# A SYMPOSIUM ON PHOTOCHEMISTRY[1]

## INTRODUCTION TO THE SYMPOSIUM

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In introducing this symposium, it is of interest to turn back to another symposium on photochemistry, held by the Faraday Society at Oxford just ten years ago (23). At that meeting the discussion was divided almost equally between what were then two of the greatest fields of interest in photochemistry: Einstein's law of photochemical equivalence, and the mechanism of photochemical reactions. The papers and discussion which comprise the present symposium, although not offered as a complete cross section of modern photochemical problems, give nevertheless a fair idea of the extent to which, in the intervening decade, the latter of these two fields of interest has absorbed the former.

Even prior to 1925 it was recognized that Einstein's derivation could be applied only to the original elementary process of absorption in a photochemical reaction, and shortly thereafter it was suggested by H. S. Taylor (6) that the relation between primary absorption and secondary reaction be generalized in the following manner,—"The absorption of light is a quantum process involving one quantum per absorbing molecule (or atom). The photochemical yield is determined by the thermal reactions of the system produced by the light absorption."

This concept has proven highly fruitful in the interpretation of photochemical phenomena. As early as 1913 it moved Bodenstein (1) to introduce the idea of chain reactions into chemistry; it has been applied to almost every photochemical reaction which has been carefully studied since that time. The principles relating absorption spectra and the primary process, due in no small part to the fundamental contributions of Franck, have become, for the simpler molecules at least, well understood and generally accepted by photochemists during recent years. Thus the Faraday Society symposium of 1925 was marked by the presentation by

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[1] Held under the auspices of the Division of Physical and Inorganic Chemistry at the Ninetieth Meeting of the American Chemical Society at San Francisco, California, August 20, 1935.

Franck of his ideas on the adiabatic dissociation of molecules by light, which have since become part of standard photochemical theory.

As a result of these developments, interest in quantum yields has become limited almost entirely to the extent to which they are useful in interpreting the secondary mechanism of photochemical reactions. It must not be assumed, however, that in every case one molecule becomes activated or dissociated for every quantum absorbed by the light sensitive species; that is to say, it must not be assumed that the primary quantum yield is always unity. In polyatomic molecules the primary yield may be reduced by an "inner filter" action due to the existence of two or more absorbing bonds in the molecule, absorption by only one of which can be effective in producing reaction (7, 13). In processes involving the primary photochemical dissociation of molecules (continuous or diffuse absorption spectra), an internal redistribution of absorbed energy may occur which prevents dissociation and so reduces the primary quantum yield (14). In solutions, as Franck and Rabinowitsch (8) have emphasized, the primary yield may be reduced by collisional deactivation during the period between absorption and dissociation. Although the extent to which these possibilities may be effective is as yet uncertain, they must be kept in mind whenever use is made of quantum yields in interpreting photochemical reaction mechanisms.

It is well known that in general the larger the number of atoms in a molecule the more difficult it becomes to effect a reliable correlation between the absorption spectrum and the primary process. In most cases ten or twelve atoms seem to be about the limit of molecular size for which vibrational structure in absorption can be observed. For example, even though the fluorescence of acetone vapor indicated the formation of activated molecules by absorption, several attempts were made before it could be proven that the absorption spectrum was other than continuous (16). Conjugated unsaturation extends the limit of molecular size for which distinct structure can be observed.

A comparison of the absorption spectra of several of the aldehydes is of interest in this respect. In figure 1 the band reproduced is the near ultra-violet absorption characteristic of the carbonyl bond. Although the structure becomes progressively weaker as the alkyl residue becomes larger, there is no photochemical evidence to indicate any marked difference in the primary process in the different aldehydes. It seems likely that the disappearance of structure in the higher aldehydes is due to an actual overlapping of the energy levels in the molecule rather than to a lack of sufficient dispersion in the spectrograph used. Contrasted with this behavior is the effect of introducing a conjugated double bond into the molecule. Figure 2 compares the absorption of crotonaldehyde (eleven atoms) with that of propionaldehyde (ten atoms).[2] In crotonaldehyde the carbonyl absorption band is shifted several hundred Ångström units toward the red, and its vibrational fine structure is distinctly sharpened as compared with propionaldehyde.

