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# THIRD REPORT
OF THE
# COMMITTEE ON PHOTOCHEMISTRY

*Contents*

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# THIRD REPORT OF THE COMMITTEE ON PHOTOCHEMISTRY,[1] NATIONAL RESEARCH COUNCIL

## INTRODUCTION

HUGH S. TAYLOR

*Department of Chemistry, Princeton University, Princeton, New Jersey*

*Received May 25, 1938*

The First Report of the Committee on Photochemistry presented six papers dealing with the quantitative technique of photoreactions, the classical point of view with respect to these processes, and the relation between the physical concept of quantized absorption and the chemical processes which succeed such absorption. The Second Report summarized the researches of the physicist with respect to the absorption process and their implications in the primary absorption process in photochemistry, and gave some examples of the secondary processes consequent upon such initial processes of absorption. The discussion was necessarily confined to gaseous systems since, at that time, knowledge of the nature of the individual steps in condensed systems was less certain.

In the seven years that have elapsed since the previous report there have been a large number of contributions to the subject and the technique of photochemistry. These have served to broaden the bases upon which the science rests, to add to our techniques, to increase the quantitative nature of our knowledge, to permit an extension of our investigations to the more complex condensed systems, and to make possible a more scientific presentation of important problems in the field of applied photochemistry. Some phases of this activity are summarized in the present report, in which some eleven papers dealing with various topics are assembled. Professor Daniels reviews some of the contributions to experimental technique (page 701) and has prepared with the assistance of the Committee a critical table of quantum yields (page 713). Professor Rollefson has summarized the more recent aspects of the primary absorption process (page 733). In the analysis of reactions subsequent to the primary process, Professor Dickin-

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[1] This Committee of the National Research Council, Division of Chemistry and Chemical Technology, is composed (1937–38) of the following members: Hugh S. Taylor, *Chairman*, Wilder D. Bancroft, Farrington Daniels, Roscoe G. Dickinson, Philip A. Leighton, Samuel C. Lind, George K. Rollefson. Contributions to this report have also been kindly prepared by Gertrud Kornfeld and Winston M. Manning.

son has discussed the correlation of photoprocesses in the gaseous phase with those in solutions (page 739). Recent researches into a variety of photoprocesses have considerably increased our knowledge of the secondary processes in which free radicals are produced in the primary process. From this standpoint Professor Leighton has summarized the researches on aldehyde and ketone photolysis (page 749), and the writer has dealt with the reactions in alkyl iodides, metal alkyls, mercury-photosensitized hydrogenations and decompositions of hydrocarbons, and the photolysis of azo compounds (page 763). Professor Rollefson has dealt generally with the problem of the evaluation of specific reaction rate constants (page 773), and the writer has summarized present knowledge in the case of ammonia decomposition (page 783) and the reactions involving the photochlorination of hydrogen and of carbon monoxide (page 789). Two final contributions in the domain of applied photochemistry, that of Dr. Gertrud Kornfeld on "The Action of Optical Sensitizers on the Photographic Plate" (page 795) and of Dr. W. M. Manning on "Photosynthesis" (page 815), complete the series of contributions.

It is not intended that this report shall represent an exhaustive summary of the photochemical work which has accumulated since the issue of the preceding report. Many publications in the field have not been covered, even though the papers here reviewed exceed six hundred. Other topics undoubtedly merit attention equal to that given to the subjects here discussed. That this is so indicates both a healthy state of photochemical science and a continuing task for the Committee.

# EXPERIMENTAL TECHNIQUE IN PHOTOCHEMISTRY[1]

FARRINGTON DANIELS

*Department of Chemistry, University of Wisconsin, Madison, Wisconsin*

*Received May 25, 1938*

Ten years ago, when G. S. Forbes (12) wrote the first report of the Committee on Photochemistry of the National Research Council, most of the principles of experimental photochemistry had been enunciated, but quantitative photochemical measurements had just begun. Since that time a few new techniques have been invented and old ones have been improved; over a hundred quantitative researches have given us the amount of chemical action produced and the amount of radiation of restricted wave length used. It is gratifying that workers in different laboratories are now able to check each other's results when the working conditions are the same.

The production of monochromatic light, the measurement of the energy absorbed and the chemical reaction produced, and the determination of the nature of the spectrum are the chief problems of the experimental photochemist. Because the monochromatic light is of reduced intensity, the first problem has led to the development of semi-micro methods of analysis.

It is not the purpose of this report to give a complete description of the methods used in photochemical investigations, for they may be found in the first report of this Committee (12) and elsewhere (10, 11, 15), or to include a bibliography of researches that have been published on this subject. It is planned merely to build on the first report giving trends of the past decade in experimental photochemistry, to record advances in technique, and to refer to a few selected researches where further details and additional references may be found.

## LIGHT SOURCES

### *Arcs*

The quartz mercury-vapor arc lamp is the almost universal standard for photochemical investigations when monochromatic light is necessary. It can be used, however, for only a few selected wave lengths extending from 2000 Å to 10,000 Å. Several types of arc lamps are commercially available.

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[1] Contribution No. 1 to the Third Report of the Committee on Photochemistry, National Research Council.

A small 80-watt lamp which operates on alternating current with a transformer has been put on the market recently at a low price. It is about 4 mm. by 20 mm. and is suitable for many photochemical experiments.

Intense light, for illuminating monochromator slits or small cells, is best supplied by capillary lamps (9, 21), in which the light is concentrated in a small region. These lamps are so inexpensive that one can afford to run them at a heavy overload, even though their life is short. At these overloads, up to a kilowatt in 10 cubic millimeters of space, the lamps must be water-cooled.

For the line at 2537 Å. a high-voltage lamp filled with mercury vapor and argon and neon is particularly suitable (32, 45). It operates on alternating current at about 6000 volts. Eighty-eight per cent of all the radiation is given off at this wave length, all the other lines being quite weak.

Arc lamps of other metals comparable in intensity and practicality with the mercury lamp have long been needed. Sodium arc lamps in glass are now available ("Sodium Lab-arc") and are useful for many purposes, but the demands for high intensities in photochemical work are hardly met by them.

Neon lamps are also available in convenient form for producing red light, but it is difficult to obtain a highly concentrated radiation from a small area of these lamps.

Quartz capillary lamps of cadmium, zinc, thallium, bismuth, and lead can be made to give light at several different lines which is practically as intense as that of the capillary mercury lamp. These lamps (25) are troublesome to make and operate, however, and the intensity falls off because of the formation of an inner coating of silicate; moreover they break when the current is turned off.

Tungsten filament lamps are used when continuous light is needed in the red or throughout the visible spectrum. Concentrated filaments are preferred. The intensity of the lamps may be increased considerably by operating them for short times at voltages considerably above their rated voltage.

Steadiness of a lamp can be achieved through the use of storage batteries, storage batteries floated across a dynamo, an isolated dynamo, or a dynamo operated by a synchronous motor. Voltage regulators are available operating with electron tubes or with a ballast coil of iron wire in series with the lamp.

### *Sparks*

For the shorter ultraviolet in the region of 2000 Å. and below, spark discharges between electrodes of aluminum, magnesium, and zinc are used (13, 26). Several types have been described. It is possible, though troublesome, to obtain from them intensities equal to those of the mercury lamp. Large transformers up to 10,000 volts and 5 kilowatts have been used together with large condensers. A blast of cooling air is directed against the spark. The noise and oxide dust are seriously annoying. Large discs of metal rotating at right angles may be used to confine the arc to one position and yet give constantly replaced surfaces (50).

## PRODUCTION OF MONOCHROMATIC LIGHT

### *Filters*

Filters are the cheapest and most convenient means for restricting the radiation to a narrow range of frequencies. A complete assortment of glass filters is available with which the various lines of mercury, helium, or hydrogen can be isolated (19).

A filter of chlorine and bromine gas in quartz is used for filtering out the longer ultraviolet and leaving the 2536 Å. line of mercury. Acetic acid cuts off all radiation below 2300 Å. Additional filters for specific purposes can be made from solids, liquids, and solutions, the absorption characteristics of which can be found in the literature (11, 18, 27).

An excellent set of laboratory filters for the mercury lamp has been assembled by Bowen (5).

The infrared radiation is practically completely absorbed by 4 cm. or more of a 1 per cent aqueous solution of copper sulfate (6).

The Christiansen filter (11) consists of a mass of particles of glass or quartz in a bath of liquid having the same refractive index at a given wave length, but a different dispersion. Particles of crown glass (1 to 2 mm. in size) are immersed in a mixture of carbon disulfide and benzene of such a composition that it will have the same refractive index at 5000 Å., for example. A beam of light of this wave length will pass through, but light of all other wave lengths will be dispersed. A different composition will pass light of a different wave length. Close temperature control is essential and the range of wave lengths transmitted is not as narrow as might be desired, but the filter can be adjusted to any wave length and the loss of energy in the transmitted light is not great.

### *Monochromators*

Monochromators, their requirements, and their limitations, have been described by Forbes (12). Large aperture and short focus are desirable for photochemical work (16, 22) in order to conserve as much energy as possible. Glass and quartz prisms are commonly used, but large hollow prisms filled with a liquid are satisfactory. Ethyl cinnamate is an excellent liquid for this purpose on account of its high refractive index and its ability to withstand photochemical decomposition. Water is used sometimes, but its refractive index is comparatively low. These liquid prisms give lines which are slightly distorted unless the prisms are thermostated with great care, but they are satisfactory for most photochemical work and they are comparatively inexpensive. A large monochromator using a water prism has been described by Harrison (20).

A double monochromator, in which the light from the exit slit of the first one passes into the entrance slit of the second, is much more effective than a single one in giving monochromatic light of great purity. Obviously the intensity is decreased. A double monochromator making use of ethyl cinnamate prisms is on the market.

In the focal isolation method the light of different wave lengths is separated by refraction with a lens instead of a prism. The light of short wave length is brought to a focus closer to the lens and passes through a small hole in a plate, while the longer rays are stopped. The apparatus is simpler to construct and in the short ultraviolet it is probably more effective. It has been used in several investigations making use of spark emission in the ultraviolet (23, 50). This method has been compared critically with the monochromator method (23).

When mirrors are used, as with the Wadsworth mounting for a monochromator, the sputtering of a clean glass surface with aluminum or other vapor in a vacuum is found to be superior to the ordinary silvering process.

## MEASUREMENT OF RADIATION

Thermopiles are usually the simplest and best instruments for measuring the intensity of radiation. Bismuth–silver, copper–constantan, and tellurium–platinum are among the combinations of metals which have been used, each being soldered to a thin, blackened metal receiver.

High sensitivity is not a very important characteristic of a thermopile, because the limiting factor in photochemical measurement is more likely to be the accuracy of the chemical analysis. The thermopile should be absolutely reproducible, with little drifting of the zero point. The theory and practice of thermopile construction have been discussed critically by Leighton and Leighton (32). The construction of a small thermopile has been described by Beckmann and Dickinson (1). The ordinary linear thermopile is smaller than the chemical reaction cell behind which it is placed, and it is necessary to move the thermopile over the whole area in order to obtain an average value. Large-area thermopiles which do their own integrating are simpler for photochemical investigations. The thermocouples, thoroughly protected with glyptal lacquer, are attached with de Khotinsky cement to the back of a blackened receiver 10 by 40 mm. in area.

High sensitivity galvanometers of the d'Arsonval type, giving deflections at 1 meter of 5 to 10 mm. per microvolt, are sufficiently sensitive. Galvanometers of the Paaschen type are more sensitive but more troublesome. If necessary the sensitivity can be pushed to the theoretical limit of $10^{-10}$ volt imposed by the Brownian motion of the electrons (28), by amplification with two galvanometers. A beam of light from the first galvanometer hits a thermopile or photoelectric cell connected to a second galvanometer, and the system is so arranged that the deflection of the second galvanometer is directly proportional to that of the first (36).

### *Calibration*

The energy of radiation is now determined in nearly all photochemical investigations by means of the standard carbon-filament lamps obtainable from the U. S. Bureau of Standards (7, 10). Calibration of a thermopile and galvanometer is quickly and easily accomplished, and absolute values are reliable to within about 2 per cent.

As secondary standard, the uranyl oxalate actinometer (30) is widely used. It is desirable to cross check all photochemical measurements with this simple actinometer. A solution 0.05 molar in oxalic acid and 0.01 molar in uranyl sulfate is titrated with potassium permanganate. The following quantum yields (molecules reacting per quantum) apply at 25°C.:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Wave length (Å.)..... | 2550 | 2650 | 3000 | 3130 | 3660 | 4060 | 4350 |
| Quantum yield....... | 0.60 | 0.58 | 0.57 | 0.56 | 0.49 | 0.56 | 0.58 |

When the light is feeble the length of exposure may become impractically long, but more sensitive actinometers such as the mercuric oxalate actinometer, which depend on chain reactions, are not sufficiently reproducible or reliable for quantitative measurements.

### *Photoelectric cells*

Photoelectric cells and electron tube amplifiers are easy to use and are much more sensitive than thermopiles, but they are selective and one must be sure that they give responses which are directly proportional to the intensity at the particular wave length used. They should be calibrated against a thermopile at each wave length.

In the study of ultraviolet radiation of extremely low intensity, Geiger counters are used in which a photoelectric surface emits electrons into a gas space between charged electrodes. A system of electron tubes amplifies greatly the ionization current produced each time that a photoelectron is shot out.

## REACTION CELLS

A satisfactory photochemical cell should have clear windows with no distortion of light, and the light should fill practically the whole cell. Practices vary, but when a good thermopile is placed immediately behind the cell it is usually preferable to have the depth of the cell and the concentration such that a measurable part of the light is transmitted past the cell. When all the light is absorbed within the cell the calculations are somewhat simplified, but then the intensity at the front and back of the cell varies from full intensity to zero, a fact which may cause uncertainties if the intensity of the light affects the quantum yield. When a dark reaction is involved the correction factor may become too large if there is such a large excess of material as to absorb all the light.

Glass or quartz cells are conveniently made by fusing polished discs into tubing of just the right size. Both windows should be at right angles to the path of the light. Flasks or tubes can be used for approximate work when the light energy is measured with an actinometer in the cell.

The cell should be so designed that nearly all of the contents of the cell are in the path of the light. Rectangular or trapezoidal cells are preferred, and they can be made to order either in quartz or in Pyrex.

Stirring is usually unnecessary in gaseous reactions, but it may be necessary for liquid reactions, particularly if a dark reaction is involved or if the reaction is influenced by intensity of light or concentration of material. Stirring should be omitted only in case experiments show that it is not necessary under the conditions of the experiment.

## CHEMICAL ANALYSIS

The requirements for monochromatic light reduce the energy intensity to such an extent that micro or semi-micro methods of analysis are often necessary. One of the most successful micromethods for gas analysis has been developed by Blacet and Leighton (2, 3, 4), using a small bead of solid absorbent,—phosphorus for oxygen, phosphorus pentoxide for water, silver oxide for carbon monoxide, and copper oxide and potassium hydroxide for hydrogen, and other absorbents. Only 0.25 to 1 cc. of gas is needed for a complete determination.

More micromethods are needed, particularly for complex organic compounds.

The removal of gas for analysis offers a problem, particularly when the gas is at reduced pressure. Toepler pumps, which utilize the filling and emptying of a mercury reservoir, are often used (43). Sometimes the gas is pumped out and frozen in a small tube surrounded with liquid air. Boiling points and freezing points are always useful in identification. Titration methods of precision such as iodimetry find frequent use. Electrotitrations have been developed to a point which makes possible increased accuracy in the study of some photochemical reactions. Conductance methods are applicable sometimes (47).

In gaseous reactions pressure change has been the most common method for following the course of a reaction. Obviously the method is applicable only when there is a change in the number of molecules and when the stoichiometrical reaction is known to be fairly simple. The pressure is usually followed in a constant-volume cell through a flexible diaphragm of glass or quartz. Many different types are available (8, 42).

The application of Beer's law to the determination of the chemical change is receiving increasing application. The absorption of light constitutes one of the simplest methods of analysis and is particularly desirable because it does not disturb the reacting system nor demand the removal of samples. Frequently the same thermopile measurements may be used for the determination of both energy absorption and chemical change. If Beer's law applies, the concentration at any time can be calculated directly from the absorption coefficient, or interpolation may be made on a logarithmic graph. Even when Beer's law does not apply, graphical interpolation on an experimentally determined logarithmic graph will give the concentration.

Thermopile-galvanometer readings may be summed up over long periods of time to give both energy absorbed and chemical change produced (24).

The analysis by absorption of light may be applied not only in the case of the light used in the photochemical reaction but to any other wave length. For example, the production of iodine or chlorine in a photolysis by ultraviolet light can be followed by the absorption of light in the visible. It must be proved experimentally that the materials actually absorbing the light are directly involved in the reaction. For example, Vesper and Rollefson (48) showed that earlier calculations involving the chlorination of monobromotrichloromethane were erroneous because it had been assumed that chlorine was the only substance absorbing the light, whereas in reality it was being absorbed by a bromine-chlorine compound having an entirely different absorption spectrum. Analysis by infrared absorption has been very accurate and successful in the case of the nitrogen oxides (49) and carbon dioxide (34).

Direct analysis with a colorimeter is often possible, and the increasing use of the photoelectric colorimeter will certainly find further application in photochemical investigations.

## HIGH AND LOW TEMPERATURES

Most photochemical investigations have been limited to temperatures in the neighborhood of room temperature. Data over a wide range of temperature are needed. Particularly with the new interest in free-radical chain reactions it is desirable to obtain quantum yields and chain lengths at high temperatures,—at 300° to 400°C., for example (29, 35). Special techniques have been developed. It is a good plan to have the thermopile back of the heated reaction chamber completely immersed in water to prevent radiations from the heated walls striking the thermopile.

Low temperature halogenations have been carried out in "freon" surrounded by dry ice (14).

### ABSORPTION SPECTRA

Intelligent planning of a photochemical investigation demands first a full knowledge of the regions in which light is absorbed. Spectrograms are essential for this purpose.

Much can be learned from absorption spectra concerning the primary photoprocess. The existence or non-existence of fine structure in the spectrum is often sufficient to decide between different photochemical mechanisms. Grating spectrographs give the greatest dispersion, but prism spectrographs of the best type are often adequate. The fine structure of the spectrum of acetone vapor offers an illustration (38, 39).

The more complex organic compounds and substances in the liquid phase are not likely to show fine structure, but a complete knowledge of the various absorption bands is helpful. Sometimes the finer details of the spectrum can be brought out by lowering the temperature of the absorbing substances with dry ice or liquid air.

Absorption spectra can be mapped in the usual way by splitting the beam of light into two paths, passing one through the absorbing material and reducing the intensity of the other until the two become equal. On a photographic plate the two are matched. Again the amount of absorption can be determined by the density of the lines or regions on the photographic plate as measured with a photoelectric cell or thermopile. Excellent recording apparatus is available for giving in full detail the intensity of absorption throughout the spectrum.

An important new development is the adaptation of the photoelectric cell to the direct determination of the percentage absorption in the different parts of the spectrum (53). Quantitative absorption measurements on chlorophyll have been obtained by this means (52) without the uncertainty of the photographic plate. In some ways this method is less expensive and more direct than the photographic method.

The emission spectra of fluorescent materials may give information regarding the photomechanisms. Since the light is weak, large apertures and long exposures are necessary with a photographic plate. Quantitative measurements of the energy emitted in fluorescence may be made with the photoelectric cell (53).

For the light needed in making absorption spectra tungsten filaments are suitable down to about 3600 Å., but the intensity is low at the shorter wave lengths. Quartz windows may be attached to the glass bulbs surrounding the filament. The iron arc gives many lines throughout the whole spectrum and is widely used in absorption spectra, but it is obviously unsuited for studying fine structure.

Improvements have been made in continuous sources of light in the ultraviolet. The spectrum of molecular hydrogen is most commonly used. Vessels are so arranged that an intense electrical discharge is passed through hydrogen at a low pressure in a tube which allows recombination of the atoms by collision with a metallic surface. An efficient tube of simple design has been described by Munch (37).

### *Isotopic tracers*

The new techniques by which atoms can be traced through chemical reactions by means of radioactivity or abnormal (isotopic) atomic weights are destined to settle many problems of photochemistry. To date only a few experiments of this type are on record.

Taylor and Jungers (46) mixed deuterium with ammonia and mercury vapor and subjected the mixture to illumination with the resonance radiation at 2536 Å. Deuterium entered the ammonia under the influence of the radiation, and the results showed that the low quantum yield obtained in the photolysis of ammonia is due to the recombination of hydrogen atoms and the $NH_2$ radicals formed by the photochemical reaction.

Leighton and Mortensen (33) used radioactive lead in their study of the mechanism of the photolysis of lead tetramethyl.

### *Free radicals*

Many photochemical reactions are now believed to involve the production of free radicals as a first step. There is a great deal of indirect evidence and some direct evidence for this theory. A test has been applied, for example, in the photolysis of acetone, in which removal of a lead or antimony mirror is used to support the view that free methyl radicals are produced in the photolysis (40, 44).

The existence of OH and other free radicals in the electrical discharge has been proved by characteristic absorption bands (17).

One of the most complete researches on absorption has given experimental proof of the production of iodine atoms when iodine molecules are illuminated. Rabinowitch (41) has described a delicately balanced colorimeter, with an amplifying circuit of electron tubes, which measures with great accuracy the change in absorption produced by a photochemical reaction.

The conversion of ortho–para hydrogen has been used also as a test for the independent existence of free radicals containing an odd number of electrons (51).

## REMARKS

Quantitative methods for measuring photochemical reactions are now well established, but more intense sources of monochromatic light are needed. Also, the further development of the spectroscopy of polyatomic molecules will lead to advances in photochemistry. Improvements are needed in methods for the analysis of the complex products of photochemical reactions. Special care must be exercised in certain reactions to remove impurities such as oxygen and moisture, which sometimes affect the reaction. Interesting developments are to be expected in photochemical studies at high and low temperatures, and at low gas pressures.

Greater accuracy in determining quantum yields is useless unless the conditions of temperature, pressure or concentration, and light intensity are clearly defined.

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# A TABLE OF QUANTUM YIELDS IN EXPERIMENTAL PHOTOCHEMISTRY[1]

FARRINGTON DANIELS

*Department of Chemistry, University of Wisconsin, Madison, Wisconsin*

*Received May 25, 1938*

In the early development of quantitative photochemistry it was believed by some that the Einstein relation would apply in many cases not only to the primary process of photoexcitations but to the overall reaction as well. Quantum yields were summarized with the purpose of testing this hypothesis. Any hope of simplicity in chemical kinetics disappeared long ago, and the present table has been assembled not to emphasize the almost universal occurrence of secondary effects which follow the primary process of quantum absorption, but to record the experimental facts of photochemistry in the simplest possible manner. The primary excitation is usually followed by rearrangements and degradation of the energy as heat, by reverse or competing reactions which make the overall quantum yield less than unity, or by continuing reactions which produce a chain and give a value greater than unity. Sometimes it is possible to study these factors from the magnitude of the quantum yield and its response to influences such as temperature, wave length, concentration, and chemical reagents.

The amount of chemical reaction produced by the absorption of radiation will change with the duration of exposure, the intensity of the light, the thickness and condition of the absorbing material, and other factors. The fundamental simple relation between light and chemical action, however, is the quantum yield $\Phi$, i.e., the number of molecules of substance reacting for each quantum of radiation, or photon, absorbed. When this is known the extent of the chemical reaction produced by the absorption of a given amount of light is easily calculated.

In table 1 are summarized the findings of most of the quantitative photochemical researches in which the results are expressed in terms of quantum yields. Many excellent researches are not included, simply because the results were not given in these terms. Photochemistry has been greatly stimulated by hypotheses in chemical kinetics, and the testing of these hypotheses has been the chief aim in many cases. For

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[1] Contribution No. 2 to the Third Report of the Committee on Photochemistry, National Research Council.

TABLE 1

*Table of quantum yields in photochemistry*

| REACTION AND PRODUCTS | SOLVENT | ABSORBER | WAVE LENGTH | TEMPERATURE | QUANTUM YIELD | REMARKS AND REFERENCES* |
|---|---|---|---|---|---|---|
| | | | Å | °C. | | |
| Acetaldehyde decomposition → $CH_4$; CO | Gas | $CH_3CHO$ | 2537 | 30 | 0.9 | Polymerization accompanies reaction; Φ changes with pressure; some hydrogen produced (12, 71) |
| | | | 2804 | 30 | 0.5 | |
| | | | 3130 | 30 | 0.2 | |
| | | | 3130 | 310 | 300 | (69) |
| Acetaldehyde decomposition → $CH_4$; $C_2H_6$; CO | | $CH_3CHO$ | | 300 | 103$^{(1)}$ | $^{(1)}$ at 100 mm.; |
| | | | | | 409$^{(2)}$ | $^{(2)}$at 700 mm.; |
| | | | | 350 | 196$^{(1)}$ | Φ decreased by addition of NO |
| | | | | | 710$^{(2)}$ | |
| | | | | 400 | 338$^{(1)}$ | |
| | | | | | 1374$^{(2)}$ | |
| | | | | 450 | 589$^{(1)}$ | † |
| | | | | | 2278$^{(2)}$ | (84) |
| Acetic acid decomposition → $CH_4$; $CO_2$ | $H_2O$ | $CH_3COOH$ | 1850–2300 | | 0.5 | 0.1 *M* solution (38) |
| Acetone decomposition → $C_2H_6$; CO | Gas | $(CH_3)_2CO$ | 3130–2650 | 56 | 0.17 | 680–760 mm. (27) |
| | | | 3130 | 60 | 0.2 | 10 per cent $CH_4$ |
| | | | 2480–2770 | 60 | 0.4 | (89) |
| | | | 2200–3300 | 60–100 | 0.2–1 | (135) |
| | | | | 160–400 | 1 | |
| | | | 1900 | 25 | 0.66 | At 0.2 mm. |
| | | | | | 0.46 | At 52.3 mm. (58) |

| | | | | | | |
|---|---|---|---|---|---|---|
| Acetone decomposition → alcohol, etc. | $n\text{-}C_6H_{14}$ | $(CH_3)_2CO$ | 2480–3135 | | 0.27 | 10 per cent solution (21) |
| Acetone hydrolysis → $CH_3COOH$; $CH_4$ | $H_2O$ | $(CH_3)_2CO$ | Hg arc | 30<br>40 | (0.12)<br>(0.17) | In 0.05 molar solution; decreases in more concentrated solutions (97) |
| Acetylene polymerization | | | | | | |
| → $(C_2H_2)_n$ | Gas | $C_2H_2$ | 2150 | 25 | 9.2 | (77) |
| → $(C_2H_2)_n$ | | Hg | 2636 | 25 | 6.5 | Mercury-sensitized; pressure 1–40 mm. (61) |
| → $(C_2D_2)_n$ | | Hg | | | 5 | |
| Acraldehyde decomposition → CO; $C_2H_2$ | Gas | $C_3H_4O$ | 3130<br>3660 | 17 | 0.15<br>0.01 | (115) |
| Acraldehyde polymerization → $(C_3H_4O)_n$ | | $C_3H_4O$ | 2537–3660 | 30 | <0.04 | Banded absorption 3130–3660; continuous absorption below 2804 |
| | | | 2537 | 30 | 19 | |
| | | | 2654 | | 19 | |
| | | | 2804 | | 10 | |
| | | | 3020 | | 1 | |
| | | | 3130 | | 0.5 | |
| | | | 3660 | | 0.3 | (10) |
| | | | 3130 | 17 | 2.3 | |
| | | | 3660 | | 0.4 | (115) |
| Allene polymerization → $(H_2C{:}C{:}CH_2)_n$ | Gas | $H_2C{:}C{:}CH_2$ | Hg arc | 25–29 | 2.5 | (78) |
| Amino acids deamination → $NH_3$; $RC(OH)HCOOH$ | $H_2O$ | Alanine | Hg arc | 30 | 1.0 | |
| | | Betaine | | | 0.5 | |
| | | Glycine | | | 0.9 | (129) |

* A reference, given in parentheses in the last column, applies to all the material between it and the preceding reference.

TABLE 1—*Continued*

| REACTION AND PRODUCTS | SOLVENT | ABSORBER | WAVE LENGTH | TEMPERATURE | QUANTUM YIELD | REMARKS AND REFERENCES |
|---|---|---|---|---|---|---|
|  |  |  | Å | °C. |  |  |
| Ammonia decomposition → $N_2$; $H_2$ | Gas | $NH_3$ | 2099–2194 | 20 | 0.14 | Pressure 1–8 atm. |
|  |  |  |  | 400 | 0.6 | (95) |
|  |  |  | 2000–2200 | 19–400 | 0.25 | Followed by ortho-para hydrogen conversion (39) |
|  |  |  | 2026–2138 | 21–31 | 0.10 | At 0.1 mm. |
|  |  |  |  |  | 0.30 | At 65 to 120 mm. |
|  |  |  |  |  | 0.18 | At 760 mm. (133) |
|  | Liquid | $NH_3$ |  |  | $<0.02$ | (94) |
|  | Gas | Hg | 1990 |  | 0.87 | Mercury-sensitized; Φ approaches zero at low pressures (126) |
|  |  |  | 2537 |  | 0.12 |  |
| Anthracene polymerization → $(C_{14}H_{10})_2$ | $C_6H_6$ | $C_{14}H_{10}$ | 3130–3665 | 80 | 1 to 0<br>(0.5) | Reaction reverses in dark (128) |
| Arsine decomposition → As; $H_2$ | Gas | Hg | 2537 | 24–27 | 1.03 | Mercury-sensitized (107) |
| Azomethane decomposition → $C_2H_6$; $N_2$ | Gas | $(CH_3)_2N_2$ | 3665 | 20–226 | 1.0 | At 181 mm. |
|  |  |  |  |  | 0.77 | At 684 mm. |
|  |  |  | 2540 |  | 0.25 | Primary products $CH_3$ and $N_2$; products complex (43, 28) |
|  |  |  | 2080 |  | 0.24 |  |
| Bromination of acetylene → $C_2H_2Br_2$ | Gas | $Br_2$ | 4358–5791 | 20 | 3000 |  |
|  |  |  |  | 150 | 500 | (19) |

| | | | | | | |
|---|---|---|---|---|---|---|
| Bromination of acetylene dichloride → CHClBr·CHClBr | Gas<br>$CCl_4$ | $Br_2$<br>$Br_2$ | 4060–5460<br>4060–5460 | 30–40<br>30–40 | (100)<br>(1.8–3.0) | (47) |
| Bromination of benzene → $C_6H_6Br_6$ | Liquid | $Br_2$ | 3000–5500 | 17–50 | 0.4–0.9 | (98) |
| Bromination of cinnamic acid → $C_6H_5CHBr \cdot CHBrCOOH$ | $CCl_4$ | $Br_2$ | 4060–5460 | 0–30 | 1–30 | Saturated with air; increases with concentration of bromine; in absence of oxygen Φ is large (5) |
| Bromination of hydrogen → HBr | Gas | $Br_2$ | 5000–5780 | $<150$<br>$>150$ | 0<br>1–2 | Several factors involved (16, 60) |
| Bromination of tetrachloroethylene → $C_2Cl_4Br_2$ | Liquid | $Br_2$ | 4360 | 25–135 | 0.1 to 24 | Depends on concentration of products and on oxygen (134) |
| Bromophosgene decomposition → CO; $Br_2$ | Gas | $COBr_2$ | $<3200$ | 10–40 | 1 | (103) |
| Chlorination of benzene → $C_6H_6Cl_6$ | Gas | $Cl_2$ | 3660 and 3130 | 25 | 12–46 | Depends on pressures; $Cl_2$, 95–126 mm.; $C_6H_6$, 8–40 mm. (110) |
| Chlorination of formic acid → HCl; $CO_2$ | Gas | $Cl_2$ | 3660 | 20–30 | 2000 | HCOOH, 65–100 mm.; $Cl_2$, 200–300 mm. (131) |
| Chlorination of chlorom for → $CCl_4$; HCl | Gas | $Cl_2$ | 4358 | 60 | 300 | $Cl_2$, 77 mm.; $CHCl_3$, 32–128 mm. (105) |

TABLE 1—*Continued*

| REACTION AND PRODUCTS | SOLVENT | ABSORBER | WAVE LENGTH | TEMPERATURE | QUANTUM YIELD | REMARKS AND REFERENCES |
|---|---|---|---|---|---|---|
| | | | Å | °C. | | |
| Chlorination of cinnamic acid → $C_6H_5CHCl \cdot CHClCOOH$ | $CCl_4$ | $Cl_2$ | 3660 | 25 | 2.4 | Depends on $Cl_2$ concentration. Probably oxygen-inhibited (9) |
| Chlorination of dichlorobenzenes → $C_6Cl_6$; HCl | Gas | $Cl_2$ | 3660 | 20 | 0.39 | Depends on dichlorobenzene pressure (40) |
| Chlorination of dichloroethylene → $CHCl_2 \cdot CHCl_2$ | Gas | $Cl_2$ | 4360 | 85–95 | 7000 | $Cl_2$, 100 mm. (86) |
| Chlorination of hydrogen → HCl | Gas | $Cl_2$ | 3660 | | ($<10^5$) | Depends on many factors; inhibited by $O_2$ and HCl (99) |
| | | | 3030–4360 | 17–27 | | (25) |
| | | | 4300–5000 | 30 | $4 \times 10^6$ | Silver walls. Oxygen removed (17) |
| Chlorination of methane → $CH_xCl_{4-x}$ | Gas | $Cl_2$ | 2537<br>4360 | | (100,000) | (24) |
| Chlorination of pentane → $C_5H_{11}Cl$; HCl | Gas | $Cl_2$ | 3660 | 25 | (190) | Oxygen excluded (114) |
| Chlorination of sulfur dioxide → $SO_2Cl_2$ | Gas | $Cl_2$ | 4200 | | (1) | (18) |
| Chlorination of tetrachloroethylene → $C_2Cl_6$ | Gas | $Cl_2$ | 4360 | 40 | 300–500 | In absence of oxygen |
| | $CCl_4$ | $Cl_2$ | | | 300–500 | (31) |

| | | | | | | |
|---|---|---|---|---|---|---|
| Chlorination of toluene → $C_6H_5CH_2Cl$ | Liquid | $Cl_2$ | 4050 | −80 | (27) | (20) |
| Chlorination of trichlorobromomethane → $CCl_4$; $Br_2$ | Gas | $Cl_2$ | 3660 | 28 | 30 | (119) |
| Chlorine monoxide decomposition | | | | | | |
| → $Cl_2$; $O_2$ | Gas | $Cl_2O$ | 2350–2750 | 20 | 4.5 | (104) |
| | | $Cl_2O$ or $Cl_2$ | 4030–4360 | 10–40 | 2 | (14) |
| | $CCl_4$ | | 4360 | | >1.8 | $ClO_2$ formed also (32) |
| Chlorine dioxide decomposition | | | | | | |
| → $Cl_2$; $O_2$ | Gas | $ClO_2$ | 3660 | 18 | 3.1 | Addition of water vapor gives reproducible results (112) |
| | | | 4360 | 31 | 2.7 | |
| → $Cl_2$; $O_2$ | | $Br_2$ | 5460 | 15 | 3 | Bromine-sensitized (112) |
| Cinnamic acid isomerization | $H_2O$ | $\begin{array}{l}C_6H_5CH\\ \quad\| \\ \quad HCCOOH\end{array}$ | 3130 | 28 | 0.6 | 0.003 *M* solution (117) |
| Isocinnamic acid isomerization | $H_2O$ | $\begin{array}{r}C_6H_5CH\\ \| \\ HOOCCH\end{array}$ | 3130 | 28 | 0.2 | 0.003 *M* solution (117) |
| Citraconic acid isomerization | $H_2O$ | $\begin{array}{l}CH_3CCOOH\\ \quad\| \\ \quad HCCOOH\end{array}$ | 3130 | 18 | 0.2 | 0.01 *M* solution (117) |
| Crotonaldehyde decomposition → RH; $R_2$; $H_2$; CO | Gas | Crotonaldehyde | 2400 and 3660 | 30 | <0.02 | (11) |

TABLE 1—*Continued*

| REACTION AND PRODUCTS | SOLVENT | ABSORBER | WAVE LENGTH | TEMPERATURE | QUANTUM YIELD | REMARKS AND REFERENCES |
|---|---|---|---|---|---|---|
| | | | Å | °C. | | |
| Cobalt potassium oxalate → $CO_2$; CO; $H_2O$ | $H_2O$ | $K_3Co(C_2O_4)_3$ | 3660 | 10–22 | (1.5) | |
| | | | 4050 | | (0.9) | |
| | | | 4360 | | (0.6) | (121) |
| Diazomethane decomposition → $CH_4$; $N_2$ | Gas | $CH_2N_2$ | 3650 and 4360 | 25 | 4 | (62) |
| Dibromotetrachloroethane decomposition → $C_2Cl_4$; $Br_2$ | Gas | $Br_2$ | 4360 | 100 | 0.5 | Bromine-sensitized 5–43 mm. |
| | | | | 125 | 3.2 | Products decrease Φ (22) |
| | | | | 150 | 15.2 | |
| Dimethyl ether decomposition with acetone → $CH_4$ CO; $H_2$ | Gas | $(CH_3)_2CO$ | 3130 | 200–400 | 5–230 | Depending on pressure and light intensity (70) |
| Ethyl iodide decompositions → $C_4H_{10}$; $I_2$ | Liquid | $C_2H_5I$ | 2537 | 5–58 | 0.41 | Independent of temperature |
| | | | 2654 | | 0.38 | |
| | | | 3130 | | 0.31 | (92) |
| | Gas | | 2610 | 25 | 0.01 | At 90 mm. |
| | | | 2026 | | 0.1 | |
| | | | 2026 | | 0.03 | At 0.1 mm. |
| | | | 2610 | | 0.6 | (130) |
| | $C_6H_{14}$ | | 2026 | | 0.1 | At 95 mm. (132) |
| | | | 2026 | | 0.24 | |
| | | | 2610 | | 0.6 | (130) |
| Ethylene iodide decomposition → $C_2H_4$; $I_2$ | $CCl_4$ | $C_2H_2I_2$ | 3030 and 3130 | 25 | 0.76 | 0.036 *M* solution. With correction for retarding effect of iodine produced Φ = 1 (29) |

| | | | | | | |
|---|---|---|---|---|---|---|
| Formaldehyde decomposition → $H_2$; CO | Gas | HCHO | 2540–2640 | | 0.9 | |
| | | | 3030–3130 | | 1.1 | |
| | | | 3340–3650 | | 0.7 | (91) |
| | | | Hg arc | 350 | 100 | (1) |
| Formic acid decomposition → $CO_2$; $H_2$ | | $(HCOOH)_2$ | 1900–2540 | 23–134 | 1 | Independent of temperature and pressure |
| → $CO_2$; CO; $H_2$; $H_2O$ | | HCOOH | | | 1 | $(CO + H_2O)/(CO_2 + H_2)$ varies with wave length (51) |
| Fumaric–maleic acid transformation | $H_2O$ | $\begin{array}{c} HCCOOH \\ \Vert \\ HOOCCH \end{array}$ | 2070–2820 | | (0.1) | 0.01 *M* (123) |
| | | | 3130 | 18 | 0.1 | 0.01 *M* (117) |
| Hydrazine decomposition → $NH_3$; $N_2$; $H_2$ | Gas | $N_2H_4$ | 1990 | 25 | 1.0 | At 2 mm. |
| | | | | | 1.7 | At 14 mm. (127) |
| | | Hg | 2547 | 15–45 | (13) | Hg-sensitized (36) |
| Hydrogen azide decomposition → $NH_3$; $N_2$; $H_2$ | Gas | $N_3H$ | 1990 | 22–27 | 1.74–3.89 | Pressure 0.3–131 mm. (7) |
| Hydrogen azide decomposition → $NH_3$; $N_2$; $H_2$ | Gas | Hg | 2537 | 20–23 | 2.86 | Hg-sensitized (83) |
| Hydrogen bromide decomposition → $H_2$; $Br_2$ | Gas | HBr | 2070 | | 2 | |
| | | | 2530 | | 2 | (122) |
| Hydrogen iodide decomposition → $H_2$; $I_2$ | Gas | HI | 2070–2820 | 27 | 2.0 | Simple photochemical reaction (76) |
| | Liquid | | | | 1.84 | (15) |
| | $C_6H_{14}$ | | | | 2.0 | (125) |

TABLE 1—*Continued*

| REACTION AND PRODUCTS | SOLVENT | ABSORBER | WAVE LENGTH | TEMPERATURE | QUANTUM YIELD | REMARKS AND REFERENCES |
|---|---|---|---|---|---|---|
| | | | Å | °C. | | |
| Hydrogen peroxide decomposition → $H_2O$; $O_2$ | $H_2O$ | $H_2O_2$ | 2750–3660 | 2–26 | 20–500 | Depending on concentration and pH (3) |
| | | | 3130 | 28 | (1) | At infinite dilution (55) |
| Hydrogen sulfide decomposition → $H_2$; S | Gas | $H_2S$ | 2050 | | 2 | At 250 mm.<br>(113) |
| Hypochlorous acid decomposition → HCl; $HClO_3$; $O_2$ | $H_2O$ | HClO | 3660 | | (2) | 0.03–0.05 *M* solution |
| | | | 4360 | | (2) | (2) |
| Iodine with $N_2CHCOOC_2H_5$ → $N_2$; $I_2CHCOOC_2H_5$ | $CCl_4$ | $I_2$ | 5460 and 5780 | 18 | <2 | Proportional to $I_2$ in dilute solutions (87) |
| Iodine with ferricyanide ion → $Fe(CN)_6^{--}$; $I^-$ | $H_2O$ | $I_3^-$ | 5000–6300 | 0 | 1.0 | (34) |
| Iodine with ferrous ion → $Fe^{+++}$; $I^-$ | $H_2O$ | $I_3^-$ | 3660–5790 | | 1 | (63) |
| Iodine with formate → CO | $H_2O$ | $I_3^-$ | 3450–3500 | 15–25 | (26–64) | (30) |
| Iodoform decomposition | $C_6H_6$ | $CHI_3$ | 3130 and 3660 | 16–25 | (1) | Increases with oxygen (50) |
| Ketene decomposition → $C_2H_4$; CO | Gas | $CH_2CO$ | 3130 | | 1 | (100) |
| | | | 3660 | | 0.4 | (90) |

| | | | | | | |
|---|---|---|---|---|---|---|
| Lead tetramethyl decomposition → Pb; $C_2H_6$ | Gas | $Pb(CH_3)_4$ | 2537 | 25–29 | 1.11 | Radioactive lead used; 22–31 mm. pressure. |
| | $(CH_3)_3C_5H_7$ | $Pb(CH_3)_4$ | 2537 | | 0.37<br>0.42 | 0.00067 *M*<br>0.0028 *M* (74) |
| Lead tetraphenyl decomposition → Pb; $C_{12}H_{10}$ | $C_6H_{14}$ | $Pb(C_6H_5)_4$ | 2537 | | 0.37 | Radioactive lead used (74) |
| Malachite green leucocyanide | $C_2H_5OH$ | Malachite green | 2537–3130 | 26–29 | 1.0 | Colorless to colored compound (54) |
| Maleic–fumaric acid isomerization | $H_2O$ | HCCOOH<br>‖ | 2070–2820 | 18 | (0.03) | 0.01 *M* (117, 123) |
| | | HCCOOH | 3130 | 18 | 0.05 | 0.01 *M* (117) |
| Maleic–fumaric ester isomerization | $CCl_4$ | $Br_2$ | 4360<br>5460 | 20 | 300<br>150 | Bromine-sensitized reaction accompanied by addition of bromine (35) |
| Mercury dimethyl decomposition → Hg; $C_2H_6$; $CH_4$ | Gas | $Hg(CH_3)_2$ | 2537 | 20<br>189 | 1.0<br>2.2 | 20 mm. pressure; no inhibition by nitric oxide (116) |
| Methane decomposition → $C_2H_4$; $H_2$ | Gas | $CH_4$ | 1400–1600<br>1295–1469 | 25 | (1)<br>(1.3) | Calculated from hydrogen produced (53, 75) |
| Methanol decomposition → $H_2$; $H_2CO$ | Gas | $CH_3OH$ | 1800–2000 | | (1) | (96) |

TABLE 1—*Continued*

| REACTION AND PRODUCTS | SOLVENT | ABSORBER | WAVE LENGTH | TEMPERATURE | QUANTUM YIELD | REMARKS AND REFERENCES |
|---|---|---|---|---|---|---|
| | | | Å | °C. | | |
| Methylamine decomposition → $NH_3$; $H_2$; $CH_3NCH_2$ | Gas | $CH_3NH_2$ | Hg arc | 100–105 | <0.7 | (37) |
| Methyl butyl ketone decomposition → $(CH_3)_2CO$; $C_3H_6$ | Gas | $CH_3COC_4H_9$ | 2480–2770 | 127 | 0.27 | 1 atm. pressure |
| Methyl butyl ketone polymerization | Gas | $CH_3COC_4H_9$ | 2480–2770 | 127 | 0.03 | (13) |
| Methyl iodide decomposition → $CH_4$; $C_2H_6$; $I_2$ | Gas | $CH_3I$ | Hg arc<br>2026 | <br>25 | (0.06)<br><0.01 | $H_2$ and $N_2O$ without effect (111)<br>At 140 mm. (132) |
| Methyl iodide with hydriodic acid → $CH_4$; $I_2$ | Gas | $CH_3I$ | Hg arc | | (2) | Independent of composition (59) |
| Methylacetylene polymerization → $(CH{\equiv}CCH_3)_n$ | Gas | $CH{\equiv}CCH_3$ | Hg arc | 25 | 3.5 | (78) |
| Monobromoacetic acid hydrolysis → $HOCH_2COOH$; $Br^-$; $H^+$ | $H_2O$ | $CH_2BrCOOH$ | 2537 | | 0.3 | 0.01 *M* (101) |
| Monochloroacetic acid hydrolysis → $HOCH_2COOH$; $Cl^-$; $H^+$ | $H_2O$ | $CH_2ClCOOH$ | 2537<br>1850–2300 | | 1<br>0.9 | Affected by pH (101)<br>(38) |

| | | | | | | |
|---|---|---|---|---|---|---|
| Nitrate ion decomposition → $NO_2^-$; $O_2$ | $H_2O$ | $NO_3^-$ | 2536 | 25 | 0.3 | At pH = 10 |
| | | | 3130 | | 0.01 | At pH = 10 |
| | | | 2536 | | 0.05 | At pH = 6 (120) |
| Nitric oxide → $N_2 + O_2$ | Gas | NO | 1832 | | 0.75 | (81) |
| o-Nitrobenzaldehyde rearrangement → $C_6H_4(NO)COOH$ | Liquid | $C_6H_4(NO_2)CHO$ | 2540-3660 | 45-75 | 0.5 | (136) |
| | Gas | | 3500 | 120 | 0.8 | 5 mm. pressure; with $N_2$ = 1 atm. (68) |
| | | | | 120 | 0.5 | |
| | $(CH_3)_2CO$ | | 3130-4360 | | 0.5 | |
| | Solid | | | | 0.5 | (73) |
| Nitrogen dioxide decomposition → NO; $O_2$ | Gas | $NO_2$ | 4050 | 0 | 0.5 | Decreases regularly with increasing pressure of inert foreign gas (6, 57, 88) |
| | | | 3660 | | 1.83 | |
| | | | 3130 | | 1.93 | |
| | $CCl_4$ | $NO_2$ | 3660-4050 | 0 | $<0.05$ | (57) |
| Nitrogen tetroxide decomposition → NO; $O_2$ | Gas | $N_2O_4$ | 2800 | 0 | 0.2 | (57) |
| | | | 2650 | | 0.4 | |
| Nitrogen pentoxide decomposition → $NO_2$; $O_2$ | Gas | $N_2O_5$ | 2800 | 0 | 0.6 | |
| | | | 2650 | | 0.6 | (57) |
| | $CCl_4$ | | 2650-2800 | 0 | $<0.05$ | |
| Nitrogen pentoxide with dioxide → $NO_2$; $O_2$ | Gas | $NO_2$ | 3130-4050 | 0 | | Results same as given under $NO_2$ decomposition (57) |
| Nitrous oxide decomposition → $N_2$; $O_2$; NO | Gas | $N_2O$ | Al spark | | 1 | (93) |
| β-Nitroso-β,ε-dimethylhexane decomposition → $H_2N_2O_2$, etc. | $C_6H_6$ | | 6850 | | (1) | (4) |

TABLE 1—*Continued*

| REACTION AND PRODUCTS | SOLVENT | ABSORBER | WAVE LENGTH | TEMPERATURE | QUANTUM YIELD | REMARKS AND REFERENCES |
|---|---|---|---|---|---|---|
| | | | Å | °*C.* | | |
| Nitrosoisopropylacetone decomposition → $H_2N_2O_2$, etc. | $C_6H_6$ | $(CH_3)_2C(NO)$-$CH_2COCH_3$ | 6850 | | (1) | (4) |
| Nitrosyl chloride decomposition → NO; $Cl_2$ | Gas | NOCl | 3650–6300 | 22 | 2 | (64) |
| Oxalic acid decomposition → $H_2O$; CO; $CO_2$ | $H_2O$ | Complex ion $UO_2^{++}$ with $H_2C_2O_4$ | 2550<br>3130<br>3660<br>4350 | 25 | 0.60<br>0.56<br>0.49<br>0.58 | Accurately known. This reaction is the universal standard for actinometry<br>(72) |
| Oxalyl chloride decomposition → $COCl_2$; CO | Gas | $(COCl)_2$ | 2537<br>3660 | 25 | 0.8<br>1.8 | (67) |
| Oxidation of acetone → $CO_2$; $H_2O$; $CH_3COOH$ | Gas | $(CH_3)_2CO$ | 3130 | 25 | 0.24 | Φ same as for decomposition (45) |
| Oxidation of carbon monoxide → $CO_2$ | Gas | $COCl_2$ | Hg arc | | 87–110 | Sensitized by phosgene. Each of three gases at 200 mm. (85) |
| | Gas | $Cl_2$ | 4050–4360 | | (1000) | Sensitized by $Cl_2$ (102) |
| Oxidation of carbon tetrachloride → $COCl_2$; $Cl_2$ | Liquid | $CCl_4$ | 2537 | 25 | 1 | (79) |
| Oxidation of chloroform → $COCl_2$; HCl; $Cl_2$ | Gas | $Cl_2$ | 4360 | 25<br>65 | (100)<br>260 | Sensitized by $Cl_2$ (23)<br>(106) |

| | | | | | | |
|---|---|---|---|---|---|---|
| Oxidation of hydrogen<br>→ $H_2O_2$; $H_2O$; $O_3$<br>→ $H_2O_2$; $H_2O$; $O_3$ | Gas | $O_2$<br>Hg | 1719–1725<br>2537 | <br>20 | 1<br>2.6 | Varies with pressure (109)<br>Sensitized by Hg. Corrected value of Φ (80) |
| Oxidation of hydrogen → $H_2O_2$; $H_2O$ | Gas | Hg | 2537 | 50–200 | 1.2 | Hg-sensitized. Light intensity 100 times that of Marshall (44, 80) |
| Oxidation of mandelic acid | $H_2O$ | $Br_2$<br>$UO_2^{++}$<br>$UO_2^{++}$ | 3660–5460<br>2560–3130<br>2547–4360 | 31<br>27 | (12.5)<br>(31.7)<br>(1) | Under certain conditions (46)<br>Under certain conditions (49)<br>For low concentration $UO_2^{++}$. Methylene blue present (48) |
| Oxidation of methylene iodide → HCOOH; CO; $H^+$; $I^-$ | Liquid | $CH_2I_2$ | 3100 | 21 | 1.4 | With respect to iodine (52) |
| Oxidation of phosgene → $CO_2$; $Cl_2$ | Gas | $COCl_2$ | Hg arc | | 1.8 | $COCl_2$, 63 mm.; $O_2$, 68 mm. (85) |
| Oxidation of phosphine → $H_2O$; $P_2O_5$ | Gas | $PH_3$ | Zn spark | 18 | 200 | At 0.05 mm. (82) |
| Oxidation of quinine and its derivatives by dichromic acid | $H_2O$ | Alkaloid | 3130<br>3660<br>4050 | 5–24 | 0.065<br>0.070<br>0.027 | Hydroquinone and ten other derivatives of quinine given also. Φ's all range from 0.002 to 0.07 (41) |
| Oxidation of rubrene → $C_{42}H_{28}O_2$ | $C_6H_6$<br>$C_5H_5N$ | $C_{42}H_{28}$ | 4360 | 0–18 | 1 | For large concentrations of rubrene and $O_2$ (65) |

TABLE 1—*Concluded*

| REACTION AND PRODUCTS | SOLVENT | ABSORBER | WAVE LENGTH | TEMPERATURE | QUANTUM YIELD | REMARKS AND REFERENCES |
|---|---|---|---|---|---|---|
| | | | Å | °C. | | |
| Oxidation of sulfur dioxide → $SO_3$ | Gas | $SO_2$ | 1860 | | 3.1 | |
| | | | 2070 | | 2.0 | (66) |
| Oxidation of tetrachloroethylene → $COCl_2$; $CCl_3COCl$ | $CCl_4$ | $Cl_2$ | 4360 | 20 | 1 | At low concentrations (33) |
| Ozone formation $O_2 \rightarrow O_3$ | Gas | $O_2$ | <2000 | | 1.3–2.0 | Depending on pressure (124) |
| | | | <1750 | | 2.0 | (118) |
| Ozone decomposition → $O_2$ | Gas | $O_3$ | 2080–3130 | 0–60 | 1.8–6.2 | Dry ozone at 177 and 390 mm. Varies with pressure (56) |
| | | | 2100–2800 | 2–20 | 1.6–130 | In presence of moisture. Depends on pressure (42) |
| Persulfate ion → $SO_4^{--}$; $O_2$; $H^+$ | $H_2O$ | $S_2O_8^{--}$ | 2536–3020 | | 1.0 | (26) |
| Phosphine decomposition → $P_4$; $H_2$ | Gas | $PH_3$ | 2300 | 20–300 | 0.56 | For 7 cm. bulb |
| | | | | | 0.49 | For 2 cm. bulb (82) |
| Propionaldehyde decomposition → $C_2H_6$; CO; $H_2$ | Gas | $C_2H_5CHO$ | 3130 | 300 | 3 | At 100 mm. |
| | | | | | 6 | At 200 mm. |
| | | | | | 8 | At 300 mm. (84) |
| Propionic acid → $C_2H_6$; $CO_2$ | $H_2O$ | $C_2H_5COOH$ | 1850–2300 | | (1) | (38) |
| *n*-Propyl iodide → $I_2$, etc. | Gas | *n*-$C_3H_7I$ | 2026–2610 | 25 | 0.01 | At 35 mm. (131) |

| | | | | | | |
|---|---|---|---|---|---|---|
| Isopropyl iodide → $I_2$, etc. | Gas | iso-$C_3H_7I$ | 2026 | 25 | 0.43 | At 56 mm. |
| | | | 2610 | | 0.17 | At 26 mm. (131) |
| Silver oxalate decomposition → Ag; $CO_2$ | Solid | $Ag_2C_2O_4$ | 3600–5200 | 100 | 0.12 | Inhibited by $O_2$ (8) |
| *trans*-Stilbene transformation → *cis*-stilbene | $C_6H_{14}$ | $C_6H_5HC{=}CHC_6H_5$ | 1930 | | 0.36 | |
| | | | 2260 | | 0.41 | |
| | | | 2650 | | 0.73 | |
| | | | 3020 | | 0.73 | |
| | | | 3130 | | 1.01 | (108) |

these purposes it is often unnecessary to express the results in absolute units (quantum yields).

In many cases the quantum yield varies with temperature, concentration, and intensity. Particularly in chain reactions the quantum yield may vary considerably with slight changes in the reacting system and with traces of impurities. Special conditions, such as concentration, are given in the last column of table 1. When the temperature is not given it may usually be taken as room temperature (about 20°C.). Parentheses around a quantum yield indicate a lesser degree of accuracy. When there is uncertainty regarding Φ, the original article should be consulted. The references are given in parentheses in the last column and include references to earlier investigations.

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# THE NATURE OF THE PRIMARY PROCESS IN PHOTOCHEMICAL REACTIONS[1]

G. K. ROLLEFSON

*Department of Chemistry, University of California, Berkeley, California*

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In the previous reports the nature of the primary action of light in photochemical reactions has been discussed in some detail. The principal developments since that time have been concerned with the determination of the products of the photodissociation processes and with the process known as predissociation. The term "predissociation" was introduced by Henri (4) in describing certain diffuse bands discovered by himself and his associates. Their choice of this name was based on their idea that these diffuse bands corresponded to excitation of the molecule to a loosely bound state in which it could dissociate readily. The present-day views are based on the picture, offered by Bonhoeffer and Farkas (2) and by Kronig (11), that the molecule in the activated state produced by the absorption of these diffuse bands undergoes a radiationless transfer to another electronic state and dissociates in a time which is short compared to the period of rotation. Such changes have been expressed graphically by Herzberg (6) by means of potential energy diagrams (figure 1). The transition from one state to another by this predissociation process must occur without any appreciable change in the separation of the atomic nuclei or in the energy of the system. From the standpoint of the diagrams, this means that we have radiationless transitions occurring only at the intersection of two curves. In our diagram (figure 1), if the excitation by light takes the molecule from the normal state, *n*, to a state represented by a point on the curve *a* above the level of the intersection of that curve with *a′*, then as the molecule vibrates in the excited state we have the possibility of a transfer from *a* to *a′* occurring. If this intersection point is above the level corresponding to the dissociation of the state represented by *a′*, the molecule will dissociate within the next vibration.

The diagrams (figure 1) must be looked upon as schematic only, since, actually, we cannot specify the positions and energies of the atoms with the precision indicated by the curves. According to Heisenberg's Uncertainty Principle, the product of the uncertainties of position and mo-

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mentum is $h/2\pi$. A more convenient form for us to use in the discussion of predissociation is that the uncertainty in the energy multiplied by the uncertainty of the time is $h/2\pi$. Our curves therefore should be looked upon as representing mean values only. Furthermore the intersections of two curves must be considered not as points but rather as regions within which the molecule may be thought of as being in an indeterminate state. The probability of a transfer occurring will depend upon the time that the molecule is in this indeterminate condition. This time will depend on the kinetic energy of vibration and the range over which the transition may occur. Thus in figure 1a we should expect the transition to occur only if the condition of the molecule corresponds to a point rather close to the intersection. On the other hand, in figure 1b, where the two curves cross at a small angle, when we take into consideration the blurring called for by the Uncertainty Principle, we see that there will be a long region along the curve *a* which is in the indeterminate area. Hence we should expect, other things being equal, that molecules represented by diagrams similar to figure 1b will show predissociation over a wider range and more frequently than those corresponding to the other diagrams. At the present time we do not know enough about these potential curves to make any quantitative calculations concerning predissociation. Furthermore, these curves must be considered as only schematic for polyatomic molecules, as they are far from simple vibrators.

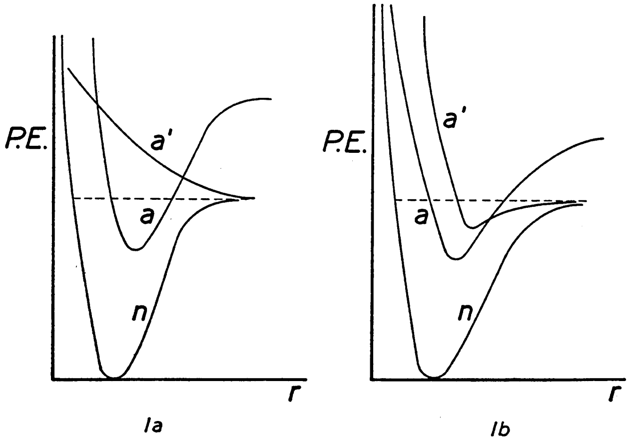

FIG. 1. Potential energy diagrams

The Uncertainty Principle also accounts for the appearance of a diffuse spectrum. If the excited state dissociates within a time $\tau$ the width, $w$, of the spectrum line which put the molecule into that state will be given by

$w\tau = h/2\pi$ or, if we express $w$ in cm.$^{-1}$, $w\tau = h/2\pi c$. In any ordinary spectrum which shows a fine line structure, the broadening due to the Doppler effect is ten to one hundred times the natural width of the line; therefore the predissociation process must shorten the life of the excited state by a factor of this magnitude for the effect to be noticeable. It is to be expected therefore that, whenever we find a diffuse absorption spectrum, fluorescence will either be very weak or absent. If we consider the competition between fluorescence and decomposition as represented by

$$AB^* \xrightarrow{k_1} AB + h\nu$$

$$AB^* \xrightarrow{k_2} A + B + \text{k.e.}$$

the fraction of the activated molecules which radiate will be given by $\frac{1}{1 + k_2/k_1}$. Hence, the greater $k_2$ is relative to $k_1$, i.e., the shorter the life period, the weaker will be the fluorescence. As $k_2$ usually must be ten to one hundred times $k_1$ for a diffuseness to be observed, it follows that a marked weakening of fluorescence is a more sensitive indicator of predissociation than a diffuse spectrum.

It is by no means universally true that we have transitions from one state to another occurring whenever we have a crossing of the potential energy curves for those states. Kronig (11) has set up the following selection rules for diatomic molecules: (*1*) There shall be no change in the total angular momentum. (*2*) Transitions occur only between states of the same multiplicity. (Invalid for large multiplet separations.) (*3*) The quantum number $\Lambda$ changes by 0 or $\pm 1$. (*4*) Transitions occur from a positive to a positive state or from a negative to a negative. (*5*) If both atoms are the same, the states involved in a transition are either both symmetrical or both antisymmetrical. The interpretation of the spectra of polyatomic molecules has not progressed to the point where we can say whether an analogous set of rules applies or not. However, we may say that we can expect to find the probabilities of radiationless transfers occurring ranging from practically every time the molecule reaches the state represented by the intersection of the potential energy curves to practically complete prohibition of the change.

The probability of a radiationless transfer occurring is modified considerably by a magnetic field or collisions with other molecules. This gives rise to the phenomenon known as induced predissociation. Experimental evidence for the occurrence of this process was obtained by Loomis and Fuller (12) and by Kondratjew and Polak (10) in the study of the absorption spectrum of iodine. They found that the addition of inert gases increased the absorption coefficient of iodine in the vapor state for those bands involving values of $v'$, the vibrational quantum number in the upper state, greater than 12. Turner (15) found that, if iodine vapor were illuminated with light absorbed in the band region in the presence of a magnetic field or inert gases, there was a marked absorption of the spectrum lines characteristic of iodine atoms. More recently, Rabinowitch and Wood (13) have made a more quantitative study of the effect of inert gases. In their experiments, the dissociation of the iodine was determined by measuring the light absorbed by the remaining iodine molecules. They concluded that argon, nitrogen, and oxygen caused the dissociation of the activated molecule at every "gas-kinetic" collision. Helium was somewhat less effective but, with a pressure of 500 mm. of that gas, all of the molecules absorbing light were dissociated.

In the case of bromine we have some evidence that dissociation occurs in the band region even without the aid of collisions. Urmston and Badger (16) found in their experiments on the photochemical reaction of bromine with platinum that the rate of the reaction was independent of the distance between the platinum and the illuminated zone. Their experiments were performed at low pressures, so that induced predissociation did not need to be considered. Neither could their results be accounted for on the basis of active molecules, as they were able to demonstrate that fluorescence was confined to the illuminated zone. It is possible that the reaction was due to a continuum underlying the band absorption, a situation analogous to that in the hydrogen–chlorine reaction which has been discussed recently by Bayliss (1). However, no appreciable difference was noted in rates whether blue or yellow light was used. Other reactions in which no effect was noted on comparing the rates using blue and yellow light are the bromination of acetylene (3) and the formation of hydrogen bromide (8). The effect of inert gases on the latter reaction has been studied in considerable detail. Instead of finding an accelerating effect, which could be attributed to induced predissociation, a retarding effect was noted, due to an increased rate of recombination of bromine atoms (7, 8, 14). This is understandable if we assume that with bromine, as has been found with iodine, every collision of an activated molecule results in dissociation. Under such conditions, no effect assignable to induced predissociation would be detectable above about 10 mm. pressure.

A quite different result has been reported for the hydrogen–chlorine reaction by Hertel (5). He found that, if the light absorption occurred in the banded region of the spectrum, this reaction was accelerated by the addition of inert gases. This effect was believed to be due to the activated molecules being dissociated by collisions. The mechanism of such a dissociation is probably induced predissociation.

The examples which we have just discussed show no sign of predissociation in their absorption spectra, indicating that the life of the undisturbed activated molecule is at least of the order of $10^{-9}$ sec.; with iodine, studies of the fluorescence indicate a life of $10^{-7}$ sec. It is apparent, therefore, that spontaneous or induced predissociation may occur with any kind of light absorption. Hence, the possibility of dissociation in the primary step of a photochemical reaction cannot be excluded on the basis of well-defined lines in the absorption bands nor even on the basis of fluorescence observations.

Another interesting example is furnished by tellurium vapor, $Te_2$. In this case the limits of the natural and induced predissociation do not coincide. The difference must be due to the induced effect involving a lower lying level than the spontaneous process (9).

If the light is absorbed by a complex molecule it is much more difficult to demonstrate an effect due to induced predissociation on account of the complexities introduced by secondary reactions. Usually, the photochemical experiments are carried out at such high pressures that the induced predissociation is a maximum if it is anything like that with simple molecules. Any effects of this type must therefore be sought for at low pressures, particularly in systems for which the quantum yield of the primary process is less than 1.

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# SOME COMPARISONS BETWEEN PHOTOCHEMICAL PROCESSES IN GASES AND SOLUTIONS[1, 2]

ROSCOE G. DICKINSON

*Department of Chemistry, California Institute of Technology, Pasadena, California*

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The chief purpose of the present section of this report is a comparison of photochemical reactions in the gaseous state with those in solution or in the liquid state. It is not proposed to enter into a detailed discussion of photochemical processes in solution but rather to indicate the relation of such processes, when possible, to those occurring in the gaseous state. This section accordingly contains a brief statement of viewpoints involved in comparing gaseous and solution or liquid reaction, together with some discussion of pertinent experimental results.

In recent years theories of the liquid state and of various phenomena occurring in liquids have undergone active development; this may, for example, be seen in the general discussion of the liquid state published by the Faraday Society (43) as well as in other papers to which specific reference will be made. Theoretical approaches to the liquid state have sometimes started with the gaseous state and have sometimes started with the crystalline state; Bernal (4), however, has given reasons for believing that liquid structure, while having points of close resemblance to the crystalline, is of a character that can not be reached by continuous transition from the crystalline state.

Current views are that a liquid, at not too high a temperature, aside from differing from a gas in the matter of coherence, possesses a somewhat quasi-crystalline structure. This does not necessarily show itself in any large regions with crystalline regularity but appears rather in the character of the distribution function $p(r)$, where $4\pi r^2 p(r)\mathrm{d}r$ gives the probability of finding a second molecule within the distance range $r$ to $r + \mathrm{d}r$ of a chosen molecule. This distribution function has been investigated by x-ray diffraction methods (25, 42, 5, 11, 29) and by experiments with models (30). The function does not show the monotonic character expected for a dilute gas, but rather exhibits maxima and minima which

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[1] Contribution No. 4 to the Third Report of the Committee on Photochemistry, National Research Council.

[2] Contribution No. 643 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology.

become less pronounced with increasing $r$ but are evident for a distance of several molecular diameters. The structure, at least in the case of simple non-polar liquids, may be thought of as such that a chosen molecule has immediately coördinated about it a number of other molecules at a distance corresponding to the first maximum of $p(r)$, others more loosely coördinated at a distance corresponding to the next maximum, and so on. The chosen molecule is accordingly closely confined in a "cage" of surrounding molecules, so that its motion becomes in part a pseudo-oscillatory one within this cage. (One estimate (8) places the mean displacement between the extremes of oscillation at about 0.5 Å.) This suggests that, for diffusion to occur, the molecule must acquire sufficient energy to break through the wall of immediately surrounding molecules (8), i.e., to move to the center of a new coördination complex (33).

In calculating numbers of collisions of solute molecules with each other, the custom has been to treat the solute as if it were gaseous with solvent absent; in the calculation the molecules have been ordinarily regarded as rigid. In recent theories the occurrence of collisions has been modified both as to distribution in time and as to average number per unit time. In view of the cage effect of the solvent molecules, once two solute molecules have made collision there is a greater probability of further collision between the same pair than would be the case in a gas. Thus a given solute molecule undergoes collisions with other solute molecules in sets. The occurrence of such collision sets has been found in experiments with models (35). For thermal bimolecular reactions between solutes, the number of sets per unit time is important when there is high probability of reaction at any collision, but the total number of collisions per unit time rather than the number of sets becomes important when any considerable activation energy is required (8, 33, 46). Present estimates of the total collisions per unit time between solute molecules give values rather higher (five to twenty times) than those from a gas calculation. In view of the present state of flux in these ideas, it would be premature to recommend any one mode of calculating collision numbers.

Specific information concerning primary absorption processes is considerably more abundant and certain for gaseous substances than for substances in the liquid state or in solution. This arises partly from the relative simplicity of the phenomenon in the gaseous state, where the absorption is by fairly isolated molecules, and partly from the related fact that in condensed states the fine structure of absorption spectra is lost, together with the detailed information derivable from such structure. Aside from the smoothing out of fine structure into a continuum in solution, dissolved substances frequently show spectra differing from those of the same substances in the gaseous state, both as to magnitude of absorption coefficient and as to position of absorption maxima. This is not surprising, since solution may be accompanied by such processes as solvation, dissociation, or ionization producing essentially new absorbing molecules. However, when interactions between molecules in the solution are not too great, the solution absorption spectrum becomes essentially a blurred copy of that of the gas. For example, the absorption coefficients of the halogens in non-polar solvents such as carbon tetrachloride differ little from values for the gases. In cases where this close similarity exists, it is usual to presume that absorption is accompanied by the same electronic transition in both cases, and to draw inferences concerning the primary process in solution from a knowledge of that in the gas.

When a molecule in solution absorbs a quantum of radiation, there is initially produced an excited molecule for which there exists a variety of conceivable fates. Among these are the following: The molecule may (*a*) immediately lose its excitation energy through collision of the second kind with solvent molecules, whereby the absorbed energy becomes ineffectively distributed through the solution, or it may (*b*) retain its excitation (in part at least) in spite of collisions with the solvent molecules and later fluoresce or enter into reaction; again, (*c*) the absorbing molecule may immediately enter into chemical reaction with an adjacent solvent molecule; and finally, (*d*) the molecule, after a lapse of time possibly dependent on whether a true continuous or a predissociation spectrum is involved, may dissociate.

Since molecules in solution are practically continuously in the process of collision with solvent, the effect of collisions of the second kind in degrading activation energy from light absorption may be expected to be of greater importance in solution than in the gaseous state. Indeed, the ability of a molecule to retain its excitation in solution sufficiently to fluoresce or to react with a second molecule of solute implies a considerable insensitiveness toward collisions of the second kind. Among inorganic substances only a few, such as the uranyl salts and compounds of the rare earths, are known to fluoresce in solution; among organic substances the phenomenon is largely confined to various ring compounds. The view has been that, in substances showing fluorescence in solution, the electronic transition was one protected from outside influences either because of occurring in the interior of an atom or because of occurring in a protected part of a complicated molecule. Frank and Levi (17) have remarked that this view is incomplete and does not explain how some substances may fluoresce yet have their fluorescence strongly suppressed by the addition of various substances to the solution. Using the idea that the electronic excitation energy of the absorbing molecule can be easily transformed only when it is approximately equal to that of a new electronic state (of the absorbing molecule, the collision partner, or both), Franck and Levi have discussed the conditions for fluorescence, quenching, and reaction in terms of potential energy curves. The retention of electronic excitation permitting reaction with a second molecule of solute is probably somewhat exceptional, most photochemical reactions occurring as a result of reaction with the solvent or of the formation of atoms or free radicals. In connection with these considerations, attention should be given to cases where sensitization of solute reaction by the solvent occurs. In the conversion of *o*-nitrobenzaldehyde into *o*-nitrosobenzoic acid in acetone solution (45), the gross quantum yield (molecules transformed per quantum absorbed by the system) for 3130 Å. remains near 0.5 for acetone solutions containing from 2 per cent to 0.02 per cent of aldehyde, although, at the lower concentration, 96 per cent of the absorption is due to the acetone. Again, the decomposition of ethyl iodide at a mean wave length of 2610 Å. gives a quantum yield (48) in 0.03 molar solution in benzene of 0.52, although only 1/180 of the absorption is due to the ethyl iodide; moreover in hexane solution, where the absorption is all due to the ethyl iodide, the yield is substantially the same. The mechanisms of these sensitizations are not known.

If, in the gaseous state, an induced predissociation occurs in competition with fluorescence, then, in solution, the dissociation may evidently be favored. However, even if the molecule does dissociate, there exists a possibility that the dissociating partners, in view of the fact that they are closely hemmed in by solvent molecules, will frequently immediately recombine. The greatly increased probability of this occurrence in solution has been emphasized by Franck and Rabinowitsch (18); they have called the process "primary recombination" to distinguish it from the "normal" recombination process which involves the uniting of atoms or radicals which were not previously partners. It has long been recognized that the Einstein photochemical equivalence law does not, in general, apply to the overall photochemical reaction, but frequently only to the primary process. The effect of a dissipation accompanying the absorption, or of primary recombination, would operate to prevent the occurrence of an integral relationship between the number of quanta absorbed and the number of *primary* products of the absorption process.

Existing experimental evidence which might be expected to have a bearing on the question of primary recombination may for the most part be divided into three classes: (*1*) experiments in which the stationary concentration of the primary products of dissociation is estimated by measurement of the light transmission of the solution while under irradiation; (*2*) photochemical experiments in which a reaction proceeds by a chain, with the rate of reaction interpreted as depending on the stationary concentration of transient substances resulting from the absorption process; and (*3*) photochemical experiments in which no chain is presumed to be involved and in which the stationary concentrations of transients are of secondary interest.

Extensive experiments of the first type have been carried out by Rabinowitsch, Wood, and Lehmann. In these the stationary decrease in concentration of halogen molecules under a measured strong irradiation was determined. With iodine in carbon tetrachloride or hexane solution (34), the processes apparently involved were only the photodissociation of the molecules and recombination of the atoms. If the fraction $\beta$ of absorbed photons gives dissociation

$$I_2 + h\nu \rightarrow 2I$$

so that the rate of production of atoms by dissociation is $2\beta(I_{\text{abs.}})$, and if the atoms disappear only by recombination $2I \rightarrow I_2$ with a rate $2k(\text{I})^2$, the value of $\beta$ is evidently given by

$$\beta = k(\text{I})^2/(I_{\text{abs.}})$$

at the steady state. Corresponding values of (I) and $(I_{\text{abs.}})$ have been measured experimentally; the value derived for $\beta$ then depends on what is assumed concerning $k$. If a pair of normally diffusing iodine atoms are assumed to combine on their first collision, and if it be assumed that the specific rate, $Z$, of such collisions may be calculated with the gas kinetic expression

$$Z = 2\sqrt{\pi}d^2\sqrt{RT/M}$$

then this specific collision rate may be set equal to $k$ and $\beta$ may be obtained. Taking $d = 5.0 \times 10^{-8}$ cm., the data lead to average values of $\beta$ of $0.7 \pm 0.3$ for $I_2$ in carbon tetrachloride and $1.0 \pm 0.3$ in hexane. However, if in the absence of combination, collisions between normally diffusing iodine atoms were to occur in sets of, on the average, $n$ collisions each, then, with combination at the first collision, $k$ becomes $Z/n$ and the calculated values of $\beta$ become the former values multiplied by $1/n$. Again if, in accord with ideas mentioned earlier, the total number of collisions between solute molecules is somewhat greater than the value given by the gas formula, say $m$ times that value, then the calculated values of $\beta$ become $m/n$ times the values given above. Thus, while values of $\beta$ of the order of magnitude of unity are compatible with the experimental results, more definite independent knowledge of the recombination rate is necessary in order to make a definite determination of $\beta$ from the stationary concentrations.