Although the pioneer researches of the elder Warburg have never been excelled in regard to painstaking care and accuracy of manipulation, experimental methods in photochemistry have been standardized to the extent that quantum yields for a given reaction may be measured by several independent investigators with results agreeing to within 1 or 2 per cent (10, 11, 15, 26). Improvement in analytical methods, together with standardization of methods for obtaining monochromatic radiation and measuring its intensity, have reached the point where one can confidently attach significance to small changes in reaction rates or products with changes in wave length, concentration, or temperature. Promising actinometric methods (10, 12, 26) are coming into wider use.

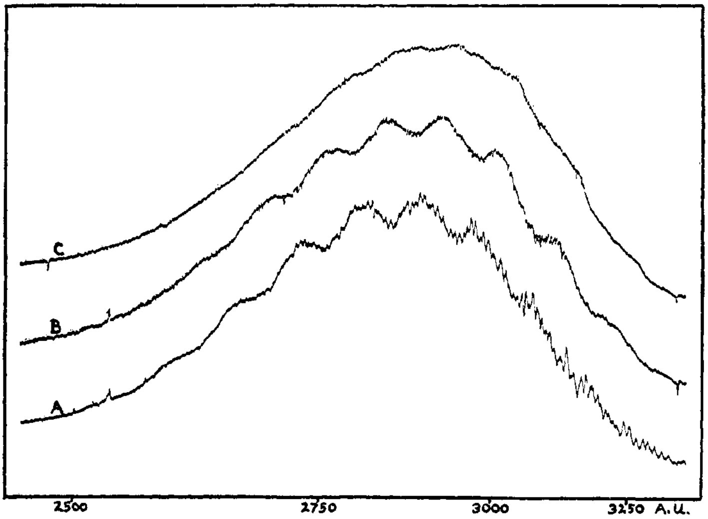

FIG. 1. Tracings of the near ultra-violet absorption spectra of (A) acetaldehyde, (B) propionaldehyde, (C) butyraldehyde.

Contrasting sharply with the progress in our understanding of the primary process, and with the development of experimental technique, the determination of secondary reaction mechanisms still remains one of the greatest problems of photochemistry. In most cases photochemical sec-

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[2] The author is indebted to Drs. F. E. Blacet and W. G. Young of the University of California at Los Angeles, and to Mr. Leo Levanas of Stanford University, for the use of the spectrograms from which these tracings were recorded.

ondary reactions, in gases at least, involve free atoms or radicals about which not enough is known. Even the detection of free atoms or radicals as intermediate products in photochemical reactions has been accomplished in only a few cases; measurement of their stationary concentration has been done scarcely at all. Methods are developing which give promise of making this possible. The para–ortho hydrogen conversion has been applied by Geib and Harteck (9) to estimate the stationary concentration of hydrogen atoms in the photosynthesis of hydrogen chloride, and by Farkas and Harteck (5) to estimate the atomic hydrogen concentration during the photolysis of ammonia. Corrections must be made for the amount of normal hydrogen produced by the reaction itself (4), and in general the method must be used with caution as paramagnetic molecules or radicals, such as $O_2$, $CH_3$, or halogen atoms, will also produce the conversion (3). In fact, this conversion has been applied by Patat and Sachsse (19) to estimate the stationary concentration of methyl radicals (or hydrogen atoms) during the thermal decomposition of acetaldehyde, and by West (25) as an indicator of the formation of methyl radicals and iodine atoms when methyl iodide and acetone are exposed to light.