The assumption that two particles just leaving a photodissociation have the same probability of immediate collision as two particles leaving an ordinary collision is doubtful when (as is usually the case) the dissociating partners have considerable excess kinetic energy. Rollefson and Libby (36) have urged that "such atoms have an excellent chance of forcing their way between the solvent molecules" so that the two probabilities would not be equal. Rabinowitsch and Wood (35) had considered such a dyssymmetry of cage effect possible when the molecules of the solvent were smaller in mass than the dissociation products but not when the solvent was greater since, from conservation of momentum, the dissociating products would be brought to rest by their first collision with the heavier particle irrespective of their kinetic energy. However, this consideration applies primarily to head-on collisions and may not seriously affect the contentions of Rollefson and Libby. In this connection it may be remarked that activation energies for diffusion of 3000 cal. and less have been calculated (8); at least this excess is often possessed by dissociating partners in photochemical experiments.

If it be admitted that the probability of separation is greater for a pair of photodissociating atoms than for a pair in normal collision, then an effect of wave length on stationary concentrations becomes possible. Such an effect was sought (34) but not certainly found.

Turning now to photochemical evidence concerning primary recombination, there are various photochemical chain reactions to which mechanisms have been assigned which are such that the rate of reaction is proportional to the steady concentration of transients produced immediately or indirectly by the light absorption process. Simple examples are the sensitized decomposition of ethylene iodide and the iodine-sensitized transformations of geometrical isomers. Attempts to draw inferences concerning primary recombination from the rates of such reactions encounter the same ambiguities, *inter alia,* as discussed above in connection with the experiments of Rabinowitsch and Wood. However, here again, if the solvent effect is not the same for primary and secondary recombination, a wave length effect is possible; for, whereas the secondary recombination is presumably unaffected by wave length, the kinetic energy of the dissociating partners will be smaller at longer wave lengths with possibly more primary recombination and a smaller rate of reaction. Reactions of the type under discussion often proceed at rates proportional to the square root of the intensity of illumination. In such cases the total material reacting per unit time depends not only on the rate of absorption of radiation but on the distribution of absorption through the reacting medium (1); this point has, unfortunately, been frequently ignored. A rather small wave length effect has been reported (14) for the iodine-sensitized ethylene iodide decomposition; the primary quantum yields for the wave lengths 4358, 5461, and 5780 Å. were found to stand in the ratios 1:0.87:0.75. Other halogen chain reactions in which yields somewhat smaller at longer wave lengths than at shorter have been reported are the following: the bromination of cinnamic acid in carbon tetrachloride solution (2); the bromination of liquid benzene (32); the bromination of maleic ester and its sensitized rearrangement to fumaric ester (15); the iodination of various olefins in chloroform solution at −55°C. (16). It is to be noted that similar wave length effects have been reported absent in the following *gaseous* reactions: the formation of hydrogen bromide (22); the bromination of acetylene (6); the bromination of cyclohexane (23); the bromine-sensitized decomposition of chlorine dioxide (40, 41). Considerable wave length effects in the same sense are often found in aqueous solution reactions, but caution must be exercised in attributing them to varying primary recombinations as opposed, for example, to reaction with solvent or to the occurrence of different electronic transitions on absorption.

The situation can be somewhat different in the case of certain reaction mechanisms not involving a chain. If conditions are such that the atoms or radicals formed in the primary process always react with some solute to give products without the intervention of a chain, then the gross quantum yield may be used to give indications of the primary quantum yield. A necessary experimental condition is evidently a constancy of gross quantum yield over a range of concentrations of reactant. Reactions which may be of this type have not been very thoroughly examined. The decomposition of ozone in carbon tetrachloride solution sensitized by chlorine has been reported (7) to occur with a quantum yield of $2O_3$ decomposed per quantum absorbed at the wave length 3660 Å. If the mechanism be such as the following (38),

$$Cl_2 + h\nu \rightarrow 2Cl$$

$$Cl + O_3 \rightarrow ClO + O_2$$

$$2ClO \rightarrow Cl_2 + O_2$$

the observed quantum yield would indicate absence of primary recombination. The gaseous reaction is complicated (21). Again the chlorination of trichlorobromomethane in carbon tetrachloride was reported (20) to proceed with a yield of 0.9 mole of bromine per quantum absorbed (wave lengths); if the mechanism is the following (38),

$$Cl_2 + h\nu \rightarrow 2\ Cl$$

$$Cl + CCl_3Br \rightarrow CCl_4 + Br$$

$$2Br \rightarrow Br_2$$

the quantum yield indicates little primary recombination. However, the compound BrCl was not known and its formation not considered in these experiments. In the gaseous reaction, chains have been found (44). The oxidation of carbon tetrachloride to phosgene by dissolved oxygen brought about by radiation (2537 Å.) absorbed by the carbon tetrachloride has been reported (28) to occur with a yield of 1 mole of carbon tetrachloride oxidized per quantum absorbed. But in the absence of dissolved oxygen the quantum yield of decomposition of carbon tetrachloride was found to be less than 0.01. Taken together, these results could mean either (*1*) no primary recombination but a low specific rate for the reaction $2CCl_3 \rightarrow C_2Cl_6$ as compared with reactions leading to reformation of carbon tetrachloride or (*2*) large primary recombination with a long chain oxidation. The second possibility would make the apparently simple yield of oxidation fortuitous. A similar result has been obtained (48) in the oxidation of ethyl iodide by oxygen in solution under the influence of radiation absorbed by the ethyl iodide. In the presence of oxygen a 1.38 molar solution of ethyl iodide in hexane irradiated with a wave length of 2610 Å. yielded "exactly 2 atoms of iodine for every quantum absorbed." In the absence of oxygen the yield was only 0.58. Franck and Rabinowitsch (18) pointed out how primary recombination might fail to operate through reaction of the dissociating molecule with the solvent. With the aid of radioactive chlorine Rollefson and Libby (36) have shown that, when chlorine absorbs visible radiation in carbon tetrachloride solution, little if any reaction with the solvent occurs.

A possibility of obtaining further information concerning primary recombination, that does not seem to have been exploited, is offered by the photochemical intermittency effect. To illustrate this possibility, suppose a photochemical solution reaction to proceed with the mechanism:

$$I_2 + h\nu \rightarrow 2I \tag{1}$$

$$I + A \rightarrow I + B \tag{2}$$

$$2I \rightarrow I_2 \tag{3}$$

This mechanism involves the same processes as those occurring in the experiments of Rabinowitsch and Wood (34), and, in addition, an iodine atom catalysis of the conversion of A into B. The steady-state rate of this process is evidently $k_2\sqrt{\beta(I_{\text{abs.}})/k}$, where $\beta$ and $k$ have their former significance. If, however, the illumination is not steady but is carried out in regularly spaced periods of light and dark of measured duration, then it can be shown[3] that for the measurable reaction A → B, the ratio of the

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[3] Complete details are too lengthy to be given here. However, the considerations are simply as follows: that in the light

$$\frac{d(I)}{dt} = 2\beta(I_{\text{abs.}}) - 2k(I)^2$$

that in the dark

$$\frac{d(I)}{dt} = -2k(I)^2$$

and that at all times

$$\frac{d(A)}{dt} = -k_2(I)(A)$$

rate under steady illumination to that under intermittent illumination is given by a complicated but known function of the measurable quantities $(I_{\text{abs.}})$, $\tau_{\text{light}}$ and $\tau_{\text{dark}}$ (the periods of light and dark in the intermittency experiment) and the unknown quantity $\beta k$. The points of importance are that, in the theory of the intermittency effect, the product of $\beta$ and $k$ occurs and may be rendered measurable by absolute measurements of $(I_{\text{abs.}})$, whereas steady-state experiments involve the ratio of $\beta$ to $k$; combination of results from both types of experiment may thus give $\beta$ and $k$ separately.

The idea of primary recombination has been employed (31) to account for some of the special complications arising in the decomposition of ketones in hydrocarbon solvents where reaction with the solvent occurs. It has also been employed in the discussion (47) of the decomposition of ethyl iodide, which occurs with a larger quantum yield in the liquid state than in the gaseous, and in a discussion (12) of the decomposition of ethylene iodide in carbon tetrachloride solution.

When a comparison of gaseous and solution photochemical reactions with respect to processes subsequent to the primary one is undertaken, the ordinary problems of chemical kinetics of thermal reactions are encountered. The literature on the effect of solvent on thermal reaction rate is, of course, large (see, for example, the symposium on the kinetics of reaction (10)). There are, however, two very simple ways in which the kinetics may undergo large apparent alteration in passing from the gas to even an inert solvent. If the gaseous reaction involves some wall reaction (for example, a chain-breaking step) this process will hardly occur in solution; the kinetics (including, for example, the dependence on light intensity) may then be considerably altered. If the gaseous reaction involves a three-body combination of two atoms or simple radicals, this process can be strongly favored in solution, owing to the abundant supply of third bodies by the solvent; if the combining bodies are sufficiently complicated, however, a third body is of little advantage (24).

In 1935, a collection was made (13) of photochemical reactions which had been examined in both the gaseous and the liquid or solution states. It was found that when the same reaction occurred in the gaseous state as in the liquid or in an inert solvent, the reaction was usually as fast or faster in the gaseous state. Additional cases for which this is true are the bromination of dichloroethylene (19), the chlorination of chloroform (9, 37, 39, 3), and the conversion of *o*-nitrobenzaldehyde into *o*-nitrosobenzoic acid (45, 26, 27).

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# THE MECHANISM OF ALDEHYDE AND KETONE PHOTOLYSIS[1]

PHILIP A. LEIGHTON

*Department of Chemistry, Stanford University, California*

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## I. ABSORPTION SPECTRA

All aldehydes and ketones show an absorption band in the near ultraviolet, extending roughly from about 3500 Å. to below 2500Å., absorption in which probably produces transitions in non-bonding electrons of the carbonyl group (27, 45). The band shows, in general, the common phenomenon of structure at longer wave lengths, changing to a continuum at shorter wave lengths (9, 12, 13, 14, 16, 17, 18, 19, 25, 33, 53). Only in the case of formaldehyde has rotational structure been definitely observed and, except for formaldehyde, the transition from structure to continuum is very gradual. In the lighter aldehydes there appears to be a region of diffuse bands or predissociation preceding the continuum and, in addition, the bands themselves appear to be underlaid with a continuum which gradually becomes stronger as wave length is decreased.

Fluorescence, where observed, is most intense for absorption in the long wave length part of the band, but the observed limits of fluorescence do not necessarily agree with the observed limits of structure in absorption (14, 18, 19, 53). The structure becomes less marked with increase in magnitude of the hydrocarbon residue, while among the three classes, ketones, saturated aldehydes, and unsaturated aldehydes, it is interesting to note that ketones show the least structure but the most fluorescence, while the unsaturated aldehydes show the most structure and the least fluorescence.

A second and much stronger region of absorption begins at about 2000 Å. (2300 Å. for unsaturated aldehydes). In those cases which have been investigated this is found to consist of series of either diffuse or discrete bands (49, 53), some of which fit a Rydberg formula (36). The bands are underlaid with faint continuous absorption and are followed at still shorter wave lengths ($<$1500 Å.) by a strong continuum (14). Photochemical investigations have been confined almost entirely to the near ultraviolet

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region, absorption in which produces two reactions,—decomposition and polymerization.

## II. THE PRIMARY PROCESS IN DECOMPOSITION

Discrete bands together with fluorescence indicate the production of a relatively long-lived molecule on absorption at longer wave lengths, while the appearance of diffuse bands and continua indicate a dissociation process at shorter wave lengths, although, as the different types of absorption overlap, the resulting processes must also overlap.

The observation that the gaseous products of photolysis in the case of the lighter aldehydes and ketones consist chiefly of carbon monoxide and hydrocarbons or hydrogen has led to the conclusion that the bond or bonds adjacent to the carbonyl group are dissociated as the result of absorption. Supporting this are energetic considerations (51) and the demonstration by Pearson and his collaborators of the production of free methyl radicals during the photolysis of acetone and, to a lesser extent, of acetaldehyde (43) as well as of ethyl, propyl, and butyl radicals during the photolyses of diethyl and higher ketones (42, 44).

Referring to photolysis through the breaking of bonds adjacent to the carbonyl group as type I, three primary processes appear energetically possible (28):

(*A*) A dissociation into hydrocarbon (or hydrogen in the case of formaldehyde) and carbon monoxide molecules in one step:

$$\mathrm{R_1R_2CO} + h\nu \rightarrow \mathrm{R_1R_2} + \mathrm{CO}(^1\Sigma \text{ or } ^3\Sigma)$$

where $R_1$, $R_2$ = an alkyl radical or a hydrogen atom.

(*B*) The dissociation of a single R—C bond to produce an alkyl and an acyl radical:

$$\mathrm{R_1R_2CO} + h\nu \rightarrow \mathrm{R_1} + \mathrm{R_2CO}$$

(*C*) The dissociation of both R—C bonds simultaneously to give the corresponding radicals and normal ($^1\Sigma$) carbon monoxide:

$$\mathrm{R_1R_2CO} + h\nu \rightarrow \mathrm{R_1} + \mathrm{R_2} + \mathrm{CO}(^1\Sigma)$$

The decision as to the relative importance of these different dissociation processes constitutes one of the present problems in the photochemistry of aldehydes and ketones. The fact that aldehydes, RCHO, give predominantly a single hydrocarbon of composition RH, while mixed ketones give a mixture of three hydrocarbons $R_1R_1$, $R_1R_2$, and $R_2R_2$, led Norrish and Kirkbride (34) to the conclusion that the primary process is represented by process A for aldehydes and process C for ketones. More recent observations, however, necessitate the modification of both of these suggestions.

The isolation of diacetyl by Barak and Style (4), the demonstration by

Spence and Wild (50) that, for absorption in the continuum, the $C_2H_6/CO$ ratio in the product gas is considerably greater than unity, and that the difference is quantitatively accounted for by diacetyl formation, and the detection by Glazebrook and Pearson (15) of acetyl radicals in concentration comparable to that of methyl radicals, all resulting from the photolysis of acetone at room temperatures, is convincing evidence that process B, rather than process C, must be concerned in ketone photolysis, at least in the case of acetone. The production of hydrogen (7, 24, 26), as well as of alkyl radicals (41, 42, 43, 44), and the existence of a chain at higher temperatures (1, 21, 26) all indicate that process B or process C must be concerned to some extent in aldehyde photolysis. The low stationary concentration of atomic hydrogen compared to that of methyl radicals (11, 40) is an indication that this dissociation occurs by process B, with the splitting of the C—C rather than the H—C bond, but the existing evidence is inconclusive in this regard.

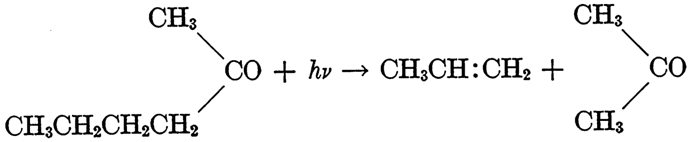
The quantum yield of decomposition of the aldehydes at temperatures below 100°C. has been found to increase with decreasing wave length in all cases studied except that of formaldehyde (24, 25, 26, 35). Accompanying the increase in quantum yield is a marked increase in the yield of hydrogen (7, 24, 26). These facts have been explained by Rollefson (48) on the basis of a competition, following absorption, between four possible paths which determine the fate of the activated molecule: (*1*) deactivation by fluorescence or collision, (*2*) dissociation into hydrocarbon and carbon monoxide by process A, (*3*) dissociation into radicals by process B or process C, and (*4*) reaction with another molecule or molecules to form a polymer. At longer wave lengths, or in the region of banded absorption, processes 1 and 4 are predominant; with decreasing wave length, in agreement with the disappearance of structure and fluorescence, processes 2 and 3 become the more important, with 3 increasing more rapidly than 2. Rollefson estimates in the case of acetaldehyde that, at 3130 Å., 90 per cent of the molecules dissociating do so by process 2 and 10 per cent by process 3, while at 2537 Å. 75 per cent dissociate by process 2 and 25 per cent by process 3. The probability of dissociation into finished molecules compared to that of dissociation into radicals is thus 9:1 at 3130 Å., decreasing to 3:1 at 2537 Å. Although the magnitude of these ratios depends upon arbitrary assumptions as to the rates of the secondary reactions (26), the predominance of the dissociation into finished molecules, particularly at longer wave lengths, is in accordance with the smaller number of methyl radicals produced in acetaldehyde as compared with acetone (43), the small number of hydrogen atoms produced by absorption in the predissociation region as compared with the continuum in formaldehyde (39), and with the observation of Norrish and Bamford (30, 32) that, except as there is a reaction with the solvent, for dipropyl ketone type I photolysis is almost completely inhibited in solution (owing presumably to primary recombination of the radicals produced), while for isovaleraldehyde the solvent has relatively little effect. On the other hand, the report of Bowen and de la Praudiere (10) that the photolysis of acetaldehyde to yield gaseous products is virtually completely inhibited in the pure liquid would indicate a dissociation into radicals as predominant, while the statement of Akeroyd and Norrish (1) that, in the chain photolysis of acetaldehyde in the presence of acetone, it makes little difference which of these substances absorbs the light, suggests that dissociation into radicals is as efficient a process for acetaldehyde as for acetone.

Little evidence is available as to whether A and B are distinct processes (48), or whether process A results from a rapid secondary reaction following process B (7), *viz.*,

$$\mathrm{RCHO} + h\nu \rightarrow \mathrm{R} + \mathrm{CHO} \rightarrow \mathrm{RH} + \mathrm{CO}$$

In the former case the increase in B with decreasing wave length would arise from the changing potential energy of the excited molecule and the resultant change in relative probability of transition into different unstable states; in the latter case, it would arise from a more rapid separation of the radicals with increasing energy absorbed, with resultant change in the secondary reactions. By extending the latter point of view the data thus far discussed are capable of explanation entirely on the basis of a primary dissociation into free radicals, followed by appropriate secondary reactions (8, 20). Thus, while the production of some carbon monoxide and a hydrocarbon in the initial act more readily accounts for certain features of these reactions, there appears to be no fact which definitely requires such an act as a separate primary process.

When studying the photolysis of methyl butyl ketone, Norrish and Appleyard (31) found that an entirely different type of decomposition occurred, which can best be described as a species of cracking the hydrocarbon chain:



$$\mathrm{CH_3(CH_3CH_2CH_2CH_2)CO} + h\nu \rightarrow \mathrm{CH_3CH{:}CH_2} + \mathrm{(CH_3)_2CO}$$

Similar reactions, as judged from the decomposition products, have since been observed for a number of aldehydes and ketones containing an alkyl chain of three or more carbon atoms (3, 26, 29). In each case the bond between the carbon atoms $\alpha$ and $\beta$ to the carbonyl group is broken, and a hydrogen atom or proton migrates to the $\alpha$-carbon atom, leaving an olefin hydrocarbon and forming acetaldehyde or a methyl ketone. Following a suggestion of Norrish, this mode of decomposition may be referred to as type II. Judging from the data in table 1, type II decreases in importance with decreasing wave length, but increases in importance with increasing length of the hydrocarbon chain.

Evidence that type II dissociation results in finished molecules is furnished by the observation of Glazebrook and Pearson (15) that free radicals are apparently produced only by type I decomposition, and by the fact that, in all cases, type II decomposition occurs without modification in solution (29, 32). As suggested by Norrish, it appears that this is a true primary process involving some type of resonance between the excited carbonyl group and the $\alpha$, $\beta$ C—C bond.

TABLE 1

*Relative numbers of molecules decomposing by type I and type II photolyses, as determined by the composition of the products*

| COMPOUND | CONDITIONS | TYPE I | TYPE II |
|---|---|---|---|
| | | *per cent* | *per cent* |
| *n*-Butyraldehyde | 3130 Å.; 30°C.<br>2654 Å.; 30°C.<br>2537 Å.; 30°C. | 90<br>97<br>100 | 10<br>3<br>0 |
| Isovaleraldehyde | Full radiation of Hg arc; approximately room temperature | 47 | 53 |
| Dipropyl ketone | Full radiation of Hg arc; approximately room temperature | 37 | 63 |
| Methyl butyl ketone | 2770–2480 Å.; 127°C. | 13 | 87 |

## III. SECONDARY REACTIONS IN DECOMPOSITION

That a chain reaction follows the photodissociation of acetaldehyde was demonstrated by Leermakers (21), who found that the quantum yield increases from less than unity at room temperature to values of 100 or more at temperatures around 300°C. A similar increase has been observed for formaldehyde (1); it is less marked for the butyraldehydes (26) and absent for valeraldehyde (21, 23).

For acetaldehyde, in the temperature region of long chains, the variation in yield with pressure and intensity is given by the equation, after Leermakers,

$$-\frac{\mathrm{d}(\mathrm{CH_3CHO})}{\mathrm{d}t} = k_1 I_{\mathrm{abs.}} + k_2 I_{\mathrm{abs.}}^{1/2} (\mathrm{CH_3CHO}) \tag{1}$$

Taking into account the demonstration by Allen and Sickman (2) that methyl radicals initiate a chain decomposition of acetaldehyde, Leermakers proposed a mechanism for the photolysis similar to that of Rice and Herzfeld (46) for the thermal decomposition (table 2).

Reaction a2 was divided into steps

$$HCO \rightarrow H + CO$$

and

$$H + CH_3CHO \rightarrow H_2 + CH_3CO$$

by Leermakers and by Akeroyd and Norrish (1). The lack of a carbon monoxide deficiency in the products favors this division; the low atomic hydrogen concentration during the reaction and the greater energetic stability of formyl radicals as compared with acetyl radicals do not. Reaction a7 was included by Leermakers to explain certain differences between his work and that of Allen and Sickman, but Akeroyd and Norrish prefer to eliminate this step. In any case, a rate law in agreement with equation 1 is obtained. Eliminating reaction a7, temperature coefficients of the photolyses of formaldehyde and acetaldehyde assign activation energies of 16 Cal. to reaction a2 and 10 Cal. to reaction a3 (1).

TABLE 2

*Reactions following dissociation into free radicals of acetaldehyde and acetone*

| | a. ACETALDEHYDE | b. ACETONE | |
|---|---|---|---|
| (a1) | $CH_3CHO + h\nu \rightarrow CH_3 + HCO$ | $(CH_3)_2CO + h\nu \rightarrow CH_3 + CH_3CO$ | (b1) |
| (a2) | $HCO + CH_3CHO \rightarrow H_2 + CO + CH_3CO$ | | |
| (a3) | $CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO$ | $CH_3 + (CH_3)_2CO \rightarrow CH_4 + CH_2COCH_3$ | (b3) |
| (a4) | $CH_3CO + M \rightarrow CH_3 + CO + M$ | | (b4) |
| (a5) | $2CH_3CO \rightarrow (CH_3CO)_2$ | | (b5) |
| (a6) | $2CH_3 \rightarrow C_2H_6$ | | (b6) |
| (a7) | $HCO + CH_3CHO \rightarrow CH_4 + CO + HCO$ | | |
| (a8) | $CH_3 + HCO \rightarrow CH_4 + CO$ | $CH_3 + CH_3CO \rightarrow C_2H_6 + CO$ | (b8) |

Recent analyses of Blacet and Volman (8) show that at room temperatures the gaseous products of acetaldehyde photolysis consist entirely of hydrogen, methane, and carbon monoxide, with no ethane or ethylene. The $H_2/CO$ ratio decreases toward zero with increasing wave length and increasing temperature above 30°C. and with decreasing temperature below 30°C.; it decreases but slightly with increasing pressure. These results are in accordance with the Leermakers mechanism provided that reaction a5 serves as the chief chain-breaking step at low temperatures, and indicate that, contrary to Leermakers' conclusion, reaction a3 is still effective even at room temperature.

Contrasting sharply with the aldehydes, the quantum yield of acetone decomposition remains at unity or less even up to 400°C. (1, 22). At room temperature the sole products in quantity, as demonstrated by Spence and Wild (50), are diacetyl, ethane, and carbon monoxide. With increasing temperature the yield of diacetyl decreases, disappearing entirely above 60°C., although diacetyl itself is stable at this temperature, while in the gaseous products the $C_2H_6/CO$ ratio approaches unity and considerable quantities of methane appear. For absorption in the continuum ($<$ 2900 Å.) at room temperature, the $C_2H_6/CO$ ratio increases with acetone pressure and with light intensity, approaching a constant value at high intensities. At 60°C., also for absorption in the continuum, the yield of methane increases with increasing acetone pressure and with decreasing intensity. These data may be accounted for on the basis of Rice and Herzfeld's thermal decomposition scheme (46, 47), as later applied by Leermakers (22) and Patat (38) to the high-temperature photolysis of acetone (table 2).

The analytical data of Spence and Wild are explained by an increase in importance of reactions b3 and b4 with increasing temperature. At 20°C. reaction b3 is negligible, while the observed $C_2H_6/CO$ ratio of 1.6 to 2.5 means that from 50 to 75 per cent of the acetyl radicals are reacting by reaction b5 to form diacetyl. At 60°C. absence of diacetyl indicates that the acetyl radicals are reacting entirely by reaction b4, while the amount of methane produced shows that from 15 to 40 per cent (depending on light intensity and pressure) of the methyl radicals are reacting by reaction b3. The thermal stability at room temperature and the instability at slightly higher temperatures, which are thus indicated for acetyl radicals, are verified by the report of Glazebrook and Pearson (15) that these radicals may be detected during the photolysis at room temperature but not at 60°C.

The absence of a chain in acetone photolysis signifies that the $CH_2COCH_3$ radicals produced by reaction b3 are incapable of further reaction with the acetone. Their ultimate fate is unknown. This mechanism is in harmony with Glazebrook and Pearson's observation that methyl radicals yield no diacetyl with acetone, and with the observation of Akeroyd and Norrish that, in acetone–acetaldehyde mixtures, there is neither inhibition or sensitization of the photodecomposition of one substance by the other, and that it makes little difference which compound absorbs the light.

The importance of reaction b5 at room temperatures in the acetone decomposition justifies its inclusion as the chain-breaking step in the low-temperature aldehyde photolysis. With the increase in rate of reaction 4 at higher temperatures, reaction 5 disappears and reaction 6 presumably becomes the chain-breaking step. Reaction b8 was considered necessary by Spence and Wild to account for the approach to a constant $C_2H_6/CO$ ratio at high intensities. The absence of ethane in the decomposition products of acetaldehyde (8) shows that reaction b8 is negligible in acetaldehyde photolysis.

In the discussion thus far, no means have been provided to account for the low quantum yields, particularly of acetone and of the unsaturated aldehydes. The decomposition yields of crotonaldehyde and of acrolein are below 0.04 at room temperature (5, 6). Although no direct measurements appear to have been made of the quantum yield of acetone photolysis below 56°C., at this temperature, with an incident intensity of $\sim 10^4$ ergs cm.$^{-2}$ sec.$^{-1}$ of 3130 Å., it varies from 0.17 at atmospheric pressure to 0.04 at 50 to 80 mm. of acetone (12). These values were calculated on the basis of pressure change with the assumption of two molecules of gas per molecule decomposed. That the yield is much lower at room temperature is indicated by the observation of Taylor and Jungers (52) that the rate of carbon monoxide evolution from acetone at $\sim$ 80 mm. in the presence of ethylene at 150 mm. and exposed to the full radiation of a hot mercury arc is only one-tenth as great at 25°C. as at 80°C.

Four means of accounting for these low yields have been proposed: (*a*) The primary yield is unity, but the overall yield is reduced by a recombination of radicals (6, 20, 24), e.g.,

$$R_1 + R_2CO \rightarrow R_1R_2CO$$

where $R_2$ = a hydrogen atom or an alkyl group. (*b*) A reorganization or distribution of the absorbed energy occurs over many internal degrees of freedom, with the result that the life of the activated molecule is greatly increased and the chance for dissociation before ultimate collisional stabilization occurs is correspondingly decreased (29, 33, 48). An observed continuous absorption would in this case be "experimentally continuous", owing to the overlapping of a large number of closely spaced transitions. (*c*) In the majority of cases quantum yields have been based on rate of carbon monoxide evolution. In these cases any condensation reactions (5, 12) would reduce the apparent yield. (*d*) Deactivation by collision or fluorescence may be a contributing factor following absorption at longer wave lengths (e.g., acetone at 3130 Å.) (12).

Since theory b accounts for the low overall yield on the basis of a low primary yield, the question of chain length in the secondary reactions immediately becomes concerned. If the acetaldehyde photolysis at high temperatures proceeds entirely by reactions a1, a2, a3, a4, and a6, the rate of decomposition will be

$$-\frac{d(CH_3CHO)}{dt} = 2\phi I_{abs.} + \frac{k_3\phi^{1/2}I_{abs.}^{1/2}}{k_6^{1/2}} CH_3CHO \qquad (2)$$

where $\phi$ is the primary quantum yield (reaction a1). The chain length, which will then be given by

$$\frac{k_3(CH_3CHO)}{2k_6^{1/2}\phi^{1/2}I_{abs.}^{1/2}} \qquad (3)$$

is inversely proportional to the square root of the primary yield. It follows that the absence of a chain in the high-temperature acetone photolysis cannot be inferred on the basis of the low quantum yield alone. The yield shows a high temperature coefficient from room temperature at least to 160°C., and the observed values may be due to a very inefficient primary process. The fact, however, that methyl radicals from other sources fail to initiate a chain in acetone is confirming evidence that no chain is concerned in the photolysis.

The observation of Norrish and Kirkbride (35) that formaldehyde vapor at 110°C. is decomposed by absorption of 3650 Å., which lies in the region of definite rotational structure, with a quantum yield almost as great as that for absorption in the continuum (0.7 versus 1.0) led these authors to the postulation that activated molecules may be dissociated by collision. Absence of atomic hydrogen (37) and the low energy of the absorbed quantum would both indicate a dissociation into finished molecules,

$$H_2CO + h\nu\ (> 3000\ \text{Å.}) \rightarrow H_2CO^*$$

$$H_2CO^* + M \rightarrow H_2 + CO + M$$

The increase in quantum yield with pressure for absorption in the banded region (3130 Å.) for both acetone (12, 19) and the butyraldehydes (26) has likewise been interpreted as indicating a dissociation induced by collisions. That such a phenomenon is not general is shown by the decrease in yield with increasing pressure for acetaldehyde at 3130Å. Independence between yield and pressure at shorter wave lengths indicates that these effects are related to the production of activated molecules. The decrease in yield with increasing pressure for acetaldehyde may be interpreted as indicating collisional deactivation or the removal of activated molecules by polymerization. The high decomposition quantum yield for acetaldehyde at 3342 Å., which falls in the weak continuum between two bands, as compared with the low yield at 3130 Å., which falls directly on a band, is additional evidence in support of this view (25). In the case of acetone, data as to the nature of the process at 3130 Å. are conflicting. The $C_2H_6/CO$ ratio of unity indicates a dissociation into finished molecules (50), while the known production of methyl radicals at this wave length indicates a dissociation into radicals. The change in quantum yield with intensity (12, 25) is difficult to reconcile with collisional dissociation. The data are best explained on the basis of a coexistence of two primary processes due to the overlapping of two types of absorption,—discrete absorption, with the production of activated molecules which are either deactivated or dissociated into finished molecules by collision, and continuous absorption, with direct dissociation into radicals.

## IV. POLYMERIZATION

Relatively little attention has been given to the photopolymerization of aldehydes and ketones, but the data available indicate that two distinct processes are concerned. With change in wave length from the region of structure and fluorescence to the region of continuous absorption, the quantum yield of apparent polymerization uniformly decreases for acetaldehyde (25), first decreases (3130 to 3020 Å.) then increases (3020 to 2537 Å.) for propionaldehyde (24) and *n*-butyraldehyde (26), and uniformly increases for isobutyraldehyde. At 3130 Å. the yield increases at least with the first power of the pressure, while at 2654 and 2537 Å. it may either increase (propionaldehyde) or be independent (acetaldehyde) of the pressure. The two processes thus suggested are (*a*) polymerization involving activated molecules and (*b*) polymerization induced by the radicals resulting from photodissociation by absorption in the continuum. Process a becomes successively less important and process b more important in the series from acetaldehyde to isobutyraldehyde.

A remarkable increase in the rate of polymerization with decreasing wave length has been observed by Blacet, Fielding, and Roof (5) for acrolein, the quantum yield at $P = 200$ mm. and $T = 30°$C. changing from 0.3 at 3660 Å. (structure) to $\sim 20$ at 2654–2537 Å. (continuum). Blacet, Fielding, and Roof suggest a mechanism for the polymerization involving reaction of either $CH_2CH$, HCO, H, or more complex radicals with acrolein molecules, probably at the C═C bond. The process concerned is probably to be compared with the polymerization of ethylene by methyl radicals (52).

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## *Addendum*[2]

Since the completion of the preceding discussion the results of some unpublished work carried out by E. Gorin in Moscow, U.S.S.R., have been communicated privately to the Committee. The newer data may modify some of the preceding conclusions on the problem of mechanism in such photolyses.

Gorin has studied the photolysis of acetaldehyde, acetone, formaldehyde, and methyl ethyl ketone in the presence of iodine vapor. It has been shown that a few tenths of a millimeter pressure of iodine molecules is sufficient to react with all the free radicals formed in the primary process.

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[2] Contributed by Hugh S. Taylor.

From analyses for the products RI and HI so produced, the number of radicals produced by the action of the light can be deduced.

With acetaldehyde–iodine systems Gorin finds methane and carbon monoxide in addition to methyl iodide. At a given wave length the ratio $CH_4:CH_3I$ is constant, independent of the temperature and of the pressure of iodine and aldehyde. There are, therefore, on this evidence, two primary processes

$$\begin{tikzcd}[row sep=small] & CH_4 + CO \qquad (I) \\ CH_3CHO \arrow[ur] \arrow[dr] & \\ & CH_3 + CHO \quad (II) \end{tikzcd}$$

Gorin concludes that at 3130 Å. reaction II is 2.6 times as probable as I, but that at 2537 Å. reaction I is 2.9 times more probable. The quantum yield is unity for the formation of $CH_4 + CH_3I$ at both wave lengths. Gorin finds that HCO radicals do not react with iodine molecules below 100°C., but do react to give $H_2CO + CO$. The formaldehyde formed was equal to half the methyl iodide formed, and equal to the excess of carbon monoxide over methane formed by reaction I. Above 100°C. hydrogen iodide begins to be formed, suggesting that formyl radicals decompose at these temperatures. This gives a minimum value of 26 kg-cal. for the activation energy of the reaction $HCO = H + CO$.

The evidence as to the influence of wave length on the alternative modes of decomposition is not in accord with other evidence on the relative amounts obtained from other studies (see page 751).

In the photolysis of acetone in presence of traces of molecular iodine no appreciable carbon monoxide formation was observed by Gorin below 60°C. Methyl iodide is formed, with a quantum yield of unity, at all wave lengths. Acetyl iodide in small amounts and diacetyl were qualitatively detected. This supports the conclusion that the primary process is represented entirely by process B of the preceding paper (page 750). The quantum yield of unity would appear to eliminate theories b and d (page 756) of the discussion by Leighton.

With formaldehyde and iodine, at all wave lengths below 3650 Å., only carbon monoxide and hydrogen iodide are formed in the ratio 2HI:CO. The primary process should therefore be, exclusively,

$$H_2CO + h\nu = H + HCO \qquad (I)$$

At 3650 Å. hydrogen is also found, indicating the additional process

$$H_2CO + h\nu_{(3650)} = H_2 + CO \qquad (II)$$

The relative probabilities are 2.5 for reaction I to 1 for reaction II. The ratio is not changed by replacing iodine with mercuric iodide as acceptor.

With methyl ethyl ketone and iodine, Gorin's results indicate that not more than a few per cent of the total primary process produces saturated hydrocarbon and carbon monoxide; the radical-producing processes are therefore overwhelmingly predominant. With acetaldehyde and iodine no polymerization was found by Gorin, indicating that it is the free radicals which are largely responsible for the polymerization observed during photolysis in the absence of iodine.

# HYDROCARBON FREE RADICALS IN PHOTOPROCESSES[1]

HUGH S. TAYLOR

*Department of Chemistry, Princeton University, Princeton, New Jersey*

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The communication by Leighton (10) on the mechanism of aldehyde and ketone photolysis has discussed in detail one group of photoreactions in which the primary process leads, at least in part, to the production of hydrocarbon free radicals. In the present communication will be reviewed a group of other photoprocesses in which the absorption of light also gives rise to the production of hydrocarbon free radicals, from the secondary reactions of which further data on the properties of such radicals and their reactivities with various atomic and molecular species can be deduced. From such studies are slowly accumulating a series of data, first qualitative and later quantitative, with the aid of which a more certain interpretation of secondary reaction paths can be deduced.

The photoprocesses leading, in the primary process of absorption, to the production of free radicals include the photolysis of alkyl iodides, the photodecomposition of metal alkyls, the mercury-photosensitized hydrogenations of unsaturated hydrocarbons, and the mercury-photosensitized decompositions of saturated hydrocarbons. As yet, the majority of the studies are confined to the simpler homologs of the several series of compounds, and the radicals for which the studies are least equivocal are the methyl and ethyl radicals.

## THE PRIMARY PROCESSES

With the lighter alkyl iodides, which show regions of continuous absorption in the ultraviolet with well-developed band spectra of greater intensity than the continua, beginning near 2000 Å. and extending into the Schumann region, it is quite generally postulated (2, 7, 8, 22, 24) that the primary process leads to dissociation into a free radical and an iodine atom. Thus, with methyl iodide we assume the formation of $CH_3 + I$, and with ethyl iodide the formation of $C_2H_5 + I$. There are no data which conflict with this point of view. Differences in reaction product arising from such photolyses are, as we shall see, to be ascribed to secondary processes rather than to any other products of the primary absorption.

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[1] Contribution No. 6 to the Third Report of the Committee on Photochemistry, National Research Council.

Of the metal alkyls the best investigated are those of lead and mercury. The spectrum of mercury dimethyl shows diffuse bands below 2150 Å., with an overlapping continuum which extends to about 2600 Å. (12). Terenin and Prileshajeva (20) interpreted this absorption as leading to primary dissociation into free radicals and detected such by their action in removing metallic mirrors. Linnett and Thompson (12), after first assuming that the major primary process was decomposition to mercury and ethane, finally decided that the facts could be best interpreted by the two possible free-radical decompositions

$$Hg(CH_3)_2 + h\nu = Hg(CH_3) + CH_3$$

$$Hg(CH_3)_2 + h\nu = Hg + 2CH_3$$

Leighton and Mortensen (11) confirmed the observations of Terenin (19) and of Duncan and Murray (5), that the absorption spectra of lead tetramethyl, tetraethyl, and tetraphenyl were all continuous, the long wave length limits of absorption by the vapors being 2800 Å. for the methyl and 3500 Å. for the ethyl compound. Lead tetraphenyl in solution in trimethylpentane gave an absorption limit around 2800 Å. These continuous spectra point to dissociation in the primary absorption act, with radicals or saturated molecules as possible products in addition to the metal atoms or metal radical complexes.

In the mercury-photosensitized hydrogenation of unsaturated hydrocarbons, when hydrogen is present in any marked amount, the primary process occurs between excited mercury and molecular hydrogen generating atomic hydrogen. The free radical arises as a secondary reaction between the atomic hydrogen and the unsaturated hydrocarbon. The simplest radical so produced is the ethyl radical from ethylene. All the recent evidence indicates that this is a process of good efficiency and that the presence of ethylene serves to reduce the stationary state concentration of atomic hydrogen to small values.

For the saturated hydrocarbons Bates (1) has shown that the quenching efficiency of methane for excited mercury is very small, but that with the higher homologs there is an increased quenching efficiency. The data of Morikawa, Benedict, and Taylor (13) suggest that quenching of methane even at room temperatures gives rise to $CH_3 + H$ either directly or by collision with metastable mercury atoms. Indirect evidence suggests that the dissociation process may require an activation energy of $\sim$4.5 kg-cal. The efficiency increases with temperature.

A recent study of Steacie and Phillips (17) is concerned with the interaction, in a circulatory process, of excited mercury and ethane. They reached the conclusion that the products of the primary interaction between excited mercury and ethane are two methyl groups. The reaction

$$C_2H_6 + Hg' = C_2H_5 + H + Hg$$

was ruled out because of the absence of molecular hydrogen in the reaction products. In the corresponding experiments with butane, Steacie and Phillips found abundant production of hydrogen. More recent experiments by these authors, not yet published, indicate that, in single-pass experiments in place of a circulatory process, the formation of hydrogen from ethane definitely occurs. This means that, with circulation, the hydrogen formed is converted into atomic hydrogen by photosensitization and is consumed in further reaction processes the nature of which will later be discussed.

### THE QUANTUM YIELD

The alkyl iodides show remarkably low quantum yields, especially in the vapor state. Methyl iodide has a yield of 0.02 in terms of iodine atoms per absorbed quantum in the gaseous state (2), and 0.05 in hexane solution in the region of continuous absorption (25). With ethyl iodide, the yield is of the order of 0.01 at 2600 Å., increasing to 0.1 at 2026 Å. In the continuous region, liquid ethyl iodide and its solution in hexane show yields of about 0.6, whereas at 2026 Å. the yield has decreased to 0.24 (24).

The low yield in the continuum points to dissociation followed by recombination. This view is supported by recent experiments of West (23), in which photolysis in the presence of silver foil as a trap for iodine atoms increased decomposition fortyfold, with a marked change in the composition of reaction products (see later discussion). The solvent molecules, in the experiments in the continuum, also should repress dissociation, according to the Franck–Rabinowitch principle, so that the large influence of solvent on quantum yield needs special consideration. In the short wave banded region, West and Ginsburg assume the production of optically excited molecules and their interaction with normal iodide molecules.

With lead tetramethyl vapor Leighton and Mortensen (11) found quantum yields at 25°C. somewhat more in excess of unity (1.01–1.13) than could be attributed to experimental error. The authors therefore suspected the existence of short chains. Linnett and Thompson (12), with mercury dimethyl, found a quantum yield of unity at room temperature, but at higher temperatures the yield increased gradually to 2.2 at 190°C. Cunningham (4) found a more than threefold increase in mercury dimethyl vapor decomposed between 50° and 300°C. These results point to the better propagation of chains with increase in temperature.

In the mercury-photosensitized hydrogenation processes the quantitative extinction of mercury fluorescence by hydrogen is well known, and hence the quantum yield of the total process is dependent on the efficiency of the secondary processes. In the hydrogenation of ethylene the evidence points to a 100 per cent utilization of the primary products in these secondary processes. In the mercury-sensitized decomposition of ethane, Steacie and Phillips found a quantum yield of approximately 0.2 in terms of ethane disappearing. This they ascribed, at least in part, to the inefficiency of the primary process of quenching by ethane. With butane a higher quantum yield, 0.55, was obtained.

## THE SECONDARY PROCESSES

The primary processes in the photolysis of methyl iodide, lead tetramethyl, mercury dimethyl and, according to Steacie and Phillips, in the photosensitized decomposition of ethane, all lead to the production of methyl radicals. There are, however, conspicuous differences in the products finally obtained.

In the case of methyl iodide, methane comprises 80 per cent of the product at room temperatures with from 4 to 12 per cent each of ethylene and ethane, for reactions in quartz vessels, packed or unpacked. With silver foil present, the methane yield fell to 28 per cent, while the ethylene and ethane yields rose to 18 and 54 per cent, respectively, ethane becoming in this case the major product. As much as 36 per cent of the methyl iodide disappearing is recoverable as $CH_2I_2$. Ethane predominates almost to the exclusion of other products in the photolyses of lead tetramethyl and mercury dimethyl. Linnett and Thompson found from 7 to 10 per cent of methane and 0 to 5 per cent of ethylene with about 90 per cent of ethane. They do not record any variation in product with temperature change. Cunningham found ethane with negligible amounts of methane and ethylene from room temperatures to 160°C. Beyond this temperature the methane yield increased to about 20 per cent of the hydrocarbon product at 300°C. In the photolysis of acetone similar results obtain. At 70° and 160°C. the hydrocarbon is more than 90 per cent ethane; at 300°C. equal volumes of ethane and methane are formed. In the Steacie–Phillips experiments with excited mercury any methyl radicals are formed in the presence of excess ethane. Hence no conclusion as to the amount of ethane which is regenerated can be given. Of the other hydrocarbons, nearly 60 per cent is methane, 23 per cent propane, and nearly 20 per cent butane. The butane undoubtedly arises from recombination of two ethyl radicals, since this gas is the predominant product in the mercury-photosensitized hydrogenation of ethylene (9).

The low quantum yield and the abnormal products in the methyl iodide decomposition are accounted for by West with the following sequence of reactions:

$$CH_3I + h\nu = CH_3 + I \qquad (1)$$

$$CH_3 + I = CH_3I \qquad (2)$$

$$CH_3 + CH_3I = CH_4 + CH_2I \qquad (3)$$

$$CH_2I + I = CH_2I_2 \quad (4)$$

$$CH_2I + CH_3 = C_2H_5I \quad (4a)$$

$$CH_2I + CH_3I = CH_2I_2 + CH_3 \quad (5)$$

$$CH_2I_2 + h\nu = CH_2 + I_2 \quad (6)$$

$$CH_2 + CH_2 = C_2H_4 \quad (7)$$

$$CH_2 + CH_3I = C_2H_5I \quad (8)$$

$$CH_3 + CH_3 = C_2H_6 \quad (9)$$

$$I + I + X = I_2 + X \quad (10)$$

It is evident that the recombination reaction (reaction 2) must be exceedingly efficient to account for the low quantum yield. All other processes are minor in comparison with processes 3, 4, and 5, the most important to account for the products found. West estimates that an activation energy of 10 kg-cal. for reaction 3 in competition with reaction 2 would account for the observed quantum yield. In agreement with this estimate are some measurements of Ginsburg (6), indicating an increase of quantum yield with temperature in the case of ethyl iodide photodecomposition.

Reaction 2 must also be rapid in comparison with reaction 9 which forms ethane. A steric factor of the order of $10^{-4}$ or $10^{-5}$ has been ascribed to the association of two methyls by Bawn (3). When, however, the iodine atoms are trapped by silver foil, reaction 9 appears to compete favorably with the methane-producing reaction (reaction 4).

A sequence of reactions to account for the photolyses of mercury and lead methyls is suggested by the following scheme of Thompson and Linnett:

$$Hg(CH_3)_2 + h\nu = Hg(CH_3) + CH_3 \quad (1)$$

$$Hg(CH_3) + X = Hg + CH_3 + X \quad (2)$$

$$Hg(CH_3) + Hg(CH_3)_2 = Hg + Hg(CH_3) + C_2H_6 \quad (3)$$

$$CH_3 + Hg(CH_3)_2 = Hg(CH_3) + C_2H_6 \quad (4)$$

$$CH_3 + Hg(CH_3)_2 = Hg + CH_3 + C_2H_6 \quad (5)$$

$$CH_3 + CH_3 = C_2H_6 \quad (6)$$

$$Hg(CH_3) + Hg(CH_3) = 2Hg + C_2H_6 \quad (7)$$

In these cases the recombination process

$$HgCH_3 + CH_3 = Hg(CH_3)_2$$

must be of lower probability than in the case of the iodide in view of the quantum yield of $\sim 1$. That it occurs to some extent is known from work of Paneth and others on the removal of mirrors by methyl radicals. Taking this into account, the quantum yield of unity at room temperatures signifies that some chain propagation is already occurring at these temperatures. Reactions 3, 4, and 5 are chain-propagating stages. They must possess an activation energy, otherwise a quantum yield of $\sim 10^6$ might be expected. Thompson and Linnett calculate that an activation energy of $\sim$ 11 kg-cal. for the chain-propagating reactions is in accord with the quantum yield of unity at ordinary temperatures and of 2.2 at 200°C. The presence of only traces of methane in the room temperature product indicates that, owing to the weakness of the Hg—C bond, this is broken in preference to the C—H bond in the mercury alkyls struck by methyl radicals. Since about 20 per cent of the hydrocarbon is found as methane at 300°C. this suggests that the breaking of the C—H bond must have an activation energy some 2 kg-cal. higher than that required for the breaking of the Hg—C bond.

Molecular hydrogen does not readily react with methyl radicals until temperatures of 160°C. and upwards are reached (13, 18, 21). The activation energy of the process has a value of 9 ± 2 kg-cal. The interaction of atomic hydrogen with methane is to be assigned a somewhat higher value (16, 21) of 13 ± 2 kg-cal. and is insignificant below 250°C. Interaction with ethane is much more easily obtained, some interaction occurring at room temperatures. Trenner, Morikawa, and Taylor (21) ascribed this to a reaction

$$H + C_2H_6 = CH_4 + CH_3 \tag{1}$$

The argument developed by them to exclude a reaction sequence

$$H + C_2H_6 = C_2H_5 + H_2 \tag{2}$$

$$C_2H_5 + H = 2CH_3 \tag{3}$$

is not entirely compelling. It is well known that F. O. Rice's free-radical mechanism (15) is incompatible with the ready occurrence of the first of these interactions.

The absence of methane, in the photosensitized hydrogenation of ethylene, until all the ethylene is hydrogenated, even though ethyl radicals and ethane are present, may be due to the low stationary state concentration of atomic hydrogen in presence of ethylene. Careful test by Jungers and Taylor (9) failed to reveal any significant amounts of methane with reaction in vessels kept carefully free from hydrocarbon deposits of higher molecular weight. Under these conditions also, the predominant product is butane, obviously by combination of ethyl radicals. The low relative production of ethane or propane is additional evidence of low hydrogen atom and methyl radical concentrations in such systems.

In the photosensitized decomposition of ethane, Steacie and Phillips now favor the C—H bond split by a reaction

$$Hg' + C_2H_6 = C_2H_5 + H + Hg \qquad (1)$$

They favor the reaction

$$C_2H_6 + H = CH_3 + CH_4 \qquad (2)$$

to account for their observed methane formation. For the reasons just discussed one is forced also to consider the possibility

$$C_2H_5 + H = 2CH_3 \qquad (3)$$

as the source of methyl radicals, subsequently converted to methane and propane by the recombination processes,

$$CH_3 + H = CH_4 \qquad (4)$$

$$CH_3 + C_2H_5 = C_3H_8 \qquad (5)$$

The recombination of ethyl radicals would produce the observed butane as in the photosensitized hydrogenation of ethylene. Unless one accepts reaction 3 as the mode of production of methyl radicals one is forced to conclude, as Steacie has called to the attention of the writer, that reaction 2 must be at least four times faster than

$$H + C_2H_6 = C_2H_5 + H_2 \qquad (6)$$

Otherwise hydrogen would not be *consumed* in the photosensitized interaction of hydrogen–ethane mixtures. The difficulties of the F. O. Rice chain mechanisms (15) would once more be acute. Rice and Teller, from a theoretical analysis, also strongly favor the mechanism. It is quite evident that there is need for further study in this field.

Contrasting with the relatively large butane formation in the photosensitization experiments are the products from the photolysis of ethyl iodide vapor. Here, as West has shown, the products are predominantly ethane and ethylene, with no butane and with minor amounts of hydrogen and methane. As in the case of the methyl radicals from methyl iodide it is the secondary processes which must account for the non-formation of butane.

The sequence of reactions suggested by West is:

$$C_2H_5I + h\nu = C_2H_5 + I \qquad (1)$$

$$C_2H_5 + I = C_2H_5I \qquad (2)$$

$$C_2H_5 + C_2H_5I = C_2H_6 + C_2H_4I \qquad (3)$$

$$C_2H_4I + I = C_2H_4I_2 \qquad (4)$$

$$C_2H_4I = C_2H_4 + I \qquad (4a)$$

$$C_2H_4I + C_2H_5I = C_2H_4I_2 + C_2H_5 \tag{5}$$

$$C_2H_4I_2 + h\nu = C_2H_4 + I_2 \tag{6}$$

$$I + I = I_2 \tag{7}$$

Of these reactions 3, 4, 4a, and 6 are the essential secondary reactions which account for the decomposition. The reactions must occur more readily than the methyl reactions, since even in presence of silver foil no butane was observed.

The increased yield in the photolyses of the alkyl iodides in the liquid or dissolved state over that in the gaseous state is ascribed by West, at any rate in part, to the action of the solvent molecules in providing third bodies for the yield-increasing radical associations. This influence must be exercised preferentially on the atom reaction I + I which certainly requires a third body, whereas the radical recombinations and $CH_3 + I$ and $C_2H_5 + I$ probably occur, at least in part, as association reactions. The interactions of the radical–iodine atom systems must be more efficient than the radical recombinations as the quantum yield is so low. West has shown that an inert gas such as carbon dioxide at a pressure of 10 to 40 atm. exercises an influence similar to solvent molecules in raising the quantum yield, a pressure of 40 atm. exercising an effect approximately 13.5 per cent of that obtaining in hexane solution.

In addition to the influence of solvent as third body in recombination processes there is a possible influence due to secondary reaction with the radicals. Recent work of Norrish and Bamford (14) has shown that radicals from the photolysis of ketones may remove hydrogen atoms from saturated hydrocarbon solvent molecules, becoming saturated thereby and producing, ultimately, unsaturation in the solvent. This possible effect has not yet been studied in alkyl iodide systems.

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## *Addendum*

The previous discussion might also have included the recent work from the New York University laboratories on the photolysis of azomethane as the source of free methyl radicals (Burton, Davis, and H. A. Taylor: J. Am. Chem. Soc. **59,** 1038, 1989 (1937); Davis, Jahn, and Burton: J. Am. Chem. Soc. **60,** 10 (1938)). The quantum yield of this photolysis has been carefully studied by Forbes, Heidt, and Sickman (J. Am. Chem. Soc. **57,** 1935 (1935)) with six monochromatic radiations at four pressures from 180 to 665 mm. The quantum yield approached unity as its upper limit for initial decomposition and a temperature increase from 20° to 226°C. had no effect on the quantum yield. The latter fell with increasing pressure. These results led the authors to the conclusion that the photolysis was not a chain reaction.

Burton, Davis, and Taylor have made a careful analytical study of products of the photolysis in the temperature range −22.5° to 223°C. In every case there is an excess of nitrogen formed, about 55 per cent at room temperatures rising to a maximum of 69 per cent at about 220°C. Methane in the hydrocarbon product is about 7 per cent by volume at room temperature and increases to 70 per cent by volume at 220°C. Ethane, which represents more than 90 per cent at room temperature, decreases to 15 per cent at 220°C. In the higher temperature range propane and possibly butane, in small amounts, are increasingly produced. Hydrogen and unsaturated hydrocarbons are not formed in measurable amounts.

There is no doubt that the majority of these results are consistent with a primary act producing free methyl radicals with minor, if any, intramolecular rearrangement to form stable molecules. The change in the character of the hydrocarbon products with temperature is consistent with the data on the reactions already discussed. In the case of the azomethane photolysis, however, there is quite evidently a more marked interaction between the free radicals and the azomethane, presumably to yield hydrazines, than is the case in several of the other substances described. The overall reaction becomes correspondingly more complex, the authors being of the opinion that the ethane formed results, not from the recombination of the methyl radicals, but from decomposition of the more complex radicals and molecules. In view of the preceding discussion this conclusion should be accepted with great reserve.

# THE EVALUATION OF SPECIFIC REACTION RATES IN CHAIN REACTIONS[1]

G. K. ROLLEFSON

*Department of Chemistry, University of California, Berkeley, California*

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One task involving photochemical chain reactions which has been undertaken by many investigators is that of evaluating the specific reaction rates (or rate constants) for the various steps which occur. The problems which arise with each reaction studied are so similar that the discussion will be simplified if we consider the three main types of processes: (*1*) chain starting, (*2*) chain terminating, (*3*) chain continuing.

## I. CHAIN-STARTING REACTIONS

A consideration of the mechanisms which have appeared in the literature leads to the conclusion that chains are started by some kind of an odd molecule, either an atom or a free radical, and are propagated by the alternate formation and disappearance of such molecules. Therefore, in this discussion, we are concerned with the rate of formation of odd molecules as a result of light absorption. In the simple cases, such as the absorption of light by diatomic molecules in the gaseous state in a continuous absorption band, it has been quite well established that dissociation occurs for every light quantum absorbed. The same may be said for the truly continuous absorption by more complex molecules, although, in such cases, it may be difficult to decide whether the spectrum is really continuous or only appears to be so because of inadequate resolution. Very often, however, we must consider a competition between the dissociation process and other processes such as fluorescence, deactivation by collision, or some reaction of the photoactivated molecule, either by itself or with other molecules, which does not involve the formation of odd molecules. For example, the photodecomposition of acetaldehyde at high temperatures is a chain reaction probably involving methyl radicals (15). From the work on this reaction at lower temperatures we know that, in the first stage, we have competition between fluorescence, a polymerization reaction, and probably a direct decomposition into methane and carbon monoxide as well as the dissociation to give methyl radicals (16, 27). It is appar-

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ent, therefore, that in this case it would be definitely inaccurate to set the number of chains started equal to the number of quanta of light absorbed. This uncertainty is involved in every reaction in which the radicals are produced by a predissociation process. A similar uncertainty is introduced if we have two overlapping absorption bands corresponding to transitions to two different excited states. Even with such a simple molecule as chlorine, Aickin and Bayliss (1) have shown that the continuous absorption is complex and there is a continuum underlying the sharp line bands. In this case Bayliss (3) has shown that the observed facts concerning the combination of hydrogen and chlorine caused by light absorbed in the banded region of the spectrum can be accounted for by assuming that only the continuous absorption starts the reaction chains.

Another source of uncertainty as to the efficiency of the dissociation process was suggested by Franck and Rabinowitch (11). They expressed the view that the quantum yield of a primary dissociation process in solution must be very low, as the surrounding molecules will prevent the separation of the parts. Rollefson and Libby (28) pointed out that such an effect should be observed if the speed of the separating parts is small, but most experiments have been performed with such energies that the parts would be separating with relatively large kinetic energies and thus be able to break through the surrounding cordon of solvent molecules, making the dissociation practically as efficient as in the gas phase. Dickinson (8) has discussed a number of reactions in solution and shown that they could be most readily explained by assuming that the first step was a dissociation of the light-absorbing molecule. Rabinowitch (22) has objected to such arguments on the grounds that the rate considerations used by Dickinson and others depend on the steady state concentrations of radicals or atoms rather than on their rates of formation, and these steady state values could be unchanged if the rates of dissociation and recombination were affected equally by the solvent. Rollefson and Libby pointed out that such a symmetrical modification was unlikely. Furthermore, it must be said that it is difficult to conceive of chains which are unaffected by dilution having a length such that the quantum yield of the overall reaction would be 2; yet such an assumption is necessary for $ClO_2$ in carbon tetrachloride solution if we do not assume a high efficiency for the primary step.

## II. CHAIN-TERMINATING REACTIONS

The best known of the chain-terminating reactions are those involving the recombination of atoms. Many studies with atomic hydrogen have shown that the recombination occurs at every collision during which a third body is present to remove some of the energy (2, 10, 32). Similarly, a comparison of the thermal and photochemical rates of formation of hydrogen bromide has led to the conclusion that bromine atoms recombine by a triple collision mechanism (5, 14). Ritchie (23) and Hilferding and Steiner (13) have studied the relative efficiencies of different molecules as the third body. Some idea of the range encountered is given by rate constants for the reaction

$$Br + Br + M = Br_2 + M + \text{k.e.}$$

taken from the paper by Hilferding and Steiner (see table 1). The variation is very similar to that found for the quenching of fluorescence by these gases. On the basis of these observations it seems reasonable to assume that any atom recombination process occurs at approximately every triple collision if the reaction is homogeneous.

The heterogeneous recombination of atoms depends quite markedly on the nature of the surface involved. It was found in the very first experiments with hydrogen atoms that dry glass or quartz surfaces are very much more effective in causing the recombination than ones which had not been dried (33). Metallic surfaces were also found to be very effective in causing recombination. Experiments with the hydrogen–bromine reaction at such pressures that the bromine atoms recombine on the wall show that the rate depends on the previous treatment of the walls (13). Another example is found in the hydrogen–chlorine reaction in which Bodenstein and Winter (6) calculated that only one collision in six thousand on a silver chloride surface resulted in removal of the chlorine atom. A comparison of their quantum yields with values obtained in the presence of glass surfaces indicates that glass is about ten times as effective. The failure of the atoms to react at every collision with the surface does not seem to be due to the requirement of any heat of activation, but rather to a low value of the accommodation coefficient. This idea is supported by a comparison of the photochemical temperature coefficients for the hydrogen–chlorine reaction as obtained by Hertel (12) and by Potts and Rollefson (21) with the value obtained by Rodebush and Klingelhoefer (24) for the reaction of chlorine atoms with hydrogen molecules, which shows that the latter reaction is capable of accounting for the entire temperature coefficient of the former. The principal difficulties in the way of securing exact values for the rate constant of such a chain-terminating reaction are the determination of the accommodation coefficient and the rate of approach to the wall. The latter rate is complicated by the fact that, usually, the heat of reaction sets up convection currents which make it

TABLE 1

*Rate constants for* $Br + Br + M$

| M | $H_2$ | He | A | $N_2$ | $Br_2$ | HBr | HCl | CO |
|---|---|---|---|---|---|---|---|---|
| $k \times 10^{-15}$ | 1.25 | 0.47 | 0.11 | 0.82 | 2.6 | 2.1 | 4.7 | 6.3 |

virtually impossible to decide on an average path length. On the whole, the error in the estimation of the rate of a chain-terminating process involving atoms is probably not greater than a factor of one hundred, whether it is a homogeneous or a heterogeneous reaction.

If the chain-terminating reaction involves more complex groups, more varieties of reaction are introduced. The surface reactions and the triple collision mechanism for association reactions are possible here as well as with atoms. However, it cannot be said with certainty that the association reactions do not involve heats of activation. Furthermore, it is possible for two radicals to combine to form a single molecule by a process which is the reverse of predissociation without having a third body present. In such a case, the quasi-molecule formed would have a sufficiently long life to lose some of its energy in a collision and become a stable molecule. Finally we have the possibility of two radicals reacting to form normal molecules. Some examples of these types of reaction which have been assumed are

$$COCl + Cl \rightarrow CO + Cl_2 \tag{1}$$

$$CH_3 + CH_3 \rightarrow C_2H_6 \tag{2}$$

$$C_2H_5 + C_2H_5 \rightarrow C_2H_4 + C_2H_6^* \tag{3}$$

The evidence for these reactions is not very conclusive, as the experiments have been such that other possibilities have been present. In support of reaction 2 we may cite the formation of ethane in the photolyses of lead tetramethyl (17), acetone (18), or methyl ethyl ketone (19). Reaction 3 has been assumed frequently, but probably the best evidence for it is the formation of ethane and ethylene in the photolysis of ethyl iodide (9). The magnitudes of the activation energies for these reactions are at present unknown. They are probably not large, but even a small activation energy would introduce a rather large uncertainty into the specific reaction rate. Until further data are available, we must conclude that the constants for reactions between two radicals are not sufficiently well known to be used in calculating rates of photochemical chain reactions.

### III. CHAIN-CONTINUING REACTIONS

The direct measurement of the rate constants for reactions of the type involved in the propagation of chains has been limited to a very few cases involving atoms. Most of these reactions involve hydrogen or one of the halogen atoms. The specific rate of the reaction

$$Br + H_2 \rightarrow HBr + H$$

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* As the concentrations of these radicals are always very low, trimolecular processes involving them must be considered improbable.

can be obtained from the thermal rate of formation of hydrogen bromide if we assume that bromine atoms and molecules are in equilibrium in the reaction mixture. On the basis of data obtained from the experimental study of both the thermal and photochemical formation of hydrogen bromide, Bodenstein and Lütkemeyer (5) give for the rate constant

$$\log k = -\frac{3859}{\mathrm{T}} + 13.862$$

which corresponds to an activation energy of 17,640 cal. The reaction is endothermic to the extent of 14,500 cal., so the activation energy is only slightly greater than the energy required to offset the endothermicity of the reaction. The study of the rate of formation of hydrogen bromide also tells us that the ratio of the rate constants for the reactions

$$H + Br_2 \rightarrow HBr + Br$$

and

$$H + HBr \rightarrow H_2 + Br$$

is 8.6 over a very wide temperature range. This fact suggests that the heats of activation for these reactions are zero, the only difference being in the so-called "steric factor".

The rate of the reaction

$$Cl + H_2 \rightarrow HCl + H$$

was measured directly by Rodebush and Klingelhoefer (24), who used a known concentration of chlorine atoms produced by an electric discharge in chlorine gas. They found that the rate was given essentially by the number of collisions multiplied by $e^{-6000/RT}$ with the uncertainty in the numerator of the exponent being approximately 1000 cal. A similar value was obtained from the measurements by Hertel (12) and by Potts and Rollefson (21) of the temperature coefficient of the photochemical reaction of oxygen-free mixtures of hydrogen and chlorine, if it was assumed that the chain-terminating step involved no heat of activation.

A number of reactions of hydrogen atoms have been studied by preparing a measurable concentration of the atoms by means of an electrical discharge and passing these atoms into some other gas. The most important reaction studied by this method is the transformation of para-hydrogen into ortho-hydrogen. The fraction of the collisions between hydrogen atoms and hydrogen molecules which result in reaction is $2 \times 10^{-6}$ and the heat of activation is approximately 7000 cal. Other reactions which have been tried include those with oxygen, water, the halogens, the hydrogen halides, some hydrocarbons, hydrogen sulfide, and methyl halides. Under these conditions most of these reactions proceed too fast to obtain accurate measurements, so the only conclusion which can be drawn is that the hydrogen atoms are destroyed in less than one hundredth of a second, which means that at least one collision in $10^4$ is effective. The activation energy is therefore either zero or very small.

Other methods which have been used to obtain estimates of the rates of the steps in a chain process are (*1*) studies of the overall rate with appropriate assumptions concerning the chain-starting and chain-terminating reactions, and (*2*) studies of systems in which two reactions compete for the same reactive intermediate. The validity of both of these methods depends on the assumption that the mechanism used in the calculation is correct. It is essential therefore that any other mechanisms be excluded on the basis of the experimental evidence before rate constants obtained by these methods may be considered valid. We may illustrate the first method by referring to the formation of hydrogen chloride from the elements. The mechanism which seems to explain the behavior of oxygen-free mixtures of hydrogen and chlorine is expressed by the following equations:

$$k_3 \quad Cl_2 + h\nu \rightarrow 2Cl \qquad (1)$$

$$k_2 \quad Cl + H_2 \rightarrow HCl + H \qquad (2)$$

$$k_3 \quad H + Cl_2 \rightarrow HCl + Cl \qquad (3)$$

$$k_4 \quad Cl \rightarrow 1/2\ Cl_2 \text{ (on the walls of the reaction vessel)} \qquad (4)$$

This leads to the rate expression

$$\frac{d(HCl)}{dt} = \frac{k_1 k_2}{k_4} I_{abs.}(H_2).$$

If the light absorbed corresponds to the continuum in the chlorine spectrum, there is plenty of evidence to support the assumption that $k_1 = 2$. The constant $k_4$ is subject to much greater uncertainty. Usually, it is assumed that every collision of an atom with a surface is effective in causing recombination, but recently Bodenstein and Winter (6) have presented data which indicate that only one collision in six thousand of chlorine atoms with a silver chloride surface leads to the formation of molecules. This effect does not seem to be due to a heat of activation but rather is an accommodation coefficient analogous to the steric factor for bimolecular reactions. Collisions with glass or quartz surfaces are much more effective, but it is probable that the erratic rates of formation of hydrogen chloride that have been reported are at least partially due to the variation of this $k_4$ in different experiments. If we assume that reaction 4 has no heat of activation, then the entire heat of activation for the overall reaction is due to reaction 2. The value of $k_2$ may be calculated approximately by multiplying the collision number by $e^{-Q/T}$, where $Q$ is the heat of activation. The efficiency factor for collisions between molecules possessing the necessary energy cannot be determined any more exactly than we know $k_4$. Usually in systems of this type the uncertainty in the heat of activation is sufficient to mask any uncertainty in the collision number or efficiency factor.

This type of calculation may be applied, with the same degree of approximation, to any other chain reaction involving atoms in the initial and final steps and having the rate determined by one step in the chain process. If radicals are involved in the initial or final steps, both of the uncertainties become much greater particularly on account of the activation energy of the chain-terminating step. Thus a reaction such as

$$2CCl_3 + Cl_2 \rightarrow 2CCl_4$$

which Schumacher and Wolf (31) assumed to be the chain-terminating step in the chlorination of chloroform probably requires some heat of activation, but the magnitude of this heat is not even approximately known. The same statement can be made about the other processes which we have discussed in the section on chain-terminating processes.

A further complication arises frequently owing to the complexity of the assumed mechanism. Thus, instead of having the overall rate constant expressed in terms of the constants for initial and final steps and one step of the chain ($k_2$ in the case of the formation of hydrogen chloride) we find that the constants of two or more steps of the chain appear in the rate equation. Such constants are indeterminate from rate measurements alone, and up to the present time no one has determined the constants for any system of this type from experimental data.[2]

The second method for evaluating the constants of steps in a chain, the use of competitive reactions, has not been used very extensively as yet. We have already cited the competition between hydrogen bromide and bromine for hydrogen atoms in the formation of hydrogen bromide. Other examples which have been studied quantitatively include the competition of carbon monoxide and hydrogen for chlorine atoms (4, 26), of oxygen and chlorine for COCl (25, 29), and of ozone and oxygen for oxygen atoms (30). The experiments determine only the ratio of the two rate constants but if one rate constant, as, for example, that for the reaction between atomic chlorine and hydrogen, is known from other studies, then the other can be calculated. We have already seen that the rate constant for the reaction

$$Cl + H_2 \rightarrow HCl + H$$

[2] Bodenstein and his students claim to have made such determinations for the formation of phosgene, but the details of their calculations have not been published. It may be remarked here that in their published work they have neither proven their mechanism to the exclusion of others nor listed enough independent equations based on experimental data to determine all of the constants involved in their rate equations. See, however, contribution No. 9 to this Report.

is pretty well known, therefore we may use this reaction as a means of measuring chlorine-atom concentrations in reaction mixtures and thus the specific rates of other reactions. Naturally this method is limited to those systems in which the chlorine atoms react at a rate comparable with that with hydrogen. Thus, the observation that in mixtures of ethylene, hydrogen, and chlorine the halogen adds to the ethylene with no appreciable formation of hydrogen chloride tells us that the first step in the addition reaction is very fast but does not permit an exact calculation of its specific rate.

Many reactions of hydrogen atoms have been studied by determining the concentration of the atoms by the rate of the conversion of para-hydrogen to ortho-hydrogen. This is essentially the method of competing rates, except that the atoms are not destroyed by the test reaction. The rate constant for this conversion has been given as $2 \times 10^9 Te^{-7000/RT}$, which indicates the order of magnitude of the rates which may be studied by this method. One point which has been overlooked in some investigations is that if the hydrogen atoms react very rapidly with other substances in the reaction mixture the concentration of the atoms may not be great enough to cause appreciable conversion of para-hydrogen to ortho-hydrogen. This method has been applied by Cremer, Curry, and Polanyi (7) to the study of reactions of atomic hydrogen with alkyl halides. Their results were only semiquantitative and their experimental method limited them to reactions for which the activation energy was in the range $2800 < Q < 7200$ cal. Farkas and Sachsse (10) studied $H + O_2 \rightarrow HO_2$ and $H + CO \rightarrow HCO$. They concluded that the former occurred once in seven hundred fifty triple collisions and the latter once in ten triple collisions. Patat (20) has also used this method to determine the concentrations of hydrogen atoms present during the decompositions of a number of organic compounds. On account of the complexity of such systems only qualitative results concerning rate constants were obtained.

In conclusion, it must be stressed that the great need at present is the determination, by methods free from assumptions, of a few rate constants for reactions of the type we have discussed. No matter how reasonable assumptions may seem, any rate constants based on them are little better than guesses. This is especially true in complex systems as, under such conditions, usually several mechanisms are capable of describing the facts, and hence there is no certainty that we are dealing with the right set of reactions. The constants which have been calculated for such systems in the literature must be looked upon as reasonable interpretations rather than as established facts.

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# THE SECONDARY PROCESSES IN THE PHOTODECOMPOSITION OF AMMONIA AND HYDRAZINE[1]

HUGH S. TAYLOR

*Department of Chemistry, Princeton University, Princeton, New Jersey*

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Since the diffuse bands of the ammonia spectrum were interpreted by Bonhoeffer and Farkas (1) as due to a dissociation of the molecule, the direction of further research on the photodissociation process has been towards an elucidation of the secondary processes in such a manner that the low quantum yield ($\sim 0.2$) might be satisfactorily explained. For the primary process, it has been generally assumed that

$$NH_3 + h\nu = NH_2 + H \tag{1}$$

though the reaction,

$$NH_3 + h\nu = NH + H_2 \tag{1a}$$

cannot be excluded on energetic grounds. It would, however, suggest an influence of molecular hydrogen which is not found experimentally in the photoreaction, although there is an effect in the reaction initiated by $\alpha$-particles and ions, in which case, at higher pressures, $NH^+$ is certainly formed by secondary processes. The first reaction accounts for the presence of atomic hydrogen, made certain by the measurements of Geib and Harteck (6) and of Farkas and Harteck (4) on para-hydrogen conversion in ammonia undergoing decomposition.

Gedye and Rideal (5), using a streaming system, obtained yields of hydrazine from the photodecomposition of ammonia of as high as 57 per cent of the stoichiometric yield by the equation

$$2NH_3 \rightarrow N_2H_4 + H_2$$

The hydrazine yield decreased rapidly as the temperature of the system was increased. Koenig and Brings (7), and more recently Welge and Beckman (16), have obtained positive confirmation of the formation of hydrazine by photolysis of ammonia in a static system. The amounts obtained, however, were very small.