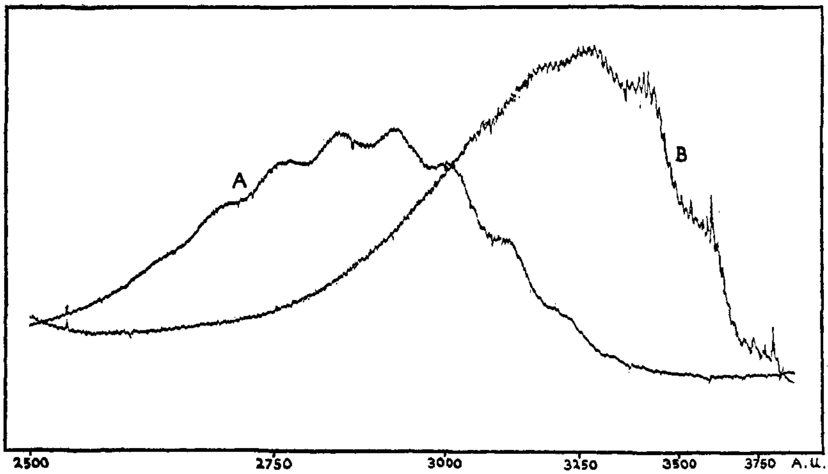

FIG. 2. Tracings of the near ultra-violet absorption spectra of (A) propionaldehyde and (B) crotonaldehyde.

Emission spectra give evidence of the primary formation of free atoms or radicals whenever the absorbed light has sufficient energy to produce dissociation into electronically excited particles which lose their excitation by emission. Terenin, for example, has recently reported (24) the emission of bands belonging to OH, CN, and $NH_2$ radicals when such molecules as $H_2O$, $CH_3OH$, HCOOH, $CH_3CN$, and $NH_3$ are exposed to radiation of 1400–1600 A.U.

Since most free radicals possess absorption spectra in the visible or near ultra-violet, observations via absorption would appear to offer one of the most direct methods for observing those radicals during the course of a reaction. Bonhoeffer and Reichardt (2) were able to observe the absorption of OH radicals in thermally dissociated water vapor, and Oldenberg (17) used absorption under high dispersion to detect and estimate the life period of non-excited hydroxyl radicals produced by the electric discharge through water vapor. Oldenberg emphasizes the necessity of high resolving power in the spectrograph used to photograph the absorption, but whether this method can be made sufficiently sensitive to observe free radicals at the concentrations in which they are produced in photochemical reactions remains to be determined.

The removal of metallic films by alkyl radicals after the method of Paneth (18, 21) presents another possibility, although more limited in scope. Difficulties arise in the application of this method to the study of free radicals produced during photochemical reactions, since the gases under observation must be streamed past the light source at low pressures in a tube of small dimensions, with the result that the amount of absorption and hence the amount of reaction are very small. Despite these difficulties, Pearson (20) reports the rapid removal of visible mirrors of antimony, tellurium, and lead by means of the radicals produced when acetone and other ketones are exposed to light. He estimates the half-life of the active agents from acetone as $5.3 \times 10^{-3}$ sec., which is in close agreement with the half-life of $5.8 \times 10^{-3}$ sec. found by Paneth and Hofeditz for free methyl.

R. A. Mortensen and the author, exposing lead tetramethyl vapor under similar conditions to the 2537 A.U. line of a high-intensity mercury arc were able to decompose only about $10^{13}$ molecules per second. Even assuming that all methyl groups from the decomposed molecules were able to survive as free radicals and react with a lead mirror further down the tube, the amount of lead so removed would amount to only 0.01 mg. per hour. By using a radioactive isotope of lead (radium D) to form the mirror and following the transfer of radioactivity from the mirror to the trap, we were able to increase the sensitivity of the method so that the formation of free radicals in the above reaction was easily followed. It is possible by observing the removal of deposits of radioactive metals to observe stationary concentrations of methyl radicals corresponding to a partial pressure of as low as $10^{-8}$ mm.

Even if the active particles, free radicals or atoms, which may be produced during a photochemical reaction, together with their stationary concentrations, are known, one is still faced with the problem of determining what reactions can occur and to what extent each possible reaction does occur. Photochemistry and chemical kinetics meet on common ground in that secondary reactions are thermal reactions and so have specific rate constants and characteristic energies of activation. As Bates points out, one of the greatest contributions that could be made to photochemistry at the present time would be a reliable codification of these constants for a number of individual reactions.