Indirect evidence of the production of amine radicals may be obtained from the photodecomposition of solutions of alkali metals in liquid am-

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[1] Contribution No. 8 to the Third Report of the Committee on Photochemistry, National Research Council.

monia (13). Liquid ammonia does not photodecompose when pure, but does decompose on the addition of alkali metals. The sole products are hydrogen and amide ion, $NH_2^-$, in equivalent amounts, and the quantum yield is well under unity. Alkali metals virtually completely dissociate in liquid ammonia into positive metal ions and free electrons which become strongly solvated with the ammonia. It would appear, therefore, that in pure liquid ammonia deactivation or primary recombination effectively retards the decomposition, while in the presence of solvated electrons the $NH_2$ radicals are stabilized by the formation of amide ion, thus permitting the decomposition to proceed. The mechanism, according to this hypothesis, would be

$$NH_3 + h\nu \rightarrow NH_2 + H$$

$$NH_2 + H + M \rightarrow NH_3 + M \quad \text{(primary recombination)}$$

$$NH_2 + (-) \rightarrow NH_2^-$$

$$H + H + M \rightarrow H_2 + M$$

The majority of workers have accounted for the low quantum yield in ammonia decomposition by a recombination process,

$$NH_2 + H = NH_3 \qquad (3)$$

though Farkas and Harteck (4) pointed out certain difficulties in accepting this, due to the low stationary state concentration of atomic hydrogen, especially if reaction 3 requires a third body. That ammonia is regenerated during the secondary processes was made definite by Taylor and Jungers (15), who showed the formation of deuteroammonias in mixtures of decomposing $NH_3$ and deuterium atoms produced from deuterium molecules by excited mercury. No exchange occurred unless the ammonia was undergoing photodecomposition. By investigating the photochemical decomposition in the region of very small decompositions Welge and Beckmann (16) found that the quantum yield measured by hydrogen produced approached unity; hence they concluded that the recombination reaction (reaction 3) does not play an important rôle. The products in such circumstances would be substantially hydrogen and hydrazine. They further assumed the secondary processes to be substantially heterogeneous, with a little of the hydrazine reacting with the atomic hydrogen to give ammonia, as shown by Dixon (2). With larger amounts of products this effect would be exaggerated and the non-condensable products would approach the stoichiometric ratio due to hydrazine decomposition.

In experiments of Elgin and Taylor (3) it was shown that the total process in both the photochemical and photosensitized decomposition of hydrazine can be with fair accuracy expressed by the stoichiometric equation

$$2N_2H_4 = 2NH_3 + N_2 + H_2 \qquad (4)$$

With hydrazine in the presence of ammonia, even when only a small fraction of the light was absorbed by the hydrazine, it was shown, by Ogg, Leighton, and Bergstrom (14), that hydrazine was the compound which disappeared, with a quantum yield of 1.28 on total quanta absorbed. Such facts provide considerable support for their conclusion, recently restated by Mund and van Tiggelen (12), that the process which regenerates ammonia and causes the low quantum yield is not reaction 3 but the reaction

$$N_2H_4 + H = NH_3 + NH_2 \qquad (5)$$

a reaction which would also explain the work of Taylor and Jungers with deuterium atoms.

The nitrogen which is formed ultimately in the photodecomposition of ammonia must arise, therefore, from further decomposition of the hydrazine or $NH_2$ radicals or both. The assumption of Ogg, Leighton, and Bergstrom that this occurs by the reaction

$$N_2H_4 + 2NH_2 = 2NH_3 + N_2 + H_2 \qquad (6)$$

has been modified by Mund and van Tiggelen in a sequence of secondary processes which more satisfactorily than any alternatives, it would appear, accounts for the kinetics of the reaction and its quantum yield. The sequence is:

$$\begin{array}{rcll}
20(NH_3 + h\nu & = & NH_2 + H) & (1)\\
17(2NH_2 + M & = & N_2H_4) & (2)\\
16(N_2H_4 + H & = & NH_3 + NH_2) & (5)\\
1(N_2H_4 + 2NH_2 & = & 2N_2 + 4H_2) & (6a)\\
\underline{2(H + H + M} & \underline{=} & \underline{H_2)} & (7)\\
20h\nu + 4NH_3 & = & 2N_2 + 6H_2 &
\end{array}$$

This sequence is based on a quantum yield of 0.2 at 1 atm. pressure, and the numerical coefficients by which the equations are multiplied must evidently be proportional to the velocities of the corresponding reactions. It leads to the following expression of Mund and van Tiggelen for the quantum yield

$$\Phi = \frac{1}{0.875 + \sqrt{0.0156 + K\sqrt{P/v}}}$$

where $v$ ($\alpha I_{\text{abs.}}$) is the velocity of reaction expressed as the number of molecules of ammonia decomposed to nitrogen and hydrogen per cubic centimeter per second, $P$ is the total pressure, and $\Phi$ the quantum yield equal to $Q/v$, where $Q$ is the number of ammonia molecules per cubic centimeter per second primarily decomposed.

This equation reproduces the tendency of $\Phi$ to vary with the pressure. With $\Phi = 0.2$ at 1 atm. one calculates a value of $\Phi = 0.314$ at 0.1 atm. and 0.126 at 8.5 atm. The former is in agreement with the data of Wiig (18) and the latter with the measurements of Ogg, Leighton, and Bergstrom. At low pressures the influence of the walls begins to predominate and will assist especially reactions 2 and 7. Its effect on the quantum yield will be equivalent to that of high pressures in the gas phase, i.e., will lower the quantum yield as Wiig observed. The influence of the intensity or the velocity of decomposition, $v$, on the quantum yield is of the same order of magnitude as the equation suggests, as elucidated in a recent research by Mund, Brenard, and Kaertkemeyer (11), and as suggested by the work of Ogg, Leighton, and Bergstrom, by Wiig and Kistiakowsky (20), and by more recent measurements of Wiig (19). The Mund–van Tiggelen numerical values for the relative rates of the several reactions do not constitute a unique solution, as is evident from an analysis by Leighton (8). For the ratios 20:17:16:1:2 of the above sequence, Leighton substitutes the sequence

$$10(NH_3 + h\nu = NH_2 + H)$$

$$7(2NH_2 + M = N_2H_4 + M)$$

$$6(H + N_2H_4 = NH_3 + NH_2)$$

$$2(2NH_2 + N_2H_4 = 2NH_3 + N_2 + H_2)$$

$$2(H + H + M = H_2 + M)$$

It will be noted that in this sequence the nitrogen-producing mechanism simultaneously regenerates ammonia, whereas the Mund–van Tiggelen reaction does not. Both yield similar expressions for the relation between quantum yield, pressure, and intensity. Leighton believes his reaction producing nitrogen to be superior, because it accounts for the 1:1 $N_2$:$H_2$ ratio observed in the ammonia-sensitized decomposition of hydrazine (see later).

It has been known since Warburg's original researches on this reaction that neither molecular nitrogen nor hydrogen influenced the quantum yield. The above mechanism is in accord with such inertness except in so far as it might influence the total pressure, $P$; this influence is small, as seen. On the other hand, atomic hydrogen was shown by Melville (9) to inhibit strongly the photodecomposition of ammonia and the same is true of the photosensitized decomposition (10). This effect, which Melville attributed to the recombination reaction (reaction 3), is rather to be ascribed to the ammonia regenerative reaction with hydrazine (reaction 5), the velocity of which, as is to be seen from the magnitude of the molecular coefficient, 16, is very high. Analysis shows that in addition to the effect of atomic hydrogen concentration there is also an effect due to the diminution in $v$, the total decomposition. The cumulative effect of these two factors is evident in the data both of Mitchell and Dickinson and of Melville.

Farkas and Harteck found a sharp maximum in the atomic hydrogen concentration from the photodecomposition of ammonia in the presence of hydrogen when the ammonia was only 10 mm. in a total pressure of 30 to 70 cm. This led these authors to the assumption of $NH_4$ radicals in equilibrium with $NH_3 + H$. The maximum should bear some relation to the maximum observed in the quantum yield but this latter, though similar in form, is displaced to higher ammonia pressures. This discrepancy is not yet elucidated.

The objection that might be raised to the Mund–van Tiggelen development, namely, that nitrogen only results from the termolecular process (from $2NH_2 + N_2H_4$, reaction 6) and not from such a process as suggested, among others, by Wiig,

$$NH_2 + NH_2 = N_2 + 2H_2 \tag{8}$$

is discussed in the original communication of Mund and van Tiggelen and more recently by them in a comment on the newer work of Wiig. They point out that reaction 8 always leads to kinetic expressions from which the observed increase of quantum yield with velocity of decomposition cannot be deduced, and, further, it fails to account for the small variation of yield between 1 and 8.5 atm. found by Ogg, Leighton, and Bergstrom. One might expect that other molecules than $N_2H_4$ could act each with a particular efficiency in the recombination–decomposition process (reaction 6) of the Mund–van Tiggelen scheme. To introduce such possibilities into the kinetic scheme would further complicate the equation derived, and the experimental data at present are not accurate enough to justify, such further refinements.

In the ammonia-sensitized hydrazine decomposition experiments of Ogg, Leighton, and Bergstrom, the two initial stages are quite clear, namely, reactions 1 and 5 of the ammonia scheme above.

$$NH_3 + h\nu = NH_2 + H \tag{1}$$

$$H + N_2H_4 = NH_3 + NH_2 \tag{5}$$

The Mund–van Tiggelen mechanism would then give

$$N_2H_4 + 2NH_2 = 2N_2 + 4H_2 \tag{6a}$$

which would mean a quantum yield of 2 at a maximum diminished by the recombination process,

$$2NH_2 + M = 2N_2H_4 \tag{2}$$

The product gas should be 33 per cent nitrogen and 66 per cent hydrogen. The Ogg, Leighton, and Bergstrom mechanism would give

$$N_2H_4 + 2NH_2 = 2NH_3 + N_2 + H_2 \tag{6}$$

again a maximum quantum yield of 2 on the hydrazine disappearing but a 1:1 ratio of nitrogen and hydrogen. This ratio was actually found by these authors and also by Elgin and Taylor. Wenner and Beckmann (17) found quantum yields ranging from 1 at low pressures to 1.7 at higher pressures and hydrogen concentrations ranging from 58 to 64 per cent in the same pressure range of 2 to 14 mm., decreasing toward 50 per cent with increasing pressure.

The primary mechanism in hydrazine decomposition is still uncertain. If it be

$$N_2H_4 + h\nu = 2NH_2$$

then it would be necessary to fall back on reaction 6 to explain the ammonia formation observed. On the other hand, a primary mechanism

$$N_2H_4 + h\nu = N_2H_3 + H$$

could by reaction 5 regenerate one-half the observed ammonia with the atomic hydrogen. The $NH_2$ and the $N_2H_3$ thus produced could, by several alternative mechanisms already proposed, but for which there is as yet no experimental test, yield $NH_3 + N_2 + H_2$ in approximate accord with the observations. The para-hydrogen conversion reaction might be employed to test these two alternative mechanisms for the primary photoprocess.

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# SECONDARY PROCESSES IN THE PHOTOCHLORINATION OF CARBON MONOXIDE AND HYDROGEN[1]

HUGH S. TAYLOR

*Department of Chemistry, Princeton University, Princeton, New Jersey*

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Since the publication of the Second Report of the Committee on Photochemistry considerable progress has been made towards a final and quantitative formulation of the secondary processes both in the hydrogen–chlorine combination and in the reactions, thermal and photochemical, of phosgene synthesis and decomposition. These several reactions have been the principal objective of the researches of Bodenstein and his school. At the present time Bodenstein (6) is occupied with the publication of the definitive conclusions of this long series of investigations and is attempting to incorporate within the framework of those conclusions, or reject for reasons ascertained, the auxiliary data that have accumulated from the investigations of other workers, notably Rollefson (15, 19, 20, 21), Ritchie (17, 18), Norrish (16), Allmand (1), and others. A discussion of the earlier work (3, 7, 8, 9, 10, 15, 22, 23, 24, 26) was included in the Second Report.

## I. THE PHOSGENE REACTIONS

For the photoreaction at room temperatures and pressures over 100 mm. the kinetic expression is

$$\frac{d[COCl_2]}{dt} = \kappa_1 I_{abs.}^{1/2} [Cl_2][CO]^{1/2}$$

This equation is derivable from the Bodenstein reaction scheme:

$$Cl_2 + E = 2Cl \qquad (1)$$

$$Cl + CO + M = COCl + M \qquad (2)$$

$$COCl + M = CO + Cl + M \qquad (3)$$

$$COCl + Cl_2 = COCl_2 + Cl \qquad (4)$$

$$COCl + Cl = CO + Cl_2 \qquad (5)$$

$$Cl + \text{wall} = 1/2\ Cl_2 \qquad (5')$$

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[1] Contribution No. 9 to the Third Report of the Committee on Photochemistry, National Research Council.

Equations 2 and 3 lead, on the Bodenstein interpretation, to an equilibrium expressed by the equation:

$$K_{\mathrm{COCl}} = [\mathrm{Cl}][\mathrm{CO}]/[\mathrm{COCl}]$$

The first five reactions, with the assumed equilibrium, yield the kinetic expression for $\kappa_1$, which is obeyed by experimental results, under the given conditions, except in the beginning of the reaction and towards the end when reaction 5′ becomes important with low concentration of COCl. The same chain-ending process (5′) becomes important also at higher temperatures and lower concentrations (< 90 mm.). At high temperatures the kinetic expression then becomes

$$\mathrm{d}[\mathrm{COCl_2}]/\mathrm{d}t = \kappa_2 I_{\mathrm{abs.}}\,[\mathrm{Cl_2}][\mathrm{CO}]$$

The reaction constants $\kappa_1$ and $\kappa_2$ are related by the following equations to the several constants of the individual reaction steps:

$$\kappa_1 = \frac{k_4}{k_5^{1/2} K_{\mathrm{COCl}}}; \qquad \kappa_2 = \frac{k_4}{k_{5'} K_{\mathrm{COCl}}}$$

By reason of the additional investigations of Bodenstein, Brenschede, and Schumacher (4, 5), Bodenstein (6) has rejected the interpretation by Rollefson (19, 20), which makes use of $\mathrm{Cl_3}$ as an intermediate, and maintains his contention that the COCl equilibrium exists in spite of reaction 4 in which this intermediate is steadily consumed.

The thermal formation and decomposition between 350° and 450°C. yield the kinetic expression

$$\mathrm{d}[\mathrm{COCl_2}]/\mathrm{d}t = \kappa_{\mathrm{th}}\,[\mathrm{Cl_2}]^{3/2}[\mathrm{CO}] - \kappa'_{\mathrm{th}}[\mathrm{Cl_2}]^{1/2}[\mathrm{COCl_2}]$$

The reaction scheme pertaining to this is

$$\mathrm{Cl_2} \rightleftarrows 2\mathrm{Cl}\ (\text{equilibrium}; K_{\mathrm{Cl_2}} = [\mathrm{Cl}]^2/[\mathrm{Cl_2}]) \qquad (1)$$

$$\mathrm{Cl} + \mathrm{CO} \rightleftarrows \mathrm{COCl}\ (\text{equilibrium}; K_{\mathrm{COCl_2}} = [\mathrm{Cl}][\mathrm{CO}]/[\mathrm{COCl}]) \qquad (2, 3)$$

$$\mathrm{COCl} + \mathrm{Cl_2} = \mathrm{COCl_2} + \mathrm{Cl}\ (\text{formation}) \qquad (4)$$

$$\mathrm{COCl_2} + \mathrm{Cl} = \mathrm{COCl} + \mathrm{Cl_2}\ (\text{decomposition}) \qquad (4')$$

The reaction constants $\kappa_{\mathrm{th}}$ and $\kappa'_{\mathrm{th}}$ are then given by the equations

$$\kappa_{\mathrm{th}} = \frac{k_4 K_{\mathrm{Cl_2}}^{1/2}}{K_{\mathrm{COCl}}} \quad \text{and} \quad \kappa'_{\mathrm{th}} = k_{4'} \cdot K_{\mathrm{Cl_2}}^{1/2}$$

### *The numerical data for the equilibrium and reaction constants*

Bodenstein, Brenschede, and Schumacher (6) have recently completed a calculation of the numerical data for the several individual reactions and for the equilibria involved. Their results are summarized in the following.

For the equilibrium between chlorine molecules and atoms the accurate data of Giauque and Overstreet (13) are available

$$\log K_{\mathrm{Cl}_2} = \frac{57156}{4.571T} + 3.820$$

For the equilibrium

$$\mathrm{COCl} \rightleftarrows \mathrm{CO} + \mathrm{Cl}$$

both the heat of reaction and the constant must be so chosen that

$$\log K_{\mathrm{COCl}} = \log k_3 - \log k_2$$

Further, $\log k_3$ must be sufficiently greater than $\log k_4$ so that the assumption of practical equilibrium in spite of reaction 4 can be maintained. By trial, the equation obtained was

$$\log K_{\mathrm{COCl}} = -\frac{5676}{4.571T} + 1.770$$

For reactions 4 and 5 the data are given in the form of equations

$$\log k = -\frac{E}{4.571T} + \log Z_1 + 1/2 \log T - \log f$$

where $E$ is the activation energy, $Z_1$ the collision yield for $T = 1°\mathrm{K.}$, and $f$ is the steric factor. In these equations $E$ and $f$ are both adjustable.

$$\log k_4 = -\frac{2612}{4.571T} + 1/2 \log T + 10.101 - 3.871$$

$$\log k_5 = -\frac{1940}{4.571T} + 1/2 \log T + 10.106 - 0.976$$

The equilibrium constant $K_{\mathrm{COCl}}$ yields the value 5676 cal. for the heat of formation of COCl. The heat of formation of phosgene from $\mathrm{CO} + \mathrm{Cl}_2$ is 26,100 cal. With these two data and the value of 2612 cal. from $\log k_4$ the expression for $k_{4'}$ becomes

$$\log k_{4'} = -\frac{23036}{4.571T} + 1/2 \log T + 10.110 - 0.171$$

With these several equations the calculated values for the overall reactions, photochemical and thermal, from room temperatures to 450°C. agree excellently with the measured values. Bodenstein sees in this concordance the best and most convincing support for the reaction schemes assumed and for the equilibrium,

$$\mathrm{CO} + \mathrm{Cl} = \mathrm{COCl}$$

which Rollefson (19) especially has questioned. The heat of formation of COCl, 5676 cal., is materially lower than the value of 10 kg-cal. originally estimated, the higher figure justifying the objection of Rollefson. With the newer numerical data, Bodenstein is of the opinion that the several reactions are described very satisfactorily and, he believes, in final and definitive form.

## II. THE HYDROGEN–CHLORINE PHOTOREACTION

The reaction sequence in the hydrogen–chlorine combination is, it is quite generally agreed, the Nernst chain mechanism, with the chains normally terminated by interaction of atomic hydrogen with oxygen impurities. The reaction scheme thus becomes

$$Cl_2 + E = 2Cl \tag{1}$$

$$Cl + H_2 = HCl + H - 800 \text{ cal.} \tag{2}$$

$$H + HCl = H_2 + Cl + 800 \text{ cal.} \tag{2'}$$

$$H + Cl_2 = HCl + Cl \tag{3}$$

$$H + O_2 + M = HO_2 + M \tag{4}$$

The numerical data for the several reactions are still subject to final revision but, according to Bodenstein, the most reliable data now available are obtained from the following equations for velocities, the units being in moles per liter per second.

$$\log k_2 = \frac{5750}{4.571T} + 1/2 \log T + 10.47 - 0.92 = 6.40 \text{ at } 288°\text{K.}$$

$$\log k_{2'} = \frac{4950}{4.571T} + 1/2 \log T + 10.48 - 1.39 = 6.55 \text{ at } 288°\text{K.}$$

$$\log k_3 = -\frac{2550}{4.571T} + 1/2 \log T + 10.50 - 0.78 = 9.01 \text{ at } 288°\text{K.}$$

$$\log k_4 = -\frac{500}{4.571T} + 1/2 \log T + 10.42 - 1.60 - \log f$$

In the last expression the datum $-1.60$ represents the logarithm of the number of three-body collisions (moles per liter). The value of $\log f$ varies with M according to the best evidence. Bodenstein assigns the following values: $\log f = -1.37$ for $M = Cl_2, H_2, O_2$; $\log f = -0.77$ for $M = HCl$; and $\log f \sim -1.07$ for $M = H_2 + Cl_2$ mixture.

The value $E_2 = 5750$ cal. is obtained from Hertel's value for the temperature coefficient for 10° = 1.37. Hence, since $E_2 - E_{2'} = 800$ cal.,

$E_{2'}$ becomes 4950 cal. From a comparison of

$$H + HCl = H_2 + Cl$$

with

$$H + Cl_2 = HCl + Cl$$

(in para-hydrogen) and the variation of $k_{2'}/k_3$ with temperature, $E_{2'} - E_3 = 2400$ cal. and so $E_3 = 2550$ cal. From Hertel's data (14) it follows also that $E_3$ would be 2060 cal. if $H + O_2 + M$ were temperature-independent. To reconcile the two data for $E_3$ we therefore can set $E_4$ equal to 500 cal.

The absolute value of $\log k_2 = 6.40$ at 288°K. comes from a comparison, by Brenschede and Schumacher (4, 5), of

$$CO + Cl + Cl_2 = COCl_2 + Cl$$

with

$$Cl + H_2 = HCl + H$$

Hence $\log f = -0.92$. The absolute value of $\log k_4 = 8.60$, in the mean, was obtained by Bodenstein from analysis of data by Frankenburger and Klinckhardt (12) and by Bates (2) on peroxide formation from atomic hydrogen. From data of Ritchie (18), with experiments in which both water and hydrogen chloride were formed, $\log k_3 - \log k_4 = 0.41$ and hence $\log k_3 = 9.01$. The steric factor corresponding is then $\log f_3 = -0.78$. From Hertel's data already discussed $\log k_3 - \log k_{2'} = 2.46$. Hence $\log k_{2'}$ at 288°K. is 6.55 and $\log f_{2'} = -1.39$. The uncertainty in the values for $\log k$ is estimated by Bodenstein to be not greater than 0.3.

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# THE ACTION OF OPTICAL SENSITIZERS ON THE PHOTOGRAPHIC PLATE[1]

G. KORNFELD

*Kodak Research Laboratories, Rochester, New York*

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In this paper a survey is given of the published work dealing with the mechanism of optical sensitizing of photographic emulsions, the connection between sensitizing and other properties, and the mechanism of desensitizing. There are some facts available concerning the first point, and a close connection has been established between light absorption and sensitizing power. Up to the present time, however, only fragmentary information has been published on the relation between sensitizing power and other properties and on the nature of desensitizing.

## I. INTRODUCTION

### *The spectral range of photographic action*

Since photochemical action in any system is necessarily connected with its light absorption, the light absorption in silver halide emulsions is of fundamental importance for determining the spectral range of photographic action.

The absorption of pure silver bromide in a microcrystalline state was measured by Slade and Toy (1) in 1920. They found absorption beginning at about 450 m$\mu$ which strongly increased towards the violet and ultraviolet regions. Eggert and Noddack (2), in 1923, found the limit towards the long wave length region at 465 m$\mu$. In 1928 Eggert and Schmidt (3) undertook a very careful investigation of thin layers of microcrystalline silver bromide and silver chloride, for which they found the absorption limits towards the longer wave lengths, at 480 m$\mu$ and 400 m$\mu$, respectively. There is no limit towards the shorter wave lengths in pure silver bromide. Absorption and photochemical action occur throughout the whole ultraviolet region and beyond it. It is well known that the photographic plate was instrumental in Roentgen's discovery of x-rays. Photographic action, however, in this region of very large quanta is essentially different from that in visible and ultraviolet light. Glocker and Traub (4) found that, with x-rays, there was no threshold of sensitivity for small intensities,

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and Bunsen's reciprocity law was found to be valid over a long range. It is not to be expected that the law of photochemical equivalence will hold in the region of x-rays, where the photochemical action corresponds to the amount of energy transferred to secondary electrons. This was the conclusion from Glocker's (5) investigation in 1927. Eggert and Noddack (6) some time before had found that one quantum of x-rays absorbed corresponds to about $10^3$ silver atoms released. That the law of equivalence does not hold in the x-ray region was also confirmed by Günther and Tittel (7). Between 0.245 Å. and 1.54 Å. the number of silver atoms per quantum absorbed changed from 920 to 148, but the ratio between the energy of the secondary electrons and the amount of reduced silver was found to be fairly constant.

The absorption of gelatin is negligible in the x-ray region, but, in the visible and ultraviolet regions, the presence of gelatin in the photographic emulsion distorts the close correlation between absorption and photographic action which can be observed in pure silver halides. Eggert and Noddack (2) determined the absorption of emulsion-coated plates in the region of the longer wave lengths and found more than 20 per cent absorption, even at 615 mμ. This absorption is of no use in photography, however, since gelatin can not act as a sensitizer. In the far ultraviolet region gelatin actually impedes photographic action by its own strong absorption. For the region below 200 mμ, therefore, Schumann plates, which do not contain any gelatin, are used.

Absorption is not so well defined in a photographic emulsion as it is in pure silver bromide. It is dependent, to some extent, on the mode of preparation. In an investigation with Frankenburger, Fajans (8) was the first to point out the deforming influence of adsorbed ions on the crystal forces which naturally must result in a spectral shift. In several succeeding investigations this spectral shift was thoroughly examined by him and his coworkers (9, 10, 11, 12, 13). Recently de Boer (14) has quantitatively connected the spectral shift with the heat of adsorption in the normal and excited state.

There is another factor which influences the absorption even more during exposure, that is, photolytically developed silver in colloidal form. The phenomenon was discovered as early as 1840 by E. Becquerel (15, 16) with a Daguerreotype plate (silver iodide on silver) which could be made sensitive to the yellow and even to the red region by long exposure. He observed the same effect with silver bromide and silver chloride papers. He therefore called the blue end of the spectrum "exciting radiation" and the yellow and red regions "continuing radiation". Lüppo-Cramer (17) and Eder (18), in 1909, explained the phenomenon as optical sensitizing by colloidal silver, and Lüppo-Cramer was able to reproduce the phenomenon by adding colloidal silver to silver chloride. The great extension of the absorption region pointed clearly to the absorption of light by the colloidal silver and to its sensitizing property. This sensitizing property of colloidal silver, as well as of colloidal silver sulfide, in analogy to the organic sensitizing dyes was extensively considered by Sheppard (19).

In 1873 H. W. Vogel (20) discovered that some of the strongly absorbing organic dyes could be used as sensitizers for the photographic plate. Corallin was the first dye used by him to sensitize the plate for the yellow and green regions. He saw at once the significant correspondence between the absorption of the dye in solution and the sensitized region, although both regions do not coincide exactly, and he foresaw its practical importance. The value of this discovery can hardly be overemphasized, since panchromatic and orthochromatic plates were developed as a result, and the extension of photography during recent years far into the infrared region can be traced to its influence.

Most of the dyes which were employed as sensitizers in the beginning are now rarely used. At present nearly all the sensitizers used belong to the polymethine group, many of them being cyanine dyes. It is not intended here to describe in detail all the work that has been done on this subject. It ought to be mentioned, however, that close connections were found between the constitution of the dyes and their spectral range of absorption in solution. Once these connections were established, sensitizing dyes were synthesized for the whole visible region of the spectrum and through the infrared as far as 1356 m$\mu$ (21).

The systematic connection, however, has been confined so far to the constitution of a dye, on the one hand, and the intensity as well as the region of its absorption, on the other. As yet no evidence has been found to connect its sensitizing property with its chemical constitution or with any other quality.

A great number of empirical facts on optical sensitizers have been found, but it seems hardly possible to fit them into a consistent picture. The conflicting results of earlier experiments can be explained partly by the fact that the sensitizers used were often not chemically pure and in some cases were even combined with various admixtures, but, even with pure materials, the complex nature of the phenomena makes it difficult to arrive at simple laws. Desensitizing was frequently regarded as optical sensitizing with a negative sign, and the difference in constitution was connected with this antagonistic behavior. It is only recently that desensitizing has been recognized as a property common to all sensitizers. It has been fairly well established, moreover, that sensitizing and desensitizing belong to different stages in the formation of the latent image and probably take place at different spots on the silver bromide grain. As early as 1907 Sheppard and Mees (22) made a very clear statement regarding the different stages for the action of sensitizers and desensitizers in the primary process, but it seems generally to have been overlooked by other investigators. Then, in 1925, Sheppard (23) emphasized the fact that desensitizing does not produce any detectable shift in the spectral sensitivity. One year later von Hübl (24) stated quite clearly that, for a special spectral region, a desensitizer might as well be considered also an optical sensitizer, since both actions were not connected with each other, optical sensitizing depending on color, whereas desensitizing as a chemical reaction can be produced by colorless substances. In 1931, writing on "Sensitizing by Desensitizers", Lüppo-Cramer (25) stated that it seemed futile to divide the dyes into sensitizers and desensitizers, since the same dye might belong to either class, according to the conditions under which it was used. He supported this statement by several facts: (*1*) Many dyes known as optical sensitizers in silver bromide emulsions act as desensitizers in silver iodide emulsions. (*2*) If an acceptor for halogen is added to a silver bromide emulsion, many dyes known as desensitizers then act only as sensitizers. (*3*) To unripened emulsions some desensitizing dyes (Capri blue, Janus green) act as sensitizers when used in low concentrations.

A very cogent argument in favor of the above statement is the existence of optimum conditions for the sensitizing baths regarding concentration and time of bathing. This fact was discovered by Sheppard (57) as early as 1908 with a solution of an isocyanine dye. In 1933 Heisenberg (26) showed for three dyes, namely, pinacyanol, thiocarbocyanine, and selenocarbocyanine, that there is an optimal concentration for the adsorption of a sensitizing dye, at which nearly all the dye is adsorbed. With concentrations increasing beyond this optimal concentration, desensitizing sets in, and Heisenberg proved that this desensitizing effect is real, since it is much too large to be accounted for merely by the increased light absorption of the dye. This desensitizing effect of sensitizing dyes when used in larger concentrations seems to be of a general nature. A very extensive and careful recent investigation by Leermakers, Carroll, and Staud (27) showed invariably the same result.

The desensitizing action, then, is to be considered a property common to all optical sensitizers and, although this statement is not reversible, because desensitizing is not exclusively a property of optical sensitizers, a study of desensitizing should contribute something to the knowledge of optical sensitizers. The connection, however, between the specific character of a sensitizer and its desensitizing property if used in excess is a little more remote than that with optical sensitizing which will, therefore, be dealt with first.

## II. SENSITIZING ACTION

### *A. The sensitizing process*

The sensitizing action has always been believed to be closely connected with the primary act of absorption, and quite recently Leermakers (28) has confirmed very accurately the close correspondence between sensitivity and absorption in a sensitized emulsion. The conclusion thus seems inevitable that sensitizing is connected with the primary act of light absorption. Now, according to the present state of the theory of the latent image, into which Webb (29) has introduced quantum mechanics, absorption in unsensitized silver bromide results first in the raising of an electron to a higher level. In this level its mobility is not blocked by other electrons and, accordingly, photoconductance results. This photoconductance was measured by Toy and Harrison (30) and was found within 0.07 sec. to reach a stationary state which was proportional to the intensity. This would be expected if the majority of the electrons left the upper level again and dropped to a lower level. It has been assumed that such lower levels are produced by impurities and that in catching the electrons they give rise to the color centers, which are called F centers, in Pohl's terminology. Hilsch and Pohl (31) found in crystals of alkali halides that these F color centers are characterized by sharp absorption bands; in silver halide crystals, the absorption bands are more diffuse and broader, overlapping the proper absorption of the silver halides. Hilsch and Pohl assume that it consists of various bands belonging to different states of aggregation, since there is evidence that, in the silver halides, the photoproduct collects into specks of varying dispersity immediately after it is formed. In this connection it is perhaps of some interest to point to the results of Wagner and Beyer (32). They found that the lattice defect in silver bromide crystals is produced by interstitial silver ions which have left their normal places in the lattice, whereas in alkali halides the ions which have left their places are not present in the lattice any more. For the photographic emulsion Sheppard (23) stressed the necessity of dividing the formation of the latent image into two stages: (*1*) the primary act of absorption and (*2*) the formation of concentration specks around the sensitivity specks. He was able to show that the relative spectral sensitivity was scarcely affected by the formation of sensitivity nuclei (such as from thiocarbamide), which greatly increased the absolute sensitivity to any wave length, and Carroll and Hubbard (33) confirmed this statement. Webb has pointed out that the results obtained by Pohl and his school, in crystals, fit very well into the concentration-speck hypothesis suggested by Sheppard, Trivelli, and Loveland (34) for the photographic emulsion. Recently experimental evidence has been found for the existence of such concentration centers in photographic emulsions. Van Kreveld and Jürriens (35) devised an extremely sensitive method for measuring the absorption of a photographic plate after exposure. They found that the characteristic absorption between 5900 Å. and 7000 Å. was proportional to the time of exposure (36). The intensity of absorption taken as a function of the time of exposure gave a straight line passing through zero. Moreover, the method was so sensitive that they could include very short exposures in their measurements. The first point was produced by an energy of $9 \times 10^{11}$ quanta per cm.$^2$ on an Ilford Process plate. This point actually lies at the beginning of the overexposure region of the H. and D. curve, but is still so near to the region of the latent image that there is a high probability that the latent image is characterized by the same absorption.[2] Now the same absorption, only increased in intensity, has also been found for the print-out region, in which Eggert and Noddack (37) found the amount of photolytically produced silver to be that required by the law of photochemical equivalence. They also extrapolated their results to the region of the latent image, and the investigations of van Kreveld and Jürriens confirmed their statement. It can be assumed, therefore, with a probability very near to certainty, that the latent image consists of silver which has been produced by light according to the law of photochemical equivalence, so that, for each electron released, one atom of silver is formed.

In a sensitized emulsion the same primary process is supposed to take place, but with one exception. The original level from which the electron is raised is higher than the original level in the unsensitized emulsion and, accordingly, the energy required for raising it is less. Sheppard and Crouch (38) attributed this electron level to the sensitizing dye, and this assumption seems amply justified by the close resemblance between the absorption spectrum of the sensitized emulsion and that of the sensitizing dye itself. Thus, in the sensitized region, the electron should originate from the adsorbed dye, whereas, in the absorption region of silver bromide, it should originate from the bromide ion in the lattice. One more fact should be mentioned as an argument in favor of this theory, i.e., the photoconductance of sensitizing dyes. As early as 1905 Joly (40) pointed out the parallelism between photoconductance and absorption in sensitizing dyes, and in 1923 Zchodro (41), in comparing the photoconductance of three sensitizing dyes (cyanine, pinaverdol, and pinachrome) in dry collodion, with their absorption, found complete correlation. This result, however, is not conclusive. The photoconductance of the dyes should be investigated in the same specific molecular state in which they are adsorbed in the silver bromide emulsions.

From the theory just outlined it should be concluded that not more than one silver atom could be produced by the light-action of one dye molecule unless this molecule could be restored to its former state, rather than be decomposed after the release of an electron. This assumption seems far-fetched, although one fact points in this direction,—the strong fluorescence which is found in sensitizing dyes. It is to be regarded, however, as one of the possible solutions for a puzzling experimental result

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[2] It must be borne in mind, however, that it would hardly be possible to discover a slight deviation of the straight line in the region of the latent image.

obtained by Leszynski (42), by Tollert (43), and recently by Bokinik and Iljina (44).

All these authors found that, in a sensitized emulsion, the number of silver atoms present after exposure was many times greater than the number of dye molecules. Leszynski found that, after the exposure of an emulsion sensitized by erythrosin, the ratio of silver atoms to dye molecules was of the order of 20. Tollert repeated Leszynski's investigation with a very fine-grained emulsion, taking care to consider only those dye molecules which had actually been adsorbed to the silver bromide, and arrived at the same result. With the dye concentrations and exposure times which were used in his experiments, a ratio of 64 was actually found. Both authors used the same analytical methods and there is a possibility, of course, that a systematic error could have been made which is responsible for the anomaly. The method used was the same as that of Eggert and Noddack (37), i.e., first dissolving the silver bromide in thiosulfate and then determining the amount of silver in the precipitate. The thiosulfate might have given rise to some silver sulfide which would increase the amount of silver in the precipitate. There is always a tendency for thiosulfate to give silver sulfide, especially in the presence of gelatin, and this might be increased by the presence of the dye.

There is, however, additional evidence for a high, although not equally high, efficiency of the sensitizing dyes, namely, the work of Bokinik and Iljina (44). These authors investigated the sensitizing action of erythrosin in silver bromide sols without gelatin and with an excess of bromide ions, with the result that the ratio of silver atoms to adsorbed dye molecules was found to lie between 4 and 15, rising with increasing alkalinity. It appears, however, that some other spectral region than the green light of the sensitizing region enhanced the effect on the silver bromide sol, for, if their curves (amount of silver against adsorbed dye) are extrapolated to a dye concentration of zero, a large and varying amount of silver seems to have been formed in every case.

Thus, although the results of all three experiments are not quite conclusive, still they are not to be considered wrong.[3] Accordingly an explanation for the results should be sought. Three different explanations have been offered, one of which has already been given, i.e., that the dye molecule is restored after the release of an electron. This restoration of the molecule could easily occur if the remaining part did not decompose in the meantime. In this connection, a study of phosphorescence in adsorbed dyes would be of interest.

Another explanation is the possibility that the absorbing dye molecule

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[3] These results were strongly supported by an experiment recently reported by Dr. Sheppard at the September, 1937, Meeting of the American Chemical Society, which will be referred to later in this paper.

imparts its energy somehow to the crystal lattice, so that an electron is released from the lattice and the dye molecule is not affected at all. This is the explanation preferred by Leermakers (28), but it does not explain why the energy required to release an electron in the silver halide lattice should be reduced to such an unusual degree by the adsorbed dye, nor why this energy should correspond so closely to the absorption of the dye itself. Recently Scheibe (44a) has tried to find a solution for this question by assuming that the dye in an aggregated state should be able to absorb more than one quantum in one elementary act.

There is a third explanation connecting the excess of silver atoms over dye molecules with a chemical reaction of these latter molecules. Sheppard and Crouch (38) suggested an explosion of the dye molecule after the release of an electron, and they produced experimental evidence for the occurring of a chemical reaction between cyanine dyes and silver halide in the presence of light. Other contributions to this question have recently been made by Semerano (45, 46) and by Mecke and Semerano (47). The most recent results of Sheppard, Lambert, and Walker (46a), however, referred to already in this paper, rule out this explanation, for these authors were able to show that in the presence of an acceptor for halogen the sensitizing action proceeds without any decomposition of the dye. Thus the decomposition of the sensitizing dye can not be connected with the actual sensitizing. The part played by the sensitizing dyes in the photographic process seems, on the whole, to be fairly well established, although some questions remain still to be answered.

The main problem, however, concerns the properties which are required to make a sensitizer out of a dye, and unfortunately very little is known about them. In the following sections a survey will be given of the attempts which have been made to correlate the various properties of dyes with their sensitizing characteristics.

### *B. Adsorption of sensitizers*

The fact that adsorption is a necessary though not a sufficient condition for sensitizing has been known for some time (22). As early as 1904 Kieser (48) studied a great number of sensitizing dyes in their relations to the surface of silver halide grains, and found that saturation was reached at very low concentrations of the dye, but it was only recently that quantitative measurements were started of the adsorption of sensitizing dyes by silver halide emulsions.

In 1925 Sheppard and Crouch (38) measured the adsorption of Orthochrome T, dissolved in water, on a silver bromide emulsion with only 1 per cent gelatin at 50°C. The adsorption was measured in two ways: (*1*) by extracting the aqueous solution of the remaining dye with chloroform and determining the dye concentration with a spectrophotometer, and (*2*) by determining directly the amount of dye adsorbed at the silver bromide grains after dissolving them in thiosulfate. The results of both methods agreed fairly well. The adsorption curves at first showed increasing adsorption with increasing concentration. Then, over a large part, the curves were parallel to the concentration axis until finally they rose steeply again with further increase in concentration. The parallel parts of the curves were interpreted by the authors as representing saturation in a single layer, and the steep rise afterwards was assumed to be due to the agglomeration of multilayers. The size-frequency of the silver bromide grains was measured, and the surface area was calculated and compared with the amount of adsorbed dye in a saturated single layer. This latter value varies according to the alkalinity. For a pH of 5.5 there were found $5 \times 10^{-10}$ gram-moles of dye per square centimeter of surface area. According to a statement of Trivelli and Sheppard (49), the authors assumed the surface area to consist mainly of bromide ions, since excess bromide was present. By calculating the number of bromide ions in the surface, they were able to establish the ratio of bromide ions to dye molecules as 2.3. In connection with the adsorption at bromide ions, the increase of adsorption in alkaline solutions presented some difficulty. For, although it would have seemed natural to assume that the dye cations were adsorbed at the bromide ions, the increase in adsorption in alkaline solution pointed to the adsorption of the molecular form. There were two forms of the dye found in a solution in water, a dissociated uncolored form which was soluble in water, and an undissociated colored form which tended to be dispersed in colloidal solution in water (50), whereas, in alcohol and other organic polar solvents, the colored form was more soluble. The equilibrium between these two forms in water depended on the acidity. The dissociated colorless form prevailed in acid solution and the colored form in alkaline solution. Thus it seemed certain that the colored form, although not actually dissociated, was still exclusively adsorbed at the bromide ions. A parallel may be drawn, perhaps, to the statement of Franck and Eucken (51), according to which energy exchange is facilitated between molecules which can react with each other, even though they can not react under the special conditions under consideration.

The connection between the basic or acid nature of a dye and the place of adsorption in silver bromide was confirmed in an investigation by Sheppard, Lambert, and Keenan (52). The acid dye dichlorofluorescein was found to be adsorbed only in the presence of an excess of silver ions, whereas, in alkaline solution, the basic dye pinacyanol was adsorbed only at the bromide ions. It should be mentioned here that the experimenters of Leermakers, Carroll, and Staud (39) gave the same results. All the basic cyanine dyes were adsorbed exclusively by the bromide ions. An investigation of the adsorption of pinacyanol (52), carried out parallel with the investigation of the adsorption of Orthochrome T, yielded a value between 1.69 and 2.78 for the ratio of bromide ions to dye molecules. (The range of variation depends on the assumption of octahedral or of cubic faces at the surface.) This value was found to be roughly in agreement with the results of other investigations, on dye adsorption at silver bromide surfaces, which had been carried on in the meantime. Having found eight bromide ions for one molecule of adsorbed methylene blue, Wulff and Seidel (53) collected other data on adsorption at the surface of salts of heavy metals. They gave the ratio 3 as the result of an experiment on the adsorption of erythrosin at silver bromide surfaces carried out by O. J. Walker and K. Fajans.

Since that time other investigators have very definitely confirmed the ratio $\frac{\mathrm{Br}^-}{\mathrm{dye}} > 1$. Bokinik (54) gave the ratio 10 for pinacyanol, and Leermakers, Carroll, and Staud (27) found the ratio 10 for two different thiocarbocyanines and 20 for a thiodicarbocyanine. Their saturation value was defined as the amount of dye adsorbed at optimal sensitization, whereas saturation in Sheppard's experiment was defined by the parallel part of the adsorption curves. Since both methods yielded different results (the ratios being 2 and 10, respectively), the authors concluded that there exists a difference between saturation considered from the point of view of adsorption, and saturation considered from the point of view of sensitizing. Their investigation was a systematic study of the correlation between the optimal concentration of a sensitizer and the available grain area, and it was carried out with three different dyes and seven emulsions. The curves obtained by plotting the sensitivity in various spectral regions against the logarithm of the dye concentration show a great increase in sensitivity towards the optimal concentration in the red region, a slighter increase in the green part of the spectrum, and no change in the blue part. At higher concentrations a decrease in sensitivity occurs throughout the whole spectrum. At the optimal concentration, practically the whole amount, i.e., 99 per cent, of the dye was found to be adsorbed. For concentrations beyond this the percentage of unadsorbed dye increased rapidly. (For pinacyanol, thiocarbococyanine, and selenocarbocyanine, Heisenberg (26) obtained exactly the same results.) The surface area for each emulsion was determined from the projective area of the average grain, the number of grains per cm.$^3$, and the volume of the average grain (obtained by finding the silver content of the emulsion, the density of silver bromide, and the number of grains). The results are shown in table 1 (taken from the paper by Leermakers, Carroll, and Staud (27)).

The fifth column shows a remarkably constant value for each dye. This constant ratio of adsorbed dye to available surface is especially remarkable, since the emulsions were prepared in various ways, both from neutral silver nitrate and from ammoniacal silver oxide. Discussing the difference in the ratio, dye to surface, for dye I and dye II, on the one hand, and dye III, on the other, Leermakers, Carroll, and Staud point out that the deviation is in the right direction, since dye III as a thiodicarbocyanine has a larger area than dye I or dye II, both of which are thiocarbocyanines. They point out at the same time, however, that the deviation is greater than could be accounted for by the difference in size. The data of table 1 are used to estimate the amount of surface saturation at the optimal concentration. For dye II, an 8-alkylthiocarbocyanine, the surface is assumed to be 150 Å., according to the values given recently for atomic radii. If the molecules are assumed to lie flat on the crystal surface, they will then cover $11.5 \times 10^{-11} \times 6 \times 10^{23} \times 150 \times 10^{-16}$ cm.$^2$ per square centimeter of surface, or 1 cm.$^2$ per square centimeter, i.e., they will form a unimolecular layer.

TABLE 1

*Optimal surface concentration of sensitizing dyes*

(From Leermakers, Carroll, and Staud (27))

| EMULSION | SURFACE | DYE | OPTIMAL CONCENTRATION | MOLES OF DYE PER CM.$^2$ OF SURFACE $\times 10^{11}$ |
|---|---|---|---|---|
| | *cm.$^2$ per cm.$^3$* | | *moles per cm.$^3$ of emulsion $\times 10^8$* | |
| 1 | 400 | I | 3.6 | 9.0 |
| 2 | 480 | | 3.8 | 7.9 |
| 3 | 580 | | 5.2 | 9.0 |
| 4 | 660 | | 6.0 | 9.1 |
| 5 | 840 | | 7.2 | 8.6 |
| 6 | 950 | | 9.0 | 9.4 |
| 7 | 1080 | | 12.0 | 11.1 |
| 1 | 400 | II | 4.4 | 11.0 |
| 3 | 580 | | 6.3 | 10.9 |
| 4 | 660 | | 8.0 | 12.1 |
| 6 | 950 | | 11.2 | 11.8 |
| 7 | 1080 | | 12.6 | 11.6 |
| 1 | 400 | III | 1.9 | 4.8 |
| 3 | 580 | | 2.3 | 4.0 |
| 4 | 660 | | 2.9 | 4.4 |
| 6 | 950 | | 4.8 | 5.0 |
| 7 | 1080 | | 4.8 | 4.4 |

This result seems fairly convincing, although the authors themselves are willing to assume that it may be a coincidence, because there are other facts (39) which seem to require the assumption of an agglomeration of the adsorbed dye. These data are connected with some spectral characteristics which will be reported later in the present paper.

Two more investigations should be mentioned in connection with adsorption measurements,—one by Bagdassarjan and Rabinovitch (55), and the other by Ščetinkina (56), which was reported by Rabinovitch. Bagdassarjan and Rabinovitch, studying the adsorption isotherms of silver bromide suspended in water, of erythrosin, eosin, rhodamine B, pyronine G, phloxine, acid rhodamine, and Bordeaux B, and their sensitizing power in silver bromide emulsions, found again that adsorption was necessary for sensitizing. In addition, they discovered that dyes (pyronine G) with adsorption isotherms which do not show any flat portions pointing to saturation are extremely weak sensitizers. Ščetinkina (56) measured the dependence of sensitizing action on the concentration of the sensitizer, and found a maximum for erythrosin and phloxine at relatively low concentrations. At very high concentrations the sensitivity decreases. These results are in good agreement with the results of the other investigators.

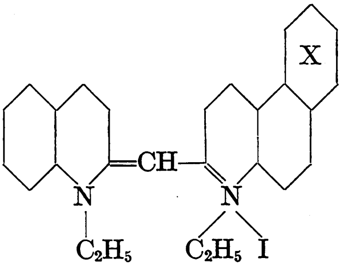
### *C. Some special spectroscopic properties of sensitizers*

That the absorption spectra of dyes vary according to the solvent has been known for a long time. In 1908 Sheppard (57) investigated the absorption of some sensitizing dyes in alcoholic solutions and in water and found a very marked difference between them. The sensitivity curves of emulsions sensitized by these dyes resembled to some extent the absorption curves in water. In another investigation Sheppard (50) obtained some ultramicroscopic evidence of the colloidal state of the dyes dissolved in water. Recent investigations of this were carried on by Scheibe (58), by Scheibe, Kandler, and Ecker (59), by Scheibe, Mareis, and Ecker (60), by Jelley (61, 62), and by Leermakers, Carroll, and Staud (39).

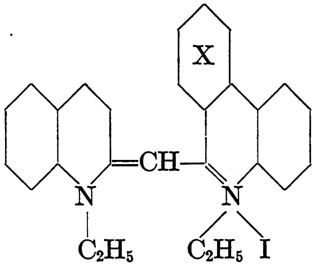
A peculiar spectroscopic phenomenon, discovered by Jelley for a special cyanine dye (1, 1′-diethylpseudocyanine chloride), was observed when the dye was changing from true solution in alcohol or a similar solvent to the crystallized state. During the change it passed through a transitory state characterized by a sharp absorption band at about 575 mμ. This absorption band was associated with a strong resonance fluorescence, an unusual phenomenon in the liquid or solid state. This transitory state of the crystal was found to be relatively stable in solutions of some salts and in the case of adsorption of the dye on various substances (59).

In investigating silver bromide emulsions sensitized by cyanine dyes, Leermakers, Carroll, and Staud found similar sharp characteristic absorption bands for many adsorbed dyes. It was this fact which made them doubtful of the unimolecular layer, since Scheibe, Kandler, and Ecker attributed these spectral characteristics to a polymerized state, and Scheibe, Mareis, and Ecker confirmed this statement. Jelley, however, assumed a nematic state, i.e., a liquid crystal with orientation along one axis only, and the question of the "aggregated" state was left open.[4] Whatever this state be called, it will still be tempting to link it with the sensitizing power. But some of the results of Leermakers, Carroll, and Staud are not in agreement with the assumption that the sensitizing action is exclusively a property of this "aggregated" state. They found parallelism between sensitivity and absorption in all spectral regions, not merely for the bands belonging to the nematic state, but also for bands in other spectral regions which were obtained in emulsions dyed from alcoholic solutions. The sensitivity, however, was always proportional to the absorption.

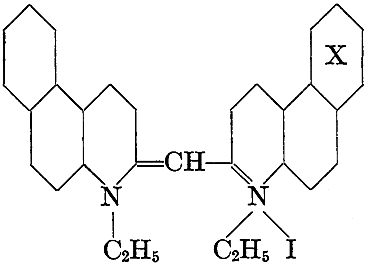
Another connection seems worth investigating, namely, that between fluorescence and sensitizing, especially with regard to the possibility (mentioned in the discussion of the sensitizing process) that the dye molecule could be quickly restored after the release of an electron. Fluorescence in solutions is known to occur very frequently in cyanine dyes (63), but it is important to know whether the dyes adsorbed to silver bromide will show fluorescence. An investigation of the fluorescence of sensitized emulsions would be especially interesting in view of some remarkable results obtained with isomers by Brooker and Keyes (64) and by Leermakers, Carroll, and Staud (39). These isomers have the following constitution:



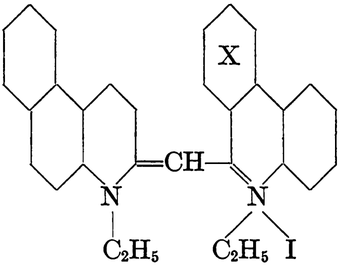
A



B



C



D

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[4] At a recent meeting (September, 1937) of the American Chemical Society Dr. Sheppard suggested a unimolecular layer in which the molecules are standing on edge, so that aggregation could take place in one dimension.

The only difference between A and B, or between C and D, lies in the position of the benzene ring marked X. Each of the dyes showed strong adsorption to silver bromide emulsions and a sharp absorption band, but only A and C were found capable of sensitizing the emulsions; B and D did not act as sensitizers. It would be interesting in this connection to know whether the isomers show any differences in fluorescence or photoconductance.

There are at present very few data which can be attributed to the sensitizing property. Bokinik (65) points out, in discussing the various explanations offered for the sensitizing action, that, of all the existing dyes, only those related to the phthalein or the cyanine groups were found to be sensitizers, but this statement is more applicable to the properties desirable for a practically useful sensitizer than to the sensitizing property itself.

Chibisoff (66), on the other hand, calls attention to some secondary effects of optical sensitizers whereby they act simultaneously as chemical sensitizers. These effects are especially marked when the dyes are added to the emulsions before ripening. They can then influence the growth of the crystal and the ripening process. Bancroft, Ackerman, and Gallagher (67) have connected the sensitizing power of a dye with its reducing action as an acceptor for halogen, and accordingly define an optical sensitizer as a dye which absorbs light in a special region and which is capable of reducing silver salts.

## III. DESENSITIZING ACTION

The desensitizing action, as a property common to all sensitizers at high concentrations, should reveal some information on their characteristics. Unfortunately, the phenomenon itself seems complex, and the variation of terminology with author and time has helped to confuse the picture still more. There is, however, one fact which seems to be fairly well established: namely, that desensitizing takes place at the developing centers and not at the places of primary absorption (68). In addition to many facts which lead to this conclusion, there is an experiment reported by Lüppo-Cramer that definitely proves this point. Pinakryptol yellow is a very strong desensitizer and is even capable of dissolving the silver of the print-out image (70, 71). Accordingly, no darkening was observed in developing a plate which had been desensitized with pinakryptol yellow before exposure, but after dissolving the silver bromide in thiosulfate, the plate could be developed physically. This demonstrates clearly that the primary act of absorption during exposure was not impeded by the desensitizer adsorbed at the surface.

According to this result Weber's theory (72, 73) can be rejected, in so far as optical sensitizers are concerned. His theory assumed that desensitizing has only an indirect influence on silver bromide by removing the optical and chemical sensitizers. This was supported by the following facts: Lüppo-Cramer (74) showed with many examples that emulsions of silver bromide in collodion were not susceptible to the action of desensitizers unless they contained a sensitizer. Mudrovčič observed that cyanine dyes and the desensitizer methylene blue reacted with each other. In water and in collodion the cyanine dye was bleached out in the presence of methylene blue. (Since, however, in gelatin the process was reversed, the methylene blue being destroyed, this effect could as well be used as an argument against Weber's theory.) Finally, Weber himself observed that, in a sensitized plate, desensitizing showed more strongly in the sensitized spectral region than the absorption region of silver bromide. Blau and Wambacher (76) strongly objected to accepting this as a general statement and pointed out that, wherever this secondary effect was found, it could be easily explained by preferential absorption of the desensitizer.

It would indeed be difficult to explain by this theory the desensitizing effect of optical sensitizers at high concentrations. With regard to the assumed effect of desensitizers on chemical sensitizers contained in gelatin, by which Weber explained the difference between gelatin and collodion in regard to the susceptibility to desensitizing, Blau and Wambacher pointed out that this explanation could not be valid. For, in the meantime, Ollendorff and Rhodius (77) had succeeded in coating plates with a silver bromide emulsion without any protective colloid which could be desensitized with methylene blue. Lüppo-Cramer confirmed (78) this result, although he did find that the number of dyes capable of acting as desensitizers is much more limited in such colloid-free emulsions. Even pinakryptol yellow, one of the strongest desensitizers, is ineffective with them. The exceptional susceptibility to desensitizing was explained for the gelatin emulsion by Lüppo-Cramer as being related to the high degree of dispersion of the latent image in gelatin.

In a special case there would, of course, always be the possibility of a complication by some of the secondary effects which have just been discussed, but desensitizing as a general phenomenon can safely be taken as a direct action on the developing centers. Even so, the range of possible reactions is still very wide and many questions remain to be answered.

There is the Herschel effect, i.e., the simple regression phenomenon produced by infrared radiation (the name, "Herschel effect," is used here for the direct regression, as it was used originally, i.e., the "visible" Herschel effect, as named by Trivelli (80)). Does desensitizing mean sensitizing of the Herschel effect? Or is it merely an oxidation of the silver in the latent image? Is it essentially an isolation of the developing nuclei (68)? Does it merely prevent the formation of the latent image, or does it also destroy it? Is the desensitizing action merely a "narcosis" (81) of the centers lasting through development? And are these reactions influenced by light absorption?

Some of these questions can be answered from the results of various investigators. Some significant results have been obtained by Sheppard (82) concerning the mechanism of reaction on the silver bromide grain. By measuring the electromotive force in concentration cells with silver salts, he found a strong tendency to form complex silver salts in several compounds used in photography either as sensitizers, desensitizers, or antifogging agents.

It is conceivable that complexes are formed with silver either *in statu nascendi* or in the very fine dispersion of the latent image when oxygen is present. In experiments by Blau and Wambacher it was found that, for desensitizing at least, oxygen was necessary, unless there was an excess of chloride ions (83, 84, 85). Pinakryptol yellow, induline scarlet, antilumine, and phenosafranine did not act as desensitizers when oxygen was completely removed, either by evacuation or by substituting nitrogen.

The strong influence of halide ions on the desensitizing action had previously been observed by Carroll and Kretchman (86) With safranine either the sensitizing or the desensitizing effect was found, depending upon the concentration of bromide ions. The investigation of Carroll and Kretchman rendered quantitative results on the influence of light on desensitizing, and they were able to show the good correlation between reversal and energy absorption. This reversal phenomenon is, of course, not related in any way to the well-known photographic reversal, the beginning of solarization. The reversal by desensitizers can be identified with the "latent Herschel effect" as Trivelli named it, contrasting it to the "visible Herschel effect", which is a direct regression of the print-out image and which was, in fact, the effect actually discovered by Herschel. Where the regions of absorption by silver bromide and the dye were sufficiently separated in wave length, maxima were found corresponding to each region. Desensitizing can, therefore, be considered as a reaction in the developing centers which can be photosensitized by the light absorbed either by silver bromide or by the desensitizing dye. The photosensitizing is not the only reaction produced by a desensitizer. Loss of developability occurs also in the dark, but at a much lower rate. This was demonstrated by Carroll (87) and confirmed by Mauz (88).

There still remains the question of whether desensitizing involves destroying the silver centers or merely making them unfit for development. Or rather, it should be asked whether there are any desensitizing dyes which impede the development of the silver centers without destroying them. For, quite aside from the dyes (such as methylene blue, Janus green, etc.) which are known to be capable of dissolving silver (89), there is pinakryptol yellow, which was found by Hübl (90) to be capable of preventing the formation of a print-out image. Lüppo-Cramer had shown that the dye can even destroy the print-out image (70). Tollert observed that a plate desensitized with pinakryptol yellow yielded a smaller amount of photolytically formed silver than a plate which had not been desensitized. If this experiment were repeated with other desensitizers, the question mentioned above could be answered. With a colorless desensitizer it could even be done in a region much nearer that of the latent image, since van Kreveld and Jürriens (35) have developed a method of determining the latent image by measuring the absorption in the red region of the spectrum.

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# PHOTOSYNTHESIS[1]

WINSTON M. MANNING

*Wisconsin Geological and Natural History Survey, Madison, Wisconsin*

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## I. INTRODUCTION

In this review major emphasis will be placed on the photochemical and kinetic aspects of photosynthesis. The influence of the various physiological factors is more fully discussed in other recent reviews of photosynthesis (23, 24, 58, 72).

Except for studies of the physical and chemical properties of extracted plant pigments, investigations of photosynthesis are practically limited to a study of living plants. This limitation introduces complications not found in non-biological photochemical studies. In the first place, other chemical reactions, thermal as well as photochemical, undoubtedly occur during a period of photosynthesis. Unless proper allowance is made, these reactions may be of sufficient magnitude to obscure the significance of the photosynthesis measurements. In the second place, variations in factors influencing photosynthesis must be limited to those which will not kill or seriously injure the plant during the time when measurements are being made. In many cases, moreover, a variation in a particular environmental (external) factor may influence photosynthesis indirectly through its effect in the plant on internal factors other than those directly connected with the photosynthetic mechanism. This is particularly true for experiments with the higher plants.

Emerson (23) has discussed more fully some of the limitations involved in photosynthesis research.

## II. THE MEASUREMENT OF PHOTOSYNTHESIS

Only a brief outline of experimental procedure will be given here. More extensive descriptions of the earlier methods which have been employed may be found in the monographs of Spoehr (70) and Stiles (74). Details of later procedures may be obtained from the original papers.

Photosynthesis is usually measured by determining either the amount of carbon dioxide consumed or the amount of oxygen liberated, or both.

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[1] Contribution No. 11 to the Third Report of the Committee on Photochemistry, National Research Council.

Less direct methods may also be used, such as the measurement of the change in dry weight or sugar content of the plant material under investigation. However, results so obtained may involve factors other than the photosynthetic process.

### *The measurement of photosynthesis in land plants*

With land plants photosynthesis may be measured by using either an entire plant or only part of the plant (often a single leaf). When a single leaf is studied, it is often detached from the rest of the plant, although many recent investigators have worked with attached leaves (41, 59, 60). In either case the material to be investigated is usually enclosed in a light-transmitting chamber.[2] The change in carbon dioxide or oxygen composition during a period of illumination or darkness may then be determined. In practice a flow method is often employed in order to maintain a nearly constant carbon dioxide concentration in the reaction chamber.

The change in gas composition during a period of darkness gives a measure of respiration. It is usually assumed that, for a given temperature, this process proceeds at the same rate in light as in darkness. A correction for respiration is therefore made in calculating absolute photosynthetic rates.

The change in oxygen and carbon dioxide may be determined by gas analysis (17), but other methods, in which only carbon dioxide is determined, are more frequently used.

In the conductivity method (43, 59, 60, 71, 76), the carbon dioxide is absorbed by a solution of alkali at constant temperature (± 0.01°C.). The conductivity of the hydroxide–carbonate mixture gives an accurate measure of the amount of carbon dioxide absorbed. With this method a continuous record of photosynthetic (or respiratory) rate may be obtained. Thomas and Hill (76) constructed a chamber large enough to enclose a field plot of wheat or alfalfa plants 6 feet square, and used the conductivity method to obtain a continuous record of photosynthesis and respiration, the measurements sometimes extending over a period of several weeks.

Instead of measuring the conductivity of the hydroxide–carbonate mixture, some investigators have titrated the mixture with standard acid (41). This method requires less apparatus than the conductivity method, but it is not as suitable for continuous measurements.

McAlister (53) has recently developed a very sensitive spectrometric method for determining carbon dioxide. This method is well adapted for continuous measurements of photosynthesis in land plants. A closed

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[2] In single leaf studies the chamber may be attached to the under side of the leaf, with the leaf forming part of the chamber wall (41, 60). This permits nearly normal air circulation and transpiration.

system is used, with the gas rapidly circulating through the plant chamber and through an optical absorption tube. The absorption by the 4.2–4.3$\mu$ band of carbon dioxide is determined with a rock salt spectrograph and a vacuum thermocouple. A notable characteristic of this method is its rapid response to changes in photosynthetic rate.

### *Photosynthesis measurements in algae and other aquatic plants*

Photosynthesis measurements in aquatic plants are usually carried out with the plant material suspended in water. However, both van den Honert (77) and van der Paauw (78) have worked with moist films of *Hormidium* (a very small filamentous blue-green alga) attached to glass plates. The rate of oxygen evolution by the suspended plant material is usually used as the criterion of photosynthetic rate.

The manometric method of Warburg (84) has been widely used for measuring changes in oxygen concentration in experiments with aquatic plants. In this method the plant material is suspended in a carbonate–bicarbonate buffer mixture (usually about 0.1 molar), and placed in a closed glass vessel connected to a manometer. The buffer concentration is high enough to maintain a practically constant carbon dioxide partial pressure in the gas phase, so that the increase in gas volume due to oxygen evolution can be read directly on the manometer. Vigorous shaking is necessary to maintain equilibrium between gas and liquid phases. With some modifications the manometric method can be applied to measurements carried out with an unbuffered nutrient solution (9, 85). This modification requires the use of two vessels and depends upon the difference in solubility of carbon dioxide and oxygen in the nutrient solution. With this differential type of manometer both oxygen and carbon dioxide changes can be measured.

Another method frequently employed, especially in ecological studies, is the determination of dissolved oxygen in closed vessels by titration (Winkler method). This method avoids the use of the somewhat nonphysiological buffer mixture and is much simpler than the differential manometric method. However, it does not permit a series of measurements on a single sample.

Petering and Daniels (62) have recently applied the dropping-mercury electrode to a determination of dissolved oxygen changes in photosynthesis. As in the manometric method, repeated measurements may be made on a single sample of plant suspension. In at least two respects, this method is superior to the usual manometric method. It does not necessitate the use of buffer mixtures and it does not involve an equilibrium between gas and liquid phases. In speed of response it compares favorably with the spectrometric method of McAlister (53).

## III. GENERAL DESCRIPTION OF THE PHOTOSYNTHETIC PROCESS

The equation for the reaction involved in photosynthesis in green plants is often written as follows:

$$CO_2 + H_2O \rightarrow 1/6\ (C_6H_{12}O_6) + O_2 \qquad \Delta H = 112{,}000 \text{ cal.} \qquad \text{(I)}$$

This equation, when reversed, becomes the one usually used to represent the normal respiratory process.

It is usually assumed that formaldehyde is the first product of photosynthesis, and that subsequent polymerization is responsible for the formation of glucose or other carbohydrates. If formaldehyde is the first product, then $\Delta H$ for equation I becomes 134,000 cal. The subsequent polymerization reaction will then be exothermic. The necessary energy for photosynthesis is assumed to come from light absorbed by the two chlorophyll pigments in the plant, although it is possible that energy absorbed by other pigments, such as carotene and xanthophyll, may sometimes be utilized.[3] It is rather remarkable that light of wave length as long as 7000 Å. (see figure 2), for which $Nh\nu$ is equal to 40,500 cal., will bring about a reaction for which $\Delta H$ is 112,000 cal. Evidently photosynthesis involves a more complex series of endothermic reactions than has been observed for any non-biological photoreaction.

### *Photosynthesis at different wave lengths*

Figures 1 and 2 show a rather close correlation between relative rates of photosynthesis at different wave lengths (Hoover (42)) and the absorption spectra (in ether solution) of chlorophylls *a* and *b* (93). Hoover's results were obtained with young wheat plants, using equal incident light intensities (less than 300 foot-candles) at the various wave lengths. A wheat leaf contains enough chlorophyll to absorb a considerable fraction of the incident radiation, even in the region between 5000 and 6000 Å.; this accounts for the relatively high minimum in the photosynthesis curve (figure 2). Chlorophyll absorbs more strongly at 3660 Å. than in the region between 5000 and 6000 Å. (90). Consequently the low rate of

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[3] Except in the *Myxophyceae* (blue-green algae) the chlorophyll pigments are found only in restricted regions of the plant cell, known as chloroplasts. These regions also contain the yellow pigments carotene and xanthophyll. Frequently a large number of the cells in a green leaf contain no chloroplasts, while in the remaining cells the number may vary from one to many. Consequently only a small fraction of the total leaf volume consists of chloroplasts and hence is able to carry on photosynthesis. In many of the algae, however, the chloroplasts constitute a much larger fraction of the total plant material. For example, the single chloroplast in the unicellular green alga *Chlorella* probably occupies half of the cell volume.

This large proportion of photosynthetically active plant material constitutes one reason for the widespread use of *Chlorella* in photosynthesis investigations.

photosynthesis at 3660 Å. (figure 2) indicates a much lower quantum efficiency for the process than in the region from 4000 to 7000 Å. Below 3000 Å. ultraviolet radiation is distinctly injurious (57, 4).

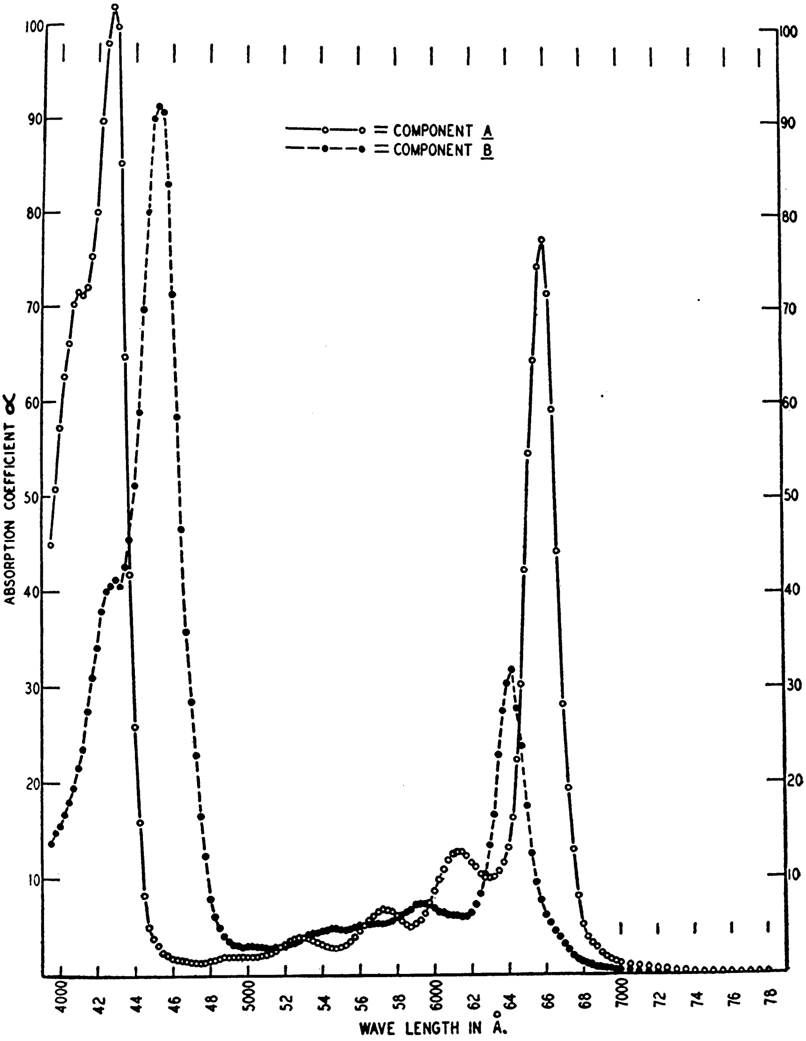

Fig. 1. The absorption spectra of chlorophylls *a* and *b* in ether (Zscheile (93))

*The formaldehyde hypothesis*

The occurrence of formaldehyde as an intermediate product of photosynthesis has been neither proved nor disproved (58). In any event its concentration must be very low, even during rapid photosynthesis, since concentrations higher than a few hundredths of a per cent are distinctly toxic. The presence of small amounts of formaldehyde in green leaves has been reported by a number of investigators. Others have found that plants in the dark can utilize low concentrations of formaldehyde to form carbohydrates. These observations add plausibility to the hypothesis that formaldehyde is an intermediate product in the photosynthetic process, but do not constitute proof of the hypothesis, since formaldehyde may be produced by other metabolic processes. Also, formaldehyde is only one of several organic compounds which may be utilized by plants in the formation of carbohydrates (58).

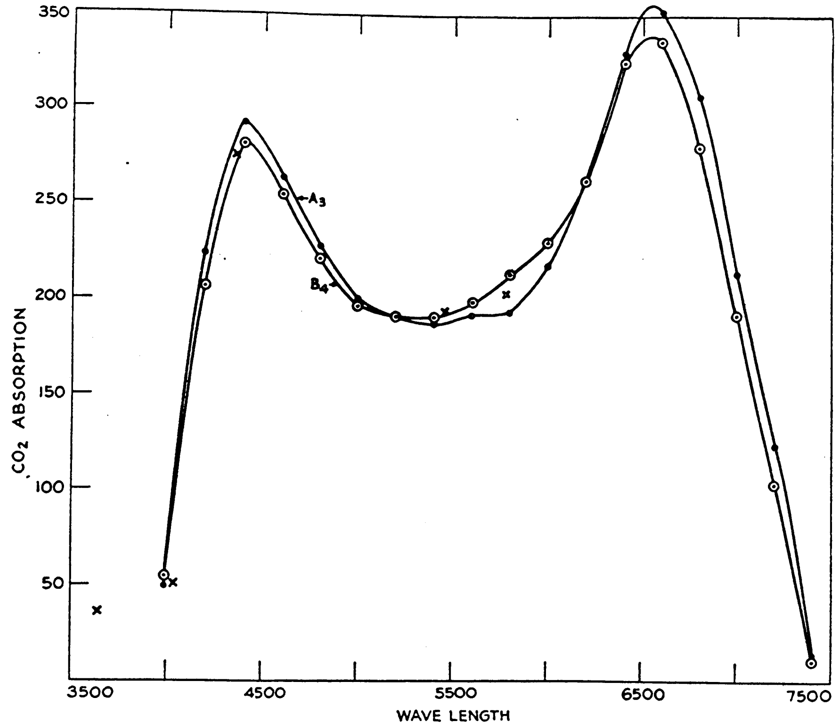

FIG. 2. Rate of photosynthesis as a function of wave length (low light intensity). $A_3$, the corrected form of the curve obtained with large Christianson filters; $B_4$, the corrected form of the curve obtained with small Christianson filters. Points marked × are the results obtained with line filters and quartz mercury arc. (Hoover (42)).

### *The photosynthetic quotient*

The ratio of the number of moles of carbon dioxide absorbed to the number of moles of oxygen produced, $\Delta CO_2/\Delta O_2$, is called the photosynthetic quotient.[4] If glucose or some other carbohydrate is the final product of photosynthesis, the photosynthetic quotient should have a value of 1, as in equation I. Maquenne and Demoussy (56) and Willstätter and Stoll (89) investigated a large number of different plants and found a quotient very close to unity. Apparent values markedly different from unity are sometimes obtained, but these may often be attributed to the effects of abnormal respiration or other processes.

The value of the photosynthetic quotient constitutes the principal proof that a carbohydrate is the first product of photosynthesis. Many investigators have attempted to identify this carbohydrate product. From present evidence it may be considered probable that a hexose is the first product formed, though the prior formation of sucrose remains as a possibility.[5]

In diatoms (and also in some other plants) the products of photosynthesis are stored principally in the form of oils rather than as carbohydrates. Barker (10) has measured the photosynthetic quotient in two species of diatoms in an effort to determine whether the oils are formed as primary products of photosynthesis or whether they are secondary metabolic products. For complete conversion of the carbon dioxide to oils, the quotient should be approximately 0.70 instead of 1.00. For both species of diatoms Barker found a quotient close to 0.95, with a tendency for the value to increase slightly with increasing light intensity. He concluded that 10 per cent or less of the photosynthetic products appeared as stored fat and that this fat production was probably the result of a secondary reaction.[6]

### *The effect of light intensity and temperature on the rate of photosynthesis*

Figure 3 shows diagrammatically the relation between the rate of photosynthesis and light intensity at high carbon dioxide concentration. Curve A represents the behavior at a relatively low temperature, perhaps 10°C.; curve B is for a higher temperature, such as 20°C.

While the type of behavior shown in figure 3 is characteristic of most

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[4] Some writers apply the term "photosynthetic quotient" to the reciprocal of this ratio, i.e., $\Delta O_2/\Delta CO_2$.

[5] More complete discussions of this problem are given by Spoehr (reference 70, page 215) and Stiles (reference 74, page 151).

[6] When a simple alga, such as *Chlorella,* is grown under long-continued constant conditions, including constant illumination, it is probable that an equilibrium is reached between the rate (per unit of plant material) at which food is manufactured by photosynthesis and the rate at which it is used in growth. Under these conditions the *apparent* photosynthetic quotient (i.e., uncorrected for respiration) should give a measure of the average state of oxidation of the entire cell material. The oxygen eliminated during the reduction of nitrates to protein material should contribute noticeably to a lowering of the apparent quotient.

plants which have been studied, the exact numerical behavior may vary widely. Thus, in many land plants the maximum photosynthetic rate may not be reached until the light intensity approaches that of sunlight, while in other plants, particularly some of the algae, one-tenth of this intensity may produce the maximum rate.[7]

The shape of a rate–light intensity curve will depend on the fraction of light absorbed by the plant material under investigation. With a thick leaf containing an abundance of chlorophyll, or with a dense suspension of algae, different portions of the plant material will be exposed to widely different light intensities. A very high incident intensity will then be necessary to produce a maximum photosynthetic rate in the chloroplasts farthest removed from the incident surface.

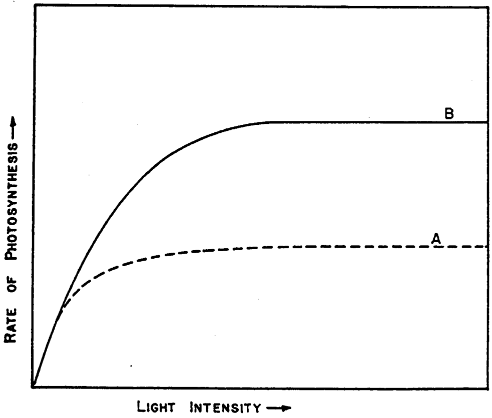

FIG. 3

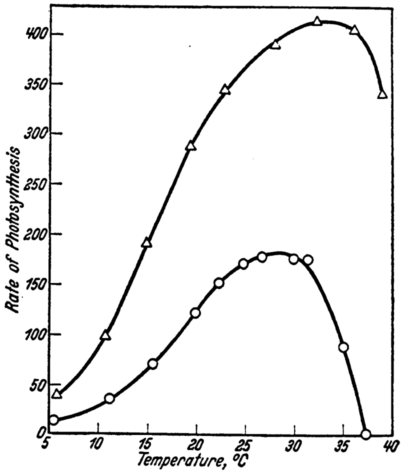

FIG. 4

FIG. 3. Rate of photosynthesis as a function of light intensity. A, low temperature curve; B, high temperature curve.

FIG. 4. Variation in rate of photosynthesis with temperature at high light intensities for *Nitzschia closterium* (O) and *Nitzschia palea* (Δ). Photosynthesis is expressed in cubic millimeters of evolved oxygen per hour per 10 cmm. of cells. (Barker (10)).

As shown in figure 3, the rate of photosynthesis is nearly independent of temperature at low light intensities, but becomes temperature-dependent at higher intensities. Thus, for *Chlorella* Warburg (82) found a temperature coefficient ($Q_{10}$) of unity at approximately $6 \times 10^3$ ergs per

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[7] In some plants the rate of photosynthesis may increase to a maximum and then decrease again as the light intensity is increased (48, 54, 72). The reason for a decrease in rate at high intensities is not definitely known. It may be caused by some form of injury, or it may be caused by the simultaneous occurrence of photoöxidation processes.

cm.$^2$ per second,[8] but a coefficient of from 2 to 5 (depending upon the temperature) at an intensity of approximately $100 \times 10^3$ ergs per cm.$^2$ per second.

From the type of behavior shown in figure 3, as well as from other evidence to be discussed below, it must be concluded that photosynthesis is a complex cyclic reaction, involving at least one thermal reaction, usually known as the Blackman reaction,[9] in addition to whatever photoreactions are necessary. According to this view, at low light intensities, where the rate of photosynthesis is approximately proportional to the intensity, the time between the absorption of successive photons, by that portion of the mechanism involved in the reduction of a single carbon dioxide molecule, will be sufficient to permit the Blackman reaction to be completed. Light is then said to be the limiting factor. But at high intensities, where the rate has practically reached its maximum value (so-called light saturation), the rate will presumably be limited only by the rate of the Blackman reaction.[10] This implies that photons are absorbed so rapidly by the mechanism that the average time between the completion of the Blackman reaction and the next light absorption will be very short compared with the average time required for the Blackman reaction. An increase in temperature will increase the rate of the Blackman reaction without appreciably altering the rate of the light reaction.[11]

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[8] In this research Warburg made only approximate estimates of absolute intensities.

[9] The term "Blackman reaction" as used in this paper refers to any reaction or reactions which contribute to the temperature dependence of the photosynthetic process. It is named for F. F. Blackman, who, in 1905 (12), formulated his principle of limiting factors in the following words: "When a process is conditioned as to its rapidity by a number of separate factors, the rate of the process is limited by the pace of the 'slowest' factor." Application of this principle did much to clarify the contradictory results of earlier research on photosynthesis.

Many subsequent investigators appear to have interpreted this principle too literally, i.e., they have assumed that for measurements under ideal conditions only a single factor could influence the rate of photosynthesis at any one time. According to this view, an increase in the intensity of a particular variable should result in an abrupt transition from direct dependence of the rate on this variable to complete independence. Such a transition is contrary to any reasonable kinetic formulation of the process.

[10] According to a recent mechanism of Franck and Herzfeld (34), the rate of the Blackman reaction is not limiting at high light intensity (see page 850).

[11] Warburg and Uyesugi (87) and Yabusoe (92) found some similarities between the Blackman reaction and the rate of decomposition of hydrogen peroxide by the enzyme catalase. There has therefore been a widespread belief that the Blackman reaction consists of a reaction between catalase and a peroxide. Hence many postulated mechanisms have included hydrogen peroxide or organic peroxides as intermediate products in photosynthesis. However, Emerson and Green (28) have recently made further comparisons of the two reactions without finding any significant similarity.

Figures 4 and 5 illustrate the effect of temperature on the rate of photosynthesis at high light intensity and high carbon dioxide concentration. Figure 4 gives the results obtained by Barker (10) with two species of diatoms; figure 5 gives the results obtained by Craig and Trelease (21) with *Chlorella vulgaris.* The lower curves in figure 5 are for rate measurements in 99.9 per cent heavy water. (The heavy water experiments will be discussed below, page 828.) The decrease in photosynthetic rate at high temperatures is probably due to injury to the plant material. Further evidence of injury is found in the fact that the photosynthetic rate at high temperatures is not constant, but decreases with time. Injury may be due to deactivation of enzymes (or of an enzyme-producing mechanism) connected with the Blackman reaction, or it may be due to a change in the physical condition of the chloroplasts.

The Arrhenius equation may be used to calculate apparent activation energies for the temperature-sensitive reaction in photosynthesis. However, in view of the complex system involved, the significance of the figures so obtained is doubtful. The apparent activation energy varies for different species and decreases with increasing temperature. The low temperature value for *Chlorella pyrenoidosa* and *Hormidium flaccidum* has been reported as being approximately 20,000 cal. (27, 78). Barker (10) found a value of about 30,000 cal. for the diatoms *Nitzschia closterium* and *Nitzschia palea* (see figure 4). Emerson and Green (27) found a value of approximately 50,000 cal. for *Chlorella vulgaris* and for the marine alga *Gigartina harveyana.*

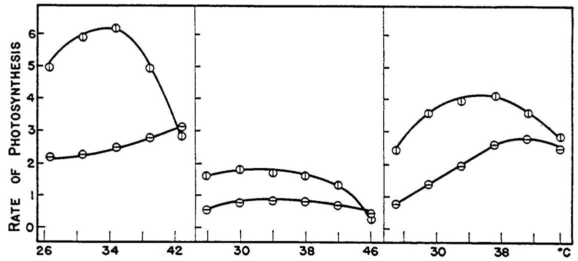

FIG. 5. Rate of photosynthesis as a function of temperature. For $H_2O$ shown by circles with vertical bars, and for $D_2O$ shown by circles with horizontal bars. (Craig and Trelease (21)).

### *The effect of carbon dioxide concentration on the rate of photosynthesis*

Variation in carbon dioxide concentration apparently affects the rate of photosynthesis in a manner similar to variation in light intensity. Van den Honert (reference 77, page 225), working with moist films of *Hormid-*

*ium* at 12° and 20°C., and using high light intensity, obtained curves essentially like those of figure 3 (with light intensity replaced by carbon dioxide concentration). In both curves the rate of photosynthesis reached its maximum value at a carbon dioxide concentration of about 0.04 per cent by volume. (Normal carbon dioxide concentration in air is approximately 0.03 per cent.) For young wheat plants Hoover, Johnston, and Brackett (43) found that a higher carbon dioxide concentration, approximately 0.15 per cent, was necessary for a maximum rate of photosynthesis (light intensity one-fourth of that of sunlight). Light saturation was not reached in this work; at higher light intensities still higher carbon dioxide concentrations would have been required. In general, the diffusion of carbon dioxide into a chloroplast will encounter more resistance in a leaf, where most of the chloroplast-containing cells are usually some distance from the leaf surface, than in a small unicellular or filamentous alga, where every vegetative cell is photosynthetically active and not surrounded by other cells. A higher carbon dioxide concentration will then be necessary for leaves in order to overcome this diffusion resistance.[12]

For *Chlorella* in liquid suspension Emerson and Green (29) found that a carbon dioxide concentration of 10 or $15 \times 10^{-6}$ moles per liter was sufficient for maximum photosynthesis.

Smith (68), using the water plant *Cabomba*, has studied the effect of light intensity and carbon dioxide concentration on the photosynthetic rate. He found that both variables affected the rate in the same way.

However, there is disagreement concerning the effect of temperature at low carbon dioxide concentrations. According to van den Honert's curves (reference 77, page 225), temperature is without effect on the rate at low concentrations, but Warburg (82) and Emerson (23) found a high temperature coefficient for *Chlorella* at low carbon dioxide concentrations. Both Warburg and Emerson used the manometric method in their measurements; the *Chlorella* was suspended in carbonate–bicarbonate buffer mixtures and the concentration of free carbon dioxide was varied by varying the ratio of carbonate to bicarbonate. At least three possible objections may be raised to the use of these buffers for regulating carbon dioxide concentration: (*1*) In varying the carbon dioxide concentration, the pH is also varied. The high pH necessary to obtain limiting carbon dioxide concentrations may influence the photosynthetic rate. (*2*) A high concentration of carbonate or bicarbonate ions may inhibit photosynthesis. (*3*) It is possible that water plants may be able to use carbonate or bicarbonate in the photosynthetic process (3). Emerson and Green (29), working with phosphate buffers, found that within the range from pH 4.6 to 8.9, neither bicarbonate nor hydrogen ion influenced the rate of photo-

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[12] The problem of diffusion resistance has been discussed by James (47).

synthesis at saturating concentrations of carbon dioxide. They concluded, however, that in carbonate mixtures at a higher pH, other factors, probably carbonate and bicarbonate concentrations as well as free carbon dioxide concentration, were influencing the rate of photosynthesis. Moreover, with the phosphate buffers, their measurements of photosynthesis in *Chlorella* as a function of carbon dioxide concentration more closely resembled van den Honert's results for *Hormidium* than Warburg's results for *Chlorella* in carbonate–bicarbonate buffers. On the basis of the results of Emerson and Green, it may be considered probable that van den Honert's curves (77), showing little or no temperature effect at low carbon dioxide concentration, are valid for *Chlorella* as well as for *Hormidium.*

Since a knowledge of the temperature effect at low carbon dioxide concentrations is of importance in choosing a mechanism for the photosynthetic process (see page 841), it appears desirable that a further study should be made of this effect in both algae and higher plants.

### *The influence of intermittent light on photosynthesis*

Warburg (82), Emerson and Arnold (25), and Pratt and Trelease (64) have studied the effect of intermittent light on photosynthesis in *Chlorella.*

Warburg used a rotating sector which cut out half of the incident light. He found that at high light intensity and abundant carbon dioxide concentration a given amount of light produced more photosynthesis when absorbed intermittently by the *Chlorella* than when it was absorbed continuously. Moreover, the improvement in yield depended upon the frequency of the flashing. At low light intensities, intermittent light produced no improvement in yield.

The effect of intermittent light can be explained on the basis of the cyclic mechanism discussed above (page 823). Thus, after a sufficiently long period of intense illumination, most of the chlorophyll molecules would be activated (or combined in an unstable compound) and waiting to undergo the so-called Blackman reaction. Photons absorbed by these molecules would presumably be without effect on the photosynthetic rate. But, if this period of intense illumination were followed by a sufficiently long period of darkness, the Blackman or thermal reaction should continue until completed. Then, at the beginning of the next light flash, all of the photons would presumably be absorbed by chlorophyll molecules ready to undergo the next photosynthetic cycle. By combining very short light flashes with long dark periods it should be possible, according to this picture, to have a plant utilize intermittent light of high intensity as efficiently as it can utilize continuous light of low intensity.

Emerson and Arnold (25) have extended considerably the observations of Warburg. They used a neon tube as a light source, with an electrical circuit which gave very short light flashes. The circuit was constructed so that the length of the dark periods could be varied without appreciable effect on the light flashes. The *Chlorella* was suspended in a buffer mixture and photosynthesis was measured manometrically.

Figure 6 shows the results obtained by Emerson and Arnold in their study of the effect of dark time on the yield of photosynthesis per flash. The lower curve was obtained at 1.1°C., while the two upper series were obtained at 25°C. All of the measurements shown in figure 6 were made with *Chlorella* cells from the same culture. It appears that at 25°C. a dark period of 0.04 sec. is sufficient for practical completion of the thermal or Blackman reaction, while at 1.1°C. a period of 0.2 or 0.3 sec. is required for practical completion. In these experiments of Emerson and Arnold, the duration of each light flash was less than $2 \times 10^{-5}$ sec., a period which is short compared with the average duration of the thermal reaction, at least at 1.1°C.

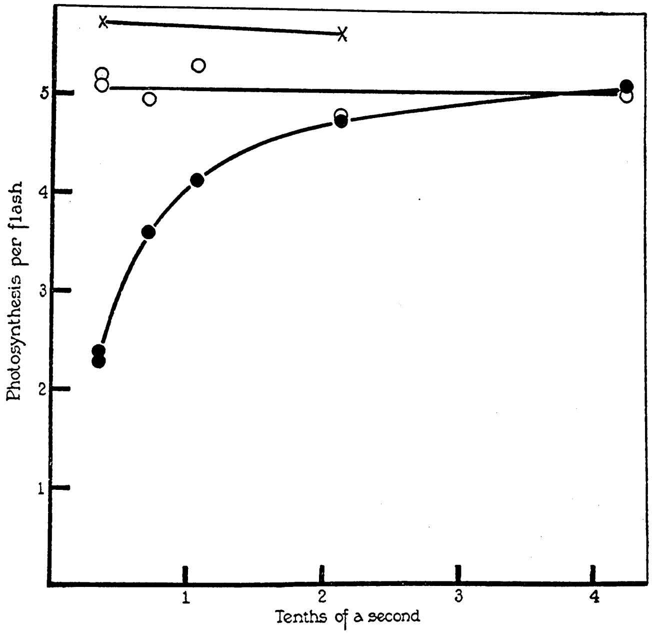

FIG. 6. The effect of dark time on the yield of photosynthesis per flash of light. Open circles are points made at 25°C.; solid circles at 1.1°C. The crosses are a check made at 25°C. (Emerson and Arnold (25)).

Figure 7 shows the results obtained with *Chlorella* at high light intensity and at 23.9°C. by Pratt and Trelease (64). Using *Chlorella* cells suspended in heavy water as well as in ordinary water, they studied the effect of flashing light on the rate of photosynthesis. Each light flash in these experiments lasted about 0.0045 sec. This period was much longer than that used by Emerson and Arnold. Consequently a considerable fraction of the chlorophyll molecules probably went through the reaction cycle more than once for each flash.

The point corresponding to a dark period of 0.0122 sec. on the upper curve in figure 7 is apparently slightly lower than the maximum, suggesting that the Blackman reaction is not quite completed in 0.01 sec. at 24°C. This is in approximate accord with indirect calculations of Emerson and Arnold (26) which indicated an *average* time of 0.012 sec. for the completion of a cycle (photochemical + Blackman reactions) in *Chlorella* at 25°C.

The lower curve in figure 7 was obtained from experiments in which the algae were suspended in heavy water. Evidently deuterium oxide retards the Blackman reaction without appreciably affecting the photochemical reaction, since, with a long dark period, the amount of photosynthesis per flash is the same in heavy water as in ordinary water.[13] These observations indicate that the specific effect of deuterium oxide is manifested in the Blackman reaction. Possibly the replacement of water by deuterium oxide may reduce the rate of the Blackman reaction by affecting a specific enzyme system.

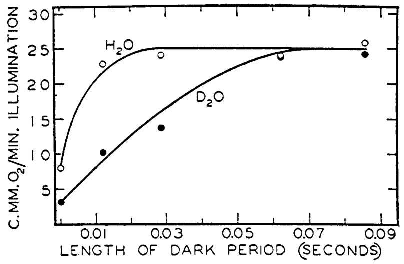

FIG. 7. Rate of photosynthesis in *Chlorella vulgaris* per minute of actual illumination as a function of the length of the dark period. The values are proportional to the photosynthesis per flash. (Pratt and Trelease (64)).

Emerson and Arnold (25) have studied the effect of low concentrations of hydrogen cyanide on photosynthesis in *Chlorella* in flashing light. With a hydrogen cyanide concentration of $1.14 \times 10^{-4}$ moles per liter, the effect was very similar to that of 99.9 per cent deuterium oxide, as reported by

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[13] With continuous light of high intensity, according to the measurements of Craig and Trelease (21), the rate of photosynthesis in $D_2O$ is about 40 per cent of the rate in $H_2O$, except at very high temperatures (see figure 5), where the rate in $H_2O$ falls more rapidly than the rate in $D_2O$. At low light intensities the rates in $D_2O$ and $H_2O$ become nearly equal. These observations are in agreement with the conclusions indicated by the flashing light experiments.

Pratt and Trelease (64) (see figure 7). The Blackman reaction was retarded but the maximum yield per flash was unchanged. But, if the hydrogen cyanide was replaced by a low concentration of phenylurethan or thymol, the maximum yield of photosynthesis per flash was decreased, with only a slight retardation of the Blackman reaction.[14]

Figure 8 shows the observations of Emerson and Arnold concerning the influence of carbon dioxide concentration on the yield of photosynthesis per flash. As before, the flash duration was less than 2 × $10^{-5}$ sec. They concluded from these experiments that carbon dioxide enters the process of photosynthesis either before or (less likely) coincident with the photochemical reaction. If chlorophyll alone were involved in the light reaction, then, according to their argument, a lower carbon dioxide concentration would not decrease the yield per flash but would necessitate longer dark periods for full utilization of the light. Since the opposite effect was actually found, Emerson and Arnold concluded that both chlorophyll and carbon dioxide (perhaps in combination) are required for the light reaction.

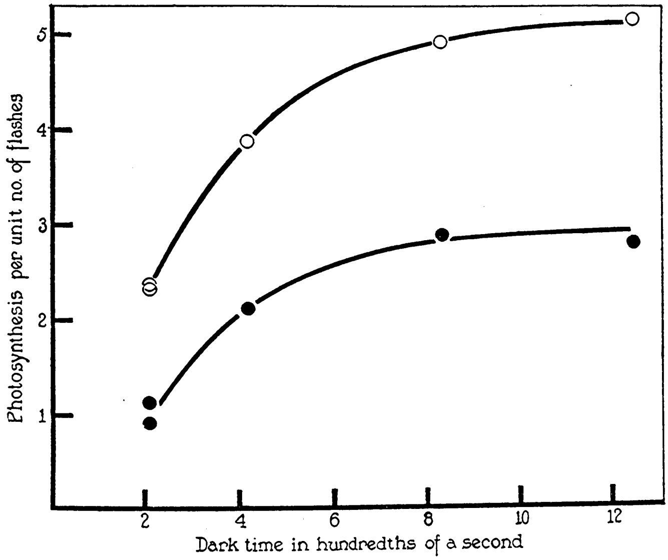

FIG. 8. The course of the dark reaction at two different concentrations of carbon dioxide. Open circles, carbon dioxide concentration = 71 × $10^{-6}$ moles per liter; solid circles, carbon dioxide concentration = 4.1 × $10^{-6}$ moles per liter. (Emerson and Arnold (25)).

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[14] In continuous light, narcotics such as phenylurethan and thymol inhibit photosynthesis at both high and low light intensities, in contrast to hydrogen cyanide, which inhibits only at high intensities (83).

However, it appears that this conclusion is open to question from two points of view. In the first place, carbon dioxide concentration was varied by changing the proportion of carbonate to bicarbonate in the buffer mixtures. Later experiments of Emerson and Green (29) have thrown doubt on the validity of this method of obtaining low carbon dioxide concentrations (see page 825). Secondly, it appears that the argument of Emerson and Arnold (given in the preceding paragraph) would be strictly valid only if the average lifetime of an activated chlorophyll molecule were much longer than the average time required for the Blackman reaction. Otherwise, the lower curve in figure 8 could be interpreted as the resultant of two curves, one a slowly rising curve, like the lower curve in figure 7, and the other a falling curve representing a decrease in concentration of activated chlorophyll.

Although the behavior illustrated in figure 8 may not give very definite evidence concerning the order in which certain steps in the reaction cycle may occur, it probably indicates, as Emerson has pointed out (reference 23, page 319), that carbon dioxide enters into a reaction in the photosynthetic cycle other than the Blackman reaction, since, if the latter reaction alone were affected by carbon dioxide concentration, the maximum yield of photosynthesis per flash should remain constant. However, this last conclusion is still subject to the uncertainty concerning the influence of carbonate–bicarbonate buffers.

Other experiments involving the use of intermittent light will be discussed below (see pages 831 and 845).

### *The induction period in photosynthesis*

A number of investigators have observed an induction period in photosynthesis, but the characteristics of this period appear to vary widely in different plant species. In the marine alga *Ulva*, Osterhout and Haas (61) found that about 2 hr. were necessary for attainment of a steady rate at high light intensity. In the moss *Mnium*, Briggs (14) found an induction period of nearly an hour. Emerson and Green (27) found a period of about 20 min. for the marine alga *Gigartina*. A period of 3 min. or less has been found in *Chlorella* (83), *Hormidium* (78), *Cabomba* (69), and wheat (53). After a 10-hr. period of darkness, however, McAlister found a longer induction period for wheat, about 12 min. Warburg found an induction period in *Chlorella* only at high light intensities, but for *Cabomba*, Smith observed an induction period at both high and low intensities. However, Warburg's measurements extended to lower intensity values than did those of Smith.

This wide diversity of characteristics suggests that the induction period may be caused by different mechanisms in different plants. Smith (69) has derived an equation for the induction period, relating the relative rate of photosynthesis to the duration of illumination, which satisfactorily describes his own data and also data obtained by several other investigators. However, the application of this equation to a particular series of data depends upon the evaluation of a constant which determines the time scale.

Most methods for measuring photosynthesis have too great a time lag to permit a satisfactory direct study of an induction period as short as 3 min. Warburg, van der Paauw, and Smith measured photosynthesis manometrically in their experiments, and resorted to an indirect integration method for studying the short induction periods which they encountered. Smith, for example, determined respiration for a 30-min. period and then exposed the plant (*Cabomba*) to light for 1 min. The manometer was not read until after a further 5- or 10-min. dark period. The rate so determined was, in effect, the resultant of 1 min. of photosynthesis superimposed on a 6- or 11-min. period of respiration. The procedure was then repeated for the same or for successively longer light exposures. The methods of Warburg and van der Paauw were similar to this. A potential source of error in this type of procedure is the possible stimulation of respiration by light. With a short light period such as 1 min., even a slight increase in respiratory rate during the subsequent 5- or 10-min. dark period would greatly reduce the apparent yield of photosynthesis.

Because of the very small time lag in his apparatus (see page 816), McAlister (53) was able to determine the induction period in wheat from continuous measurements of the photosynthetic rate. Considering the amount of carbon dioxide lost to photosynthesis as a measure of the induction period, he found that, in wheat, this quantity decreased with decreasing light intensity, apparently approaching zero at zero intensity. This result is in qualitative agreement with the behavior in *Chlorella* (83) and in *Cabomba* (69). McAlister also found the induction period in wheat to be nearly twice as long at 12°C. as at 31°C. Van der Paauw (78) observed a similar temperature effect in *Hormidium.*

In intermittent light, with equal light and dark periods, the rate of photosynthesis in wheat passes through a minimum for light and dark periods of about 1 min. (53). With longer intervals a smaller percentage of total illumination time is taken up by the induction periods, while at shorter intervals it is probable that two factors contribute to an increase in rate. One is the occurrence of the Blackman reaction during the dark periods (see page 826); the other is the probability that, after a short dark interval, the induction period is less pronounced than after a longer interval.

No very convincing mechanism has so far been advanced for the induction process in photosynthesis. Since three or more quanta of red light are necessary to supply energy for the reduction of one molecule of carbon dioxide to carbohydrate, it is often assumed that the process occurs through a series of three or more intermediate photochemical reactions (however, see page 851). On this basis it would appear probable that, after a long dark period, each reaction unit in the chloroplast would have to undergo some or all of this series of reactions before evolving oxygen or absorbing additional carbon dioxide. This should produce an induction period lasting until the establishment of equilibrium between the concentration of the various intermediates. Furthermore, the magnitude of the induction effect after a dark interval should give a measure of the extent to which the various intermediate compounds were decomposed during the dark interval.

According to this picture the induction period should last much longer at low light intensities than at high intensities. This is contrary to the observed facts. Consequently, it is evident that processes other than those considered in the preceding paragraph must play a part in the induction period.

According to the mechanism of Franck and Herzfeld (34), oxygen is evolved after the first photochemical step in the series of reduction reactions. They suggested that the induction period is the result of photo-oxidation processes (see page 850).

It appears that further data concerning the influence on the induction period of various external and internal factors are greatly to be desired.

### *Quantum efficiency of photosynthesis*

A knowledge of the quantum efficiency of the photochemical process in photosynthesis is essential to any detailed consideration of the kinetics of the process. Unfortunately, the actual measurement of this quantity is accompanied by difficulties not encountered in quantum efficiency measurements carried out in non-living systems. Some of these difficulties will be considered in the following paragraphs.

Because of the complexity of the photosynthetic process, many factors other than the efficiency of the photoprocess may influence quantum efficiency values determined from a measurement of the overall reaction. To a certain extent, the influence of these other factors may be minimized by using low light intensities, high carbon dioxide concentration, and a relatively high temperature. In this range, since the rate of photosynthesis is nearly proportional to light intensity, the quantum efficiency should be nearly constant and relatively independent of other external variables. Under these conditions, however, the necessary correction for respiration becomes relatively very large. If it were definitely established that the respiratory and photosynthetic processes are independent and unaffected by each other, and that the rate of respiration is not influenced by light, then respiration corrections, even when large, would not seriously reduce the accuracy of photosynthesis measurements. However, van der Paauw (78) found that, in *Hormidium*, respiration was more than twice as rapid immediately after an hour of strong illumination as it had been before the photosynthetic period. Two hours after exposure, the respiration had dropped to its normal rate. In an atmosphere devoid of carbon dioxide, van der Paauw found that the respiratory rate was actually increased during illumination. However, it is possible that, in the absence of carbon dioxide, light may have produced an abnormal effect. Petering and Daniels (62) have observed a temporary increase in the rate of respiration for *Chlorella* after exposure to light, the extent of the increase depending on the previous treatment. On the other hand, McAlister (53) failed to find any stimulation in wheat plants after illumination at high light intensities, despite the fact that a very sensitive method was used. The difference between the response of wheat on the one hand, and *Hormidium* and *Chlorella* on the other, may be partially due to the much larger fraction of total cell volume occupied by the chloroplasts in the case of the algae.

The measurement of light absorption in plant material is difficult. Pigments are irregularly distributed and much light is lost by refraction and scattering. From this point of view, a small unicellular alga, such as *Chlorella*, is more satisfactory than a leaf of a higher plant. *Chlorella* in suspension settles only slowly, making it easy to maintain even distribution. Moreover, by varying the concentration of the suspension, the fraction of incident light absorbed can be varied at will.

Not all of the absorbed light is absorbed by chlorophyll. The amount absorbed by other substances can be estimated from measurements made with extracted pigments, but such an estimate is uncertain, since the optical properties and distribution of the various pigments are altered by the extraction process. Moreover, it is not known whether light absorbed by chloroplast pigments other than chlorophyll can contribute to photosynthesis. At wave lengths longer than 5500 Å., the uncertainty due to these other pigments is minimized, since their absorption is very slight at longer wave lengths.

Another difficulty is found in the fact that, in some plant material, a large part of the chlorophyll may be inactive so far as ability to produce photosynthesis is concerned. After reaching maturity a leaf usually decreases in photosynthetic activity, even though the amount of chlorophyll may remain constant or increase. Because of this, it is advisable to use only young or actively growing material for quantum efficiency measurements.

Finally, there is a possibility that the mechanism of photosynthesis is not the same for all plants. In this case the overall efficiency would probably vary in different plants, even if all measurements were made under ideal conditions. However, the apparently identical nature of the pigments in many different plant species, as well as other similarities in the photosynthetic process, suggest that the photochemical reactions are the same, at least throughout the green algae (*Chlorophyceae*) and the higher divisions of the plant kingdom (mosses, ferns, and seed plants).

The first measurements of the quantum efficiency of photosynthesis were made by Warburg and Negelein (85, 86), with the alga *Chlorella* as plant material. A differential manometer was used for the photosynthesis measurements. A mercury arc with filters served as a source of monochromatic light except in the red, where a filament lamp with filters was used to obtain the region 6100–6900 Å. To avoid the necessity of measuring transmitted light, Warburg and Negelein used very heavy suspensions of the algae. Except for a small amount of reflection, practically all of the incident light was absorbed. At any one time most of the *Chlorella* cells were thus receiving only a small fraction of the incident light intensity. To reduce the value of the respiration correction, these investigators carried out their measurements at a temperature of 10°C., where respiration is much slower than at 20° or 25°C.

At wave lengths of 6600, 5780, and 5461 Å. Warburg and Negelein found a quantum efficiency of approximately 0.25 molecule of carbon dioxide per quantum. The observed value at 4360 Å. was lower, about 0.20, but an approximate correction for light absorbed by the carotene and xanthophyll pigments increased the 4360 Å. value to 0.25 or slightly higher. The incident light intensity in these experiments varied from 575 to 3500 ergs per $cm.^2$ per second. Within this range the quantum efficiency appeared to be independent of light intensity.

At 6600 Å. $Nh\nu = 43{,}000$ cal., so that a quantum efficiency of 0.25 corresponds to an energy efficiency of 65 per cent on the basis of equation I. If formaldehyde is the first product of photosynthesis, then $\Delta H$ for equation I becomes 134,000 cal. and the corresponding energy efficiency is 78 per cent. In either case the energy efficiency is surprisingly large, particularly since one or more of the intermediate reactions in photosynthesis is probably exothermic.

The quantum efficiency of photosynthesis in *Chlorella* has recently been investigated by Manning, Stauffer, Duggar, and Daniels (55). These investigators found quantum efficiencies much lower than those reported by Warburg and Negelein. Most of the experiments were carried out at 25°C., with high carbon dioxide concentrations. Light intensities varied from 830 to 24,000 ergs per $cm.^2$ per second. A mercury arc was used with a monochromator to give monochromatic light of wave lengths 5461 and 4360 Å. Other measurements were made with polychromatic light from the mercury arc, and still others with light from a tungsten filament lamp.

In some experiments a gas stream was bubbled through the algal suspension and photosynthesis measured by gas analysis, while in other experiments a closed system was used, oxygen being determined by the Winkler method. In all cases the algal suspensions were less concentrated than those of Warburg and Negelein, since from 10 to 50 per cent of the incident light was transmitted through the back of the reaction vessel.

The quantum efficiency values obtained by Manning, Stauffer, Duggar, and Daniels were quite variable, but the maximum value of approximately 0.06 is so far below the figure obtained by Warburg and Negelein that it is difficult to attribute the discrepancy to differences in experimental procedure.[15] Different strains of *Chlorella* (possibly different species) may have been used in the two investigations (reference 55, page 272), but it is unlikely that such minor differences would cause any fundamental difference in the photosynthetic mechanism.

Quantum efficiency measurements, in *Chlorella* exposed to various intensities of sunlight below the surface of a lake, have been made by Manning, Juday, and Wolf (54). The maximum value approached at low light intensities was approximately 0.05.

Burns (18) has calculated quantum efficiencies from measurements of photosynthesis in white pine trees. In his experiments the top of a young tree was enclosed in a bell jar containing 1 per cent of carbon dioxide. The decrease in carbon dioxide concentration after 2 hr. of illumination was determined by gas analysis. Light sources were the 5890 Å. line of sodium, the 5780 Å. line of mercury, and polychromatic light with filters. The quantum efficiency for the yellow lines of sodium and mercury was approximately 0.13; for the polychromatic light the value was approximately 0.11. The light intensities used were apparently greater than 10,000 ergs per cm.$^2$ per second.

In Burns' experiments it was necessary to estimate the amount of absorbed light by determining the absorption of an acetone solution of the extracted pigments. This procedure is subject to some uncertainty, since the pigment distribution is of course very different in the two cases. Such an approximation is apparently unavoidable when working with a light-absorbing system as complex as this.

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[15] In both investigations it was evident that the previous conditions of growth played an important part in determining quantum efficiency values. Warburg and Negelein found that a week of growth at high light intensity, followed by a week of growth at low light intensity, gave the most favorable results for their strain of *Chlorella*. It is especially necessary to avoid using old cultures which have passed the period of most active growth. *Chlorella* cells from such cultures often contain a high chlorophyll concentration, but nevertheless show a low photosynthetic efficiency. It is possible that much of the chlorophyll in such cells is unable to transfer absorbed energy to the photosynthetic mechanism.

Briggs (13) has determined the energy utilization for photosynthesis in the leaves of the bean (*Phaseolus vulgaris*), the elder (*Sambucus nigra*), and the elm. Most of the light intensities were in the neighborhood of 5000 ergs per cm.$^2$ per second. The higher quantum efficiencies estimated from Briggs' data are in approximate agreement with those determined by Burns.

The present data concerning the problem of the quantum efficiency of photosynthesis are in serious disagreement. Evidently a further study of the problem is greatly to be desired. It appears probable that accurate and extensive data on the variation of the quantum efficiency as a function of wave length in different species may help to dispel the uncertainty concerning the photosynthetic activity of pigments other than chlorophyll, and also serve to provide a more secure basis for the postulation of chemical and kinetic mechanisms for the process.

### *Photosynthesis in bacteria*

The problem of photosynthesis in bacteria is a very interesting one, and may have an important bearing on the problem of photosynthesis in green plants. An adequate discussion of bacterial photosynthesis would require many pages; only a few aspects of the problem will be considered here. More complete information may be obtained from recent publications of van Niel (79, 80), whose researches have contributed a large portion of our present knowledge concerning bacterial photosynthesis.

In the presence of light, hydrogen sulfide, and carbon dioxide, the green and purple sulfur bacteria are able to develop in entirely inorganic media. These bacteria grow only under anaerobic conditions, and no oxygen is given off during their development. Instead, sulfur or sulfuric acid is produced.

Assuming that formaldehyde is the first product, the equation for the process in the green sulfur bacteria may be written:

$$CO_2 + 2H_2S \xrightarrow{\text{light}} (CH_2O) + H_2O + 2S \qquad \Delta H \cong 22{,}000 \text{ cal.} \qquad \text{(II)}$$

and in the purple bacteria:

$$2CO_2 + H_2S + 2H_2O \xrightarrow{\text{light}} 2(CH_2O) + H_2SO_4 \qquad \Delta H \cong 72{,}000 \text{ cal.} \qquad \text{(III)}$$

Apparently the green sulfur bacteria can utilize only hydrogen sulfide as a hydrogen donor for the reduction of carbon dioxide, but the purple sulfur bacteria can carry on photosynthesis in the presence of a number of substances other than hydrogen sulfide. Among these are sodium sulfite, sodium thiosulfate, sulfur, hydrogen, and various organic substances

(79).[16] For the reaction with hydrogen (37), the probable equation is

$$CO_2 + 2H_2 \xrightarrow{\text{light}} (CH_2O) + H_2O \qquad \Delta H \cong 2000 \text{ cal.} \qquad \text{(IV)}$$

As Spoehr and Smith have pointed out (72), it is questionable whether the processes represented by equations II and IV can, strictly speaking, be called photosynthesis, at least if the word is used to denote an accumulation of light energy in the form of chemical energy. As in the higher plants, the formaldehyde or other intermediate product is presumably polymerized almost immediately to carbohydrates. If equations II and IV are written with glucose instead of formaldehyde as the reduction product, $\Delta H$ becomes approximately zero for equation II and negative for equation IV.

Bacterio-chlorophyll, a pigment closely related to the chlorophyll found in green plants (32), occurs in both of these groups of bacteria. The purple bacteria also contain one or more red pigments, probably related to the carotenoid pigments of green plants. Bacterio-chlorophyll shows a strong absorption in the region between 8000 and 9000 Å., in addition to its visible absorption bands. Consequently the sulfur bacteria are able to utilize infrared radiation in the reduction of carbon dioxide.

French (38) has studied the effect of different wave lengths on the rate of carbon dioxide assimilation by one of the purple bacteria (*Spirillum rubrum*). Using very thin suspensions of the bacteria, he found that the reaction rate corresponded closely to the absorption spectrum of the green pigment, even in regions where the red pigment absorbed strongly. Consequently he concluded that the red pigment is photochemically inactive in photosynthesis.

Van Niel has suggested that the various equations for photosynthesis (I to IV) should be considered as special cases of a general type reaction:

$$CO_2 + 2H_2A + nh\nu \rightarrow (CH_2O) + H_2O + 2A \qquad \text{(V)}$$

where $H_2A$ represents a substance able to furnish hydrogen for the reduction of carbon dioxide.

### *Quantum efficiency of photosynthesis in bacteria*

Roelefson (66) has made some measurements of the quantum efficiency of photosynthesis in the purple sulfur bacteria. After making corrections for light absorbed by red pigments, he concluded that the maximum quantum efficiency is approximately 0.25 molecule of carbon dioxide per

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[16] The purple bacteria referred to here are members of the *Thiorhodaceae*. Another group of photosynthetically active purple bacteria, the *Athiorhodaceae*, apparently require organic compounds instead of sulfur compounds as reducing agents.

quantum absorbed, in agreement with the measurements of Warburg and Negelein (86) for the alga *Chlorella.*

French (37), using the purple bacterium *Streptococcus varians*, has made quantum efficiency measurements in which infrared radiation (wave lengths 8520 + 8940 Å., from a cesium lamp) was used as the energy source. The red pigments do not absorb appreciably in this wave length region. The bacterial suspension was in equilibrium with an atmosphere of 5 per cent carbon dioxide and 95 per cent hydrogen. Consequently the overall reaction presumably corresponded to that of equation IV.

French's measurements were complicated by the fact that he found a sigmoid curve for the variation in reaction rate as a function of light intensity. Thus, at low intensities the rate was proportional to a higher power of intensity than the first power. Quantum efficiencies were calculated from the maximum slopes observed for his rate versus light intensity curves. The maximum slope occurred at various light intensities, depending upon the type of pretreatment of the bacteria. By extrapolation French found that as the position of the maximum slope approached zero light intensity, the quantum efficiency appeared to approach a value of 0.25 (or 0.5 on the basis of hydrogen), in agreement with the estimates of Roelefson. As Emerson has pointed out (24), there is some doubt concerning the validity of this indirect method of calculating quantum efficiencies, particularly since it yields higher efficiency values than those actually prevailing in French's experiments.

French agrees with van Niel (79) in believing that the agreement between the quantum efficiencies observed for purple bacteria and those observed for *Chlorella* by Warburg and Negelein (86) indicate that a similar sequence of photoreactions is involved, despite the great difference in energy requirements. However, recent experiments with *Chlorella* (54, 55) have created some doubt concerning the correctness of the quantum efficiency values obtained by Warburg and Negelein (see page 835).

## IV. THE RÔLE OF CHLOROPHYLL IN THE PHOTOSYNTHETIC PROCESS

### *Chlorophyll production*

The manner in which chlorophyll is manufactured by green plants is a problem of fundamental physiological importance. It will be mentioned only briefly in this review, since it probably is not a direct part of the problem of photosynthesis. Further information on chlorophyll production may be obtained from articles by Spoehr and Smith (72), Inman, Rothemund, and Kettering (46), and Rothemund (67).

In most of the higher plants light is necessary for chlorophyll production. However, other plants, particularly some of the algae, can apparently produce chlorophyll in the dark. Etiolated plants, although usually containing no chlorophyll, have been found to contain a very small amount of another green pigment which is usually called protochlorophyll. It differs spectroscopically from chlorophyll. When an etiolated plant is exposed to light, most of this green pigment disappears and is perhaps transformed into chlorophyll (67).

Most plants develop a higher chlorophyll concentration when grown in light of relatively low intensity than when grown in very bright light. Consequently several investigators have suggested that, in addition to its rôle in chlorophyll formation, light may also produce chlorophyll decomposition. According to this view, the chlorophyll concentration in a plant under given conditions can be regarded as a steady state concentration, with the rate of chlorophyll formation being approximately balanced by its rate of decomposition.

The production of chlorophyll is, of course, also dependent upon the proper supply of mineral nutrients; perhaps the most conspicuous of these are magnesium, which enters into the chlorophyll molecule, and iron, which apparently acts as a catalyst in some step in the formation process.

### *Chemical properties of chlorophyll*

The structure and chemical properties of extracted chlorophyll are now known rather completely, largely as a result of the investigations of Willstätter, Stoll, Fischer, and Conant. The subject has recently been reviewed by Fischer (30) and by Steele (73). Figure 9 shows the probable formula for chlorophyll *a* (30). Fischer's formula for chlorophyll *b* is identical with the formula for *a*, except that the methyl group in the 3-position is replaced by a formyl group.

Willstätter and Stoll (89) have found that the *a*:*b* ratio for chlorophyll in leaves is approximately 3. They found that this ratio was practically constant for many different species and for different environmental conditions. However, other investigators have found evidence that the ratio depends somewhat upon external conditions.

Working with etiolated corn seedlings, Inman (45) found that, shortly after exposure to light, the chlorophyll *a*:*b* ratio was very high, approximately 22:1. After an additional 90 min. of light exposure the ratio dropped to 17:1. Similar behavior has been observed in oat seedlings by Burr and Miller (19). The simplest explanation for this behavior would be that chlorophyll *a* is produced first, and that chlorophyll *b* is an oxidation product of chlorophyll *a*. However, this type of oxidation would be very difficult to bring about *in vitro*.

In some of the earlier theories concerning the photosynthetic mechanism, it was assumed that the *a* and *b* components formed a photo-activated oxidation–reduction system, so that the coöperation of both components would be necessary to carry on photosynthesis. Aside from the difficulty involved in the methyl-formyl oxidation, further evidence that the *a* and *b* components do not function as an oxidation–reduction system is found in the observation of Fischer and Breitner (31) that chlorophyll *b* does not occur in several of the red algae (*Porphyra tenera, Bangia fuscopurpurea,* and *Polysiphonia nigrescens*). On the other hand, Beber and Burr (11) observed no photosynthesis in etiolated oat seedlings until long after a perceptible amount of chlorophyll *a* was formed. Their experiments suggested that chlorophyll *b* is necessary for photosynthesis in oat seedlings. Further evidence concerning the degree of interdependence of the two chlorophylls might be obtained from quantum efficiency measurements with wave lengths chosen to correspond to the respective absorption maxima of the two pigments.

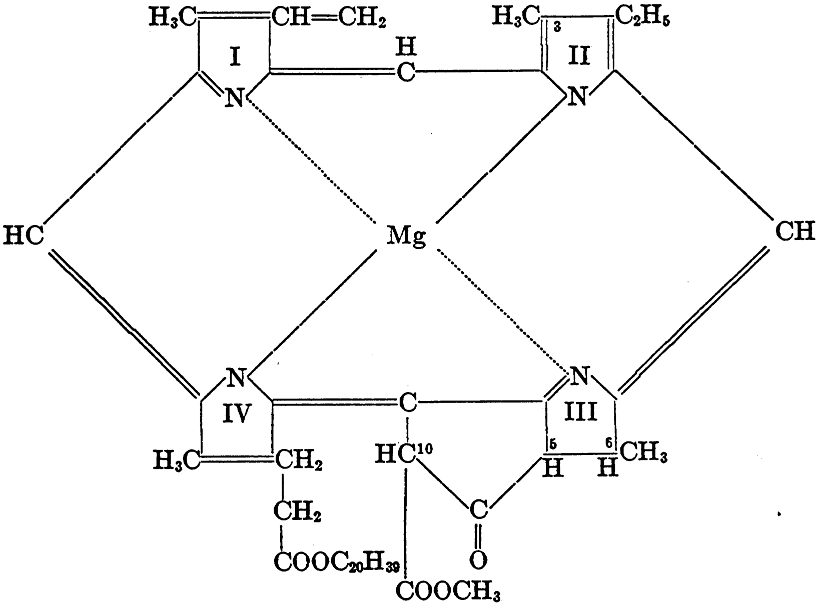

FIG. 9. Fischer's formula for chlorophyll *a* (Steele (73))

Stoll (75), on the basis of his own and other investigations, has concluded that the action of both chlorophylls in the photosynthetic process is in large part due to the labile hydrogen atom attached to the carbon atom in the 10-position (figure 9). According to his point of view, the existence of two chlorophyll components may be advantageous to a plant because of the increased range of wave lengths which can thus be absorbed (see figure 1). This might be particularly useful to a plant growing in dim light.

In the chloroplast the position of the absorption maxima for the two chlorophylls is shifted approximately 200 Å. to the red as compared to the position for the extracted pigments in ether solution. This shift is usually ascribed to differences in the optical properties of the solvents. Albers and Knorr (2) have recently studied the absorption spectra of single chloroplasts in the region from 6640 to 7040 Å. They found evidence for several maxima in the absorption band usually attributed to chlorophyll *a*. They suggested that the several maxima may be due to the presence of compounds between chlorophyll *a* and various intermediates in the photosynthetic process.

The phytyl group in the chlorophyll molecule has little influence on the optical properties. Replacement of the phytyl group by a methyl group produces only a slight change in the chlorophyll absorption spectrum. The optical properties are due principally to the ring of conjugated double bonds surrounding the central magnesium atom. The phytyl group, according to Stoll (75), may serve to make chlorophyll lipoid-soluble, thus permitting proper distribution in or on the plastid.

Stoll suggests that, in addition to maintaining the conjugated bond system, magnesium is important in maintaining the proper degree of reactivity with carbonic acid. Chlorophyll forms a complex with carbonic acid *in vitro*, and Stoll, as well as many other investigators, suggests that a similar complex is formed in the plant. As mentioned above (page 825), earlier evidence indicated that the rate of photosynthesis is temperature-dependent even at very low carbon dioxide concentrations. This was regarded as additional evidence for the formation of a carbonic acid (or carbon dioxide) complex with chlorophyll during the photosynthetic process. But the experiments of van den Honert (77) and of Emerson and Green (29) have indicated that the temperature dependence at low carbon dioxide concentrations may be only apparent, and due to complications resulting from the use of buffer mixtures. These observations weaken somewhat the evidence for participation of a carbonic acid–chlorophyll complex in photosynthesis.

It has frequently been observed that chlorophyll in solution is decomposed by the action of light. Albers and Knorr (1, 51) have followed this decomposition in the presence of various gases, by observing changes in the fluorescence spectra of chlorophylls *a* and *b*. Porret and Rabinowitch (63) have studied the bleaching of chlorophyll dissolved in methanol. In the presence of oxygen the quantum yield was approximately $10^{-6}$. This value was independent of oxygen concentration over a wide range, but the bleaching disappeared on complete removal of oxygen.

In the absence of oxygen Porret and Rabinowitch (63) found that intense light caused a reversible bleaching of the red absorption band of chlorophyll. Using a $10^{-6}$ molar solution of chlorophyll in methanol, and a light intensity such that each chlorophyll molecule absorbed about 10 quanta per second, the bleaching of the red band amounted to about

1 per cent. Therefore, assuming the quantum efficiency of the bleaching process to be 1, they estimated an average lifetime for the bleached state of about $10^{-3}$ sec. The degree of bleaching was approximately proportional to the square root of light intensity. Porret and Rabinowitch suggested that the bleaching was probably due to a dissociation into "dehydrochlorophyll" and a hydrogen atom (perhaps from carbon atom No. 10; see figure 9). In the presence of formic acid the reversible bleaching was increased to 10 per cent. With a dissolved oxygen concentration of $10^{-5}$ molar, the bleaching with formic acid was reduced about 50 per cent. Apparently the oxygen either formed a complex with chlorophyll or removed the chlorophyll excitation before dissociation could occur.

Rabinowitch and Weiss (65) have found that chlorophyll in methyl alcohol solution is transformed by certain oxidizing agents, particularly ferric chloride, into a yellow product. The chlorophyll could be restored to its original condition by the action of ferrous chloride. The oxidation process was accelerated by light. In the yellow oxidation product the red absorption bands were virtually eliminated, and the blue bands shifted toward shorter wave lengths. A rather peculiar feature of the oxidation process was that the blue band of chlorophyll *b* was changed much more slowly than the red band of *b*, and also more slowly than either the red or blue bands of the *a* component. This suggests that the blue absorption band of *b* may be produced by a chromophoric group different from those responsible for the other absorption bands of chlorophyll. Rabinowitch and Weiss consider it probable that the oxidation of a chlorophyll molecule results in the formation of a positively charged chlorophyll ion, which perhaps then breaks down into a hydrogen ion and dehydrochlorophyll.

It is probable that, in the process of extraction from plant cells, the chlorophyll pigments undergo some sort of chemical change. Some investigators (e.g., Stoll (75) and Franck and Herzfeld (34)) have suggested that, in the chloroplast, chlorophyll may be combined with a protein. Its specific effectiveness in photosynthesis would thus depend upon its attachment to a particular colloidal carrier. In any event, attempts to bring about carbon dioxide reduction by extracted chlorophyll have thus far been unsuccessful.[17] Whether this failure is due principally to changes

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[17] Baly, Stephen, and Hood (8) have reported the formation of carbohydrates from carbon dioxide and water, with visible light as the energy source. The light-absorbing agent in their experiments was not chlorophyll, but an aqueous suspension of nickel or cobalt carbonate. However, a number of other investigators have tried, without sucess, to repeat the experiment of Baly, Stephen, and Hood. It may be that these other investigators have failed to duplicate with sufficient exactness the procedure described by Baly *et al.*, but, as Emerson (23) has suggested, it seems reasonable to require that the production of photosynthesis *in vitro* should be capable of repetition before it can be regarded as an established fact.

in the chlorophyll, or to changes in the environment, or both, is as yet an unanswered problem.

### *Chlorophyll fluorescence*

Solutions of chlorophyll emit a bright red fluorescence when illuminated with visible or near ultraviolet radiation. It has been estimated that, under favorable conditions, about 10 per cent of the absorbed radiation may be recovered as fluorescence (36). Chlorophyll in living cells also fluoresces, but much less strongly than solutions of the extracted pigment. The maximum yield for chlorophyll fluorescence in living material is of the order of 0.01 per cent (81). Colloidal solutions of chlorophyll do not fluoresce. The fact that fluorescence occurs in the living cell is often regarded as an indication that chlorophyll is in a dissolved state in the chloroplast. However, the very low intensity of fluorescence in the chloroplast lessens the force of this argument.

Zscheile (94) has determined the fluorescence spectra of chlorophylls *a* and *b* in ether solution. The exciting radiation was supplied by a tungsten filament lamp. The *a* component showed two bands and the *b* component three bands in the region 6300–8200 Å. No observations were made at wave lengths below 6300 Å.

Kautsky and coworkers (49, 50) and Franck and Wood (36) have studied the effect of illumination time on the intensity of fluorescence in living leaves. In Kautsky's experiments the 3660 Å. line of mercury was used as the exciting source, while, in the experiments of Franck and Wood, a tungsten filament lamp with a blue filter was used to produce fluorescence. The results of these two series of investigations, while not identical, showed the same general type of behavior. Following a long period of darkness, the fluorescent intensity from an illuminated leaf is at first very low, but increases rapidly to a maximum after 2 to 5 sec. of illumination. The intensity then diminishes until a constant level is reached after about a minute. At a temperature of 35°C., Kautsky and Marx (50) found that this constant intensity was approximately two-thirds of the temporary maximum value, but at 0.1°C. the intensity remained constant at nearly the maximum value. In the presence of oxygen, the fluorescent intensity was reduced to about half the value observed in the absence of oxygen (49).

Franck and Levi (35) found that weak alcoholic or acetonic extracts of leaves, when irradiated in the presence of oxygen, showed a variation in fluorescent intensity similar to that found in leaves.

Kautsky concluded from his investigations that there is an intimate connection between the process of photosynthesis and the process of fluorescence. Earlier investigations (89) indicated that oxygen is necessary for photosynthesis. Consequently, Kautsky attributed the quenching of fluorescence by oxygen to the utilization of chlorophyll excitation energy in the process of photosynthesis. Kautsky and Hormuth (49) suggested that oxygen forms an addition compound with some substance in the chloroplast, and that this compound serves to transfer the chlorophyll excitation energy to carbonic acid, which is thereupon reduced to formaldehyde or carbohydrate.

Kautsky's interpretation is open to question from several points of view. In the first place, recent experiments by Gaffron (39), with *Chlorella,* indicate that oxygen is not essential for photosynthesis. Gaffron observed that when *Chlorella* was illuminated following 15 hr. in darkness in a nitrogen atmosphere, carbon dioxide consumption proceeded normally. However, oxygen production did not occur for some time, presumably because of oxidation of excess intracellular fermentation products.

Secondly, Kautsky used the 3660 Å. line of mercury to excite fluorescence. This wave length is relatively inefficient for photosynthesis (see page 818).

Thirdly, as Emerson (23) has pointed out, a plant exposed to high light intensity is using only a small fraction of the absorbed energy in the photosynthetic process. Consequently, changes in fluorescent intensity might occur quite independently of the photosynthetic process.

Franck and Wood (36), while not considering oxygen as necessary for photosynthesis, concluded that there is a close connection between the processes of photosynthesis and fluorescence. They interpreted the variation in fluorescent intensity as being due to the formation and disappearance of a strongly fluorescent radical.

According to the mechanism of Kautsky and Hormuth (49), it would appear that, at low light intensities, the percentage yield of fluorescence should increase with increasing intensity of the incident light, approaching a maximum value after the attainment of a maximum photosynthetic rate. If this type of relation could actually be established, it would constitute strong evidence for a connection between photosynthesis and fluorescence.

### *The relation between chlorophyll concentration and the maximum rate of photosynthesis*

Emerson (22) and Fleischer (33) have studied the effect of varying chlorophyll concentration on the rate of photosynthesis in *Chlorella.* Emerson grew *Chlorella* in a nutrient solution containing glucose, and varied the chlorophyll concentration by varying the concentration of iron in the nutrient solution. Fleischer varied the chlorophyll concentration in three different ways. In some of his series the iron concentration was varied, while in other series the magnesium or nitrogen concentrations were varied. Except for samples deficient in magnesium, Emerson and Fleischer both found that, at high light intensity and abundant carbon dioxide concentration, the rate of photosynthesis per unit volume of cells was approximately proportional to the amount of chlorophyll. When chlorophyll deficiency was caused by insufficient magnesium, Fleischer found an abnormally low rate of photosynthesis, and consequently concluded that magnesium influences the process of photosynthesis in some way other than by its influence on chlorophyll production.

Emerson and Arnold (26) have studied the relation in *Chlorella* between chlorophyll content and the rate of photosynthesis in intermittent light of high intensity. In these experiments the chlorophyll content was varied by varying the light conditions under which the *Chlorella* was cultured. As in previous work (25), they used light flashes which lasted only about $10^{-5}$ sec., a period which is short compared with the duration of the dark or Blackman reaction (see page 827). Sufficient time was allowed between flashes for completion of the dark reaction, so that light saturation in their intermittent light experiments implied, not that the rate of the dark reaction was limiting, as it is in the case of saturation with continuous light, but that the photochemical mechanism was saturated. Under these conditions the maximum rate was again found to be approximately proportional to the chlorophyll concentration. Emerson and Arnold calculated the ratio between the total number of chlorophyll molecules present in the reaction vessel and the number of carbon dioxide molecules reduced per single light flash. Instead of finding a value of 1 (or of 3 or 4 or 5, as would be expected in case a series of three or four or five alternate photochemical and thermal reactions were required for the photosynthetic cycle), they found a value of approximately 2500. This figure represented the average for all chlorophyll concentrations; its value was apparently independent of chlorophyll concentration. In similar experiments Kohn (52) found that light saturation was reached when only about one chlorophyll molecule in a hundred absorbed one or more quanta in a single flash. Arnold and Kohn (6) have determined the minimum value of the ratio of chlorophyll molecules to carbon dioxide molecules reduced per flash for several different species in different divisions of the plant kingdom. They found the value to lie between 2000 and 4000 in all cases.

Emerson (23, 24) has suggested that carbon dioxide probably does not combine with chlorophyll prior to the photoreaction, and that the ratio of about 2500 probably represents the ratio between chlorophyll and some other internal factor, perhaps the substance which combines with carbon dioxide. However, according to this mechanism, one would expect a very low quantum efficiency, even with low intensity continuous light. The high efficiency values reported by Warburg and Negelein (86), or even those found by Manning, Stauffer, Duggar, and Daniels (55), would thus be very difficult to explain.

### *The photosynthetic unit*

One way of reconciling the small yield of carbon dioxide reduced per flash with the relatively high quantum efficiencies observed at low light intensities is to assume that light absorbed by a large number of chlorophyll molecules can be made available to a single carbon dioxide molecule. This assumption implies (unless one postulates an extremely long life for excited chlorophyll) that, in the chloroplast, the chlorophyll molecules are distributed in the form of groups or units, each containing a large number of individual molecules. Arnold and Kohn (6), Gaffron and Wohl (40), and Weiss (88) have favored this interpretation. The postulated size of such a unit would depend upon the number of successive photochemical reactions which are required to reduce one carbon dioxide molecule, and also on the number of carbon dioxide molecules associated with each group. Weiss (88) has suggested that a single unit may have carbon dioxide molecules adsorbed on the surface, with one carbon dioxide molecule to each surface molecule of chlorophyll. Assuming four successive photoreactions, it would thus be necessary to have 500 or 600 molecules in the interior for each surface molecule of chlorophyll. Weiss calculated that, if such a unit were spherical, its radius should be of the order of $0.4\mu$. Globules of this general size have been observed in photographs of chloroplasts (44). However, it is difficult to conceive of energy transmission through a unit of this magnitude without enormous losses in the form of heat.

Gaffron and Wohl (40) obtained additional support for the existence of of a photosynthetic unit from approximate calculations in which the data of numerous investigators were used. They found that the maximum photosynthetic rate (light saturation) corresponded to the reduction of one carbon dioxide molecule by each chlorophyll molecule every 10 or 20 sec. This period is approximately 1000 times as long as the average time for the dark or Blackman reaction (25, 26). Assuming a single dark reaction in each cycle, this would indicate a unit of about 1000 chlorophyll molecules for each carbon dioxide molecule.

It has also been suggested (34, 91) that the existence of a photosynthetic unit would account for the absence of a long induction period at low light intensities. If a single chlorophyll molecule were obliged to absorb four or more quanta before oxygen could be liberated, a long induction period would be required at low light intensities. But, if a unit of 500 or 1000 chlorophyll molecules were available for the reduction of each carbon dioxide molecule, the necessary quanta would be absorbed within a second or two, even at the lowest intensities that have been used in studies of photosynthesis.

If the process of photosynthesis involves a series of photochemical reactions, any thermal decomposition of intermediate products would result in a lowering of the overall efficiency of the process. If one or more of these intermediate products were sufficiently unstable to decompose appreciably within a period of a minute or less, then a plant should be greatly benefited at low light intensities by the coöperation of more than one chlorophyll molecule in the reduction of a carbon dioxide molecule, since the time between successive photoreactions would be shortened in proportion to the number of chlorophyll molecules per unit.

As Gaffron and Wohl (40) have pointed out, a variation in the size of the photosynthetic unit might account for the phenomenon of light adaptation, by which plants of the same species may be conditioned to efficient use of either high or low light intensities. A plant accustomed to high intensities will often photosynthesize more rapidly in bright light than will one accustomed to low intensities, and *vice versa.* A large number of small units would permit more rapid photosynthesis in bright light, while, with weak light, large units would serve to minimize the possible losses due to decomposition of intermediates.

Thermal decomposition of intermediate products might account for the type of behavior shown at low light intensities by the species of purple bacteria which French (37) used in his measurements of quantum efficiency (see page 838). At low light intensities French's measurements indicated a decreasing efficiency as intensity decreased. If thermal decomposition of intermediates was responsible for this behavior, it would be expected that an increase in temperature should increase the rate of decomposition, and thus cause the diminished efficiency to occur at higher light intensities. This effect was actually observed by French (reference 37, figure 5). However, it should be remembered that the change in $\Delta H$ is small for the reaction studied by French. The only reason for assuming a series of photoreactions for the process is its apparent similarity to green plant photosynthesis.

Perhaps the strongest argument against the existence of a photosynthetic unit is the difficulty involved in picturing a model which would permit an efficient transfer of energy from every region where visible light could be absorbed to the point where it could be utilized for carbon dioxide reduction.

Franck and Herzfeld (34) considered that the fluorescence of chlorophyll in living plants is an indication of unimolecular dispersion. Since colloidal chlorophyll does not fluoresce *in vitro,* they argue that chlorophyll in units of 500 or more should not fluoresce in the chloroplast.

However, the very low intensity of fluorescence *in vivo* weakens the argument. Rabinowitch[18] has suggested that the weak chlorophyll fluorescence observed in living material may be emitted by a few "misplaced" chlorophyll molecules which may play no part in photosynthesis.

Wohl (91) has discussed in detail various arguments favoring the existence of a photosynthetic unit. He also has suggested several experiments with intermittent light which might add to our knowledge of the photoprocess involved in photosynthesis.

The existence of a photosynthetic unit has thus far been neither proved nor disproved. Its existence would offer an explanation for several different groups of experiments, but on the other hand, various arguments, largely based on physical grounds, can be offered against it.

### *The mechanism of photosynthesis*

Several recent investigators have proposed kinetic mechanisms for the process of photosynthesis, e.g., Arnold (5), Baly (7), Briggs (15), Burk and Lineweaver (16), Franck and Herzfeld (34), and Smith (68). Of these, the mechanism of Franck and Herzfeld is the only one which includes a detailed consideration of the photochemical reactions which may be involved. Other investigators have suggested a variety of chemical mechanisms without going into detail regarding the kinetics of the process (Conant, Dietz, and Kamerling (20), Gaffron and Wohl (40), James (47), Kautsky and Hormuth (49), Stoll (75), van Niel (79)).

In most of these mechanisms it is assumed that the quantum efficiency for the photochemical reaction is 0.25, in accord with the observations of Warburg and Negelein (86). However, the low efficiency values found by recent investigators (see page 835) suggest that the value 0.25 may be too high.

It has also been generally assumed that the photosynthetic process includes a series of four successive photochemical steps, $\Delta H$ for a single step being limited to the energy supplied by a single quantum. In van Niel's mechanism, however, the four photochemical steps are assumed to be identical, resulting in each case in the formation of a hydrogen atom; the four hydrogen atoms then presumably bring about the reduction of carbon dioxide to formaldehyde. Van Niel's mechanism is represented by the following equations:

$$4[\text{Chlorophyll}\cdot H_2O + h\nu \rightarrow \text{Chlorophyll}\cdot OH + H] \qquad (1)$$

$$CO_2 + 4H \rightarrow (CH_2O) + H_2O \qquad (2)$$

$$\underline{2[2\text{Chlorophyll}\cdot OH + H_2A \rightarrow 2\text{Chlorophyll}\cdot H_2O + A]} \qquad (3)$$

$$CO_2 + 2H_2A + 4h\nu \rightarrow (CH_2O) + H_2O + 2A \qquad (V)$$

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[18] Private communication.

For reaction 1 to be energetically possible, the chlorophyll·$H_2O$ compound would have to be a more intimate compound of chlorophyll and water than in the case of an ordinary hydrate. An alternative way of writing reaction 1 would be

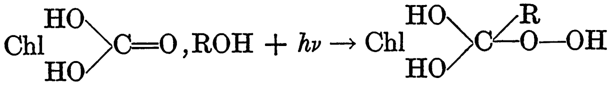
$$4[\text{Chlorophyll}\cdot H_2O + h\nu \rightarrow \text{Dehydrochlorophyll}\cdot H_2O + H]$$

the hydrogen atom thus being split from the chlorophyll portion of the hydrated molecule.

In reaction 3, $H_2A$ would be water in the case of algae and higher plants, and hydrogen sulfide in the case of the green sulfur bacteria.

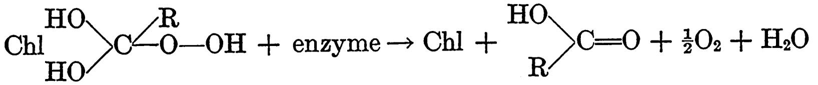
Without modification this series of reactions could not take place (except perhaps in bacteria) with a quantum efficiency as high as 0.25, since reaction 2 is exothermic to the extent of about 150,000 cal. The energy thus wasted would be nearly equivalent to the total energy supplied by four photons at 7000 Å. For $H_2A = H_2O$, reaction 3 would be endothermic. The necessary energy would presumably have to be supplied by additional photons, unless reactions 2 and 3 were considered to be coupled in some manner so that the excess energy from reaction 2 could be utilized for reaction 3.

The mechanism of Franck and Herzfeld (34) was designed to avoid the necessity of assuming a photosynthetic unit. They assumed, as did Stoll (75), that carbonic acid forms a complex with chlorophyll. This complex, in turn, was assumed to be combined with an organic molecule ROH, present in abundance. Franck and Herzfeld suggested that ROH may be a protein which forms the main body of the chloroplasts. The following equations represent the forward reactions postulated by Franck and Herzfeld. They state that the equations are suggested as a working hypothesis, not as a final solution.



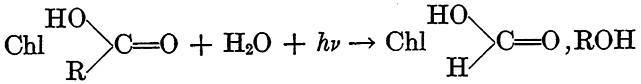
$$\mathrm{Chl}\begin{matrix}\mathrm{HO}\\ \\ \mathrm{HO}\end{matrix}\!\!>\!\mathrm{C{=}O,ROH} + h\nu \rightarrow \mathrm{Chl}\begin{matrix}\mathrm{HO}\\ \\ \mathrm{HO}\end{matrix}\!\!>\!\mathrm{C}\overset{\mathrm{R}}{\angle}\mathrm{O{-}OH} \qquad (1)$$

Carbonic acid Peracid



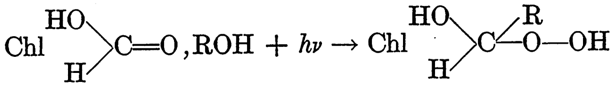
$$\mathrm{Chl}\begin{matrix}\mathrm{HO}\\ \\ \mathrm{HO}\end{matrix}\!\!>\!\mathrm{C}\overset{\mathrm{R}}{\angle}\mathrm{O{-}OH} + \text{enzyme} \rightarrow \mathrm{Chl} + \begin{matrix}\mathrm{HO}\\ \\ \mathrm{R}\end{matrix}\!\!>\!\mathrm{C{=}O} + \tfrac{1}{2}O_2 + H_2O \qquad (2)$$

Peracid R acid



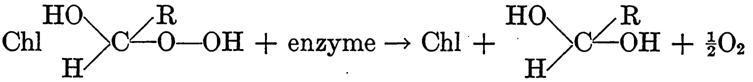
$$\mathrm{Chl}\begin{matrix}\mathrm{HO}\\ \\ \mathrm{R}\end{matrix}\!\!>\!\mathrm{C{=}O} + H_2O + h\nu \rightarrow \mathrm{Chl}\begin{matrix}\mathrm{HO}\\ \\ \mathrm{H}\end{matrix}\!\!>\!\mathrm{C{=}O,ROH} \qquad (3)$$

R acid Formic acid

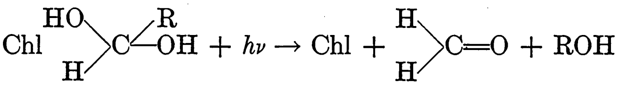


$$\mathrm{Chl}\begin{matrix}\mathrm{HO}\\ \\ \mathrm{H}\end{matrix}\!\!>\!\mathrm{C{=}O,ROH} + h\nu \rightarrow \mathrm{Chl}\begin{matrix}\mathrm{HO}\\ \\ \mathrm{H}\end{matrix}\!\!>\!\mathrm{C}\overset{\mathrm{R}}{\angle}\mathrm{O{-}OH} \qquad (4)$$

Formic acid Peraldehyde



$$\underset{\text{Peraldehyde}}{\text{Chl}\,{}^{\text{HO}}_{\text{H}}\!>\!\text{C}\!<\!{}^{\text{R}}_{\text{O—OH}}} + \text{enzyme} \rightarrow \text{Chl} + \underset{\text{R aldehyde}}{{}^{\text{HO}}_{\text{H}}\!>\!\text{C}\!<\!{}^{\text{R}}_{\text{OH}}} + \tfrac{1}{2}O_2 \qquad (5)$$



$$\underset{\text{R aldehyde}}{\text{Chl}\,{}^{\text{HO}}_{\text{H}}\!>\!\text{C}\!<\!{}^{\text{R}}_{\text{OH}}} + h\nu \rightarrow \text{Chl} + \underset{\text{Formaldehyde}}{{}^{\text{H}}_{\text{H}}\!>\!\text{C}=\text{O}} + \text{ROH} \qquad (6)$$

The two enzyme reactions, in which oxygen is evolved, constitute the temperature-sensitive or Blackman reaction.

According to Franck and Herzfeld, the calculated binding energy of —OH to —O— in the two peroxides is so weak that the —OH radical will be split off whenever the peracid or peraldehyde complexes absorb a photon. At low light intensities the probability of such an absorption would be negligible, because of the speed of the enzyme reactions. But, at intensities corresponding to light saturation in most leaves, they estimated this probability to be about $\frac{1}{10}$. According to their postulation, the photodecomposition of the permolecules into two radicals initiates chain reactions (back reactions in this case), each chain resulting in the decomposition of a large number of permolecules.

With these chains light saturation is thus reached at a much lower intensity than would be required if the rate were limited by the Blackman reactions. By assuming a sufficient chain length ($\sim 10^3$ at light saturation), saturation, both in flashing and in continuous light, can be explained without the assumption of a photosynthetic unit.

Franck and Herzfeld suggested that, after a long dark period, much of the chlorophyll may be attached to intermediate respiratory products, probably plant acids. Illumination could then cause photosynthesis, as in the case of chlorophyll–carbonic acid or chlorophyll–formic acid complexes. However, according to Franck and Herzfeld, photoöxidation of these plant acids, probably by a chain mechanism, should also take place to a large extent. Until the accumulated respiratory products were exhausted, this oxygen consumption would largely counterbalance the photosynthetic oxygen production, thus producing an induction period. Increased probability of oxidation at high light intensities would cause a more noticeable underproduction of oxygen at high intensities than at low intensities, in agreement with experimental results (53).

The kinetic equations derived by Franck and Herzfeld are in reasonable agreement with experimental facts. However, this cannot be considered as a criterion for the correctness of the mechanism, since equations derived by other investigators on the basis of various mechanisms are also in fairly good agreement with experimental results.

The reverse chain reactions of Franck and Herzfeld have been subjected to some criticism (91). Aside from doubts concerning this part of their mechanism, it is evident that to account for the high efficiencies found by Warburg and Negelein, the various forward reactions in the mechanism of Franck and Herzfeld would have to proceed with remarkable efficiency. Not only would the quantum efficiencies for each photoreaction have to be nearly unity, but the intermediate products would have to remain practically unchanged during the periods between the absorption of successive quanta by a single chlorophyll molecule. This period, according to calculations of Gaffron and Wohl (40), was about 10 min. in many of the experiments of Warburg and Negelein. But Franck and Herzfeld explained the induction period by assuming that, in the dark, a considerable fraction of the chlorophyll molecules become attached to intermediate respiratory products. The experiments of McAlister with wheat (53) indicated that 10 min. in the dark is sufficient to produce a noticeable induction period. Thus, in its present form, the mechanism of Franck and Herzfeld can hardly be reconciled with the results of Warburg and Negelein. It could much more easily account for the efficiencies found by Manning, Stauffer, Duggar, and Daniels (55). But, if the maximum quantum efficiency for photosynthesis is actually only 0.06 instead of 0.25, then there is no very good reason for choosing a mechanism involving four photoreactions, rather than one involving five or possibly more reactions.

In some respects it may be more desirable to postulate a mechanism involving only a single photoreaction, as in van Niel's mechanism (79). This result could also be obtained in a manner quite different from that suggested by van Niel. The following scheme indicates a possible mechanism of this type.

In the series of substances $A_1$, $A_2$, $\cdots$ $A_{n-1}$, $A_n$, carbon dioxide or carbonic acid is represented by $A_1$ and formaldehyde or other product is represented by $A_n$, with the other symbols representing intermediate substances. Assuming for simplicity that there are three intermediates, the following series of changes might conceivably take place:

$$A_1 + A_5 \rightarrow 2A_3 \tag{1}$$

$$2[A_3 + A_5 \rightarrow 2A_4] \tag{2}$$

$$4[A_4 + h\nu \rightarrow A_5] \tag{3}$$

The overall equation would then be $A_1 + 4h\nu \rightarrow A_5$. Water, oxygen, and other possible reactants are ignored in the above equations. Reactions 1 and 2 would presumably be enzyme reactions. The Blackman reaction might consist of one or more reactions like reaction 1 or 2, or it might be due to intermediate reactions not included in this or the following scheme.

To avoid postulating an enzyme reaction involving carbonic acid, one might use the following type of scheme:

$$4[A_1 + h\nu \rightarrow A_2] \tag{1'}$$

$$2[2A_2 \rightarrow A_1 + A_3] \tag{2'}$$

$$2A_3 \rightarrow A_1 + A_5 \tag{3'}$$

The sum of these reactions again gives the equation $A_1 + 4h\nu \rightarrow A_5$. Disproportionation reactions similar in principle to 2′ and 3′ are probably necessary in the production, by a plant, of such compounds as fats and oils, where presumably much of the energy comes from the oxidation of glucose.

If the maximum quantum efficiency is much lower than 0.25, many mechanisms of this type are possible, particularly ones involving more than three intermediate products.

With a mechanism of the type just proposed, a relatively high quantum efficiency could be maintained at very low light intensities without necessitating stable intermediate substances, such as would be necessary with a mechanism like that of Franck and Herzfeld.

Perhaps the principal value of this discussion has been to give an indication of how little actually is known concerning the chemistry of the photosynthetic process. When such entirely different mechanisms can possess even a small degree of plausibility, the need for further definite information becomes evident.

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