The difficulties in the way of determining these constants are discussed by Bates. The direct study of individual processes, as, for example, the study of the reaction between chlorine atoms and hydrogen molecules by Rodebush and Klingelhofer (22), or the reaction between oxygen atoms and nitric oxide reported by Rodebush, is one of the most satisfying ways of obtaining the desired information. Unfortunately, the results of different investigators on the same individual reaction, as, for example, the studies of the recombination of hydrogen atoms discussed by Bates, are in wide disagreement. Moreover, it is uncertain as to whether the constants determined for a given reaction occurring alone can be applied to that same reaction occurring in the presence of other molecules.

In photochemistry, as in reaction kinetics, the theoretical treatment of reactions in solution has progressed less rapidly than the treatment of reactions in gases. As Dickinson shows, direct comparison of reactions in the gas phase and in solution, at least in inert solvents, provides one of the most valuable methods of approach to the latter. Photochemistry, through the information given by absorption spectra and quantum yields, perhaps has the advantage over thermal reaction kinetics in comparisons of this sort.

When dealing with reactions in active or ionizing solvents, where ions, ionic complexes, or solvated molecules may be involved, comparisons between gas and solution become strictly limited. The application of kinetic rate laws, as discussed by Rollefson, appears to offer one of the most powerful tools for unraveling the mechanism of reactions in non-ideal solutions.

Of all reactions which may be classed as photochemical, none has been more subtle in resisting solution by investigation than has the carbohydrate photosynthesis in green plants. Nor has any other photochemical reaction more far-flung significance than photosynthesis. Franck has suggested a mechanism, based on recognized photochemical principles, which will explain the unique energetic relations as well as other characteristics of the photosynthetic process, and which is certain to stimulate further thought and experiment on this important problem.

## REFERENCES

(1) BODENSTEIN: Z. physik. Chem. **85**, 329 (1913).
(2) BONHOEFFER AND REICHARDT: Z. physik. Chem. **139**, 75 (1928).
(3) FARKAS, A.: Ortho Hydrogen, Para Hydrogen, and Heavy Hydrogen, p. 79. Cambridge University Press, Cambridge (1935).
(4) FARKAS, A.: ibid. p. 104.
(5) FARKAS AND HARTECK: Z. physik. Chem. **25B**, 257 (1934).
(6) First Report of the Committee on Photochemistry, National Research Council, Circular 81 (1928). J. Phys. Chem. **32**, 527 (1928).
(7) FORBES AND HEIDT: J. Am. Chem. Soc. **55**, 2407, 2701 (1933).
(8) FRANCK AND RABINOWITSCH: Trans. Faraday Soc. **30**, 120 (1934).
(9) GEIB AND HARTECK: Z. physik. Chem. **15B**, 116 (1931).
(10) HARRIS AND KAMINSKY: J. Am. Chem. Soc. **57**, 1154 (1935).
(11) HOLMES AND DANIELS: J. Am. Chem. Soc. **56**, 630 (1934).
(12) LEIGHTON, W. G., AND FORBES, G. S.: J. Am. Chem. Soc. **52**, 3139 (1930).
(13) LEIGHTON, P. A., AND LUCY, A.: J. Chem. Physics **2**, 759 (1934).
(14) NORRISH, CRONE, AND SALTMARSH: J. Chem. Soc. **1934**, 1463.
(15) NORTON: J. Am. Chem. Soc. **56**, 2295 (1934).
(16) NOYES, DUNCAN, AND MANNING: J. Chem. Physics **2**, 717 (1934).
(17) OLDENBERG: J. Chem. Physics **3**, 266 (1935).
(18) PANETH AND HOFEDITZ: Ber. **62**, 1335 (1929).
(19) PATAT AND SACHSSE: Naturwissenschaften **15**, 247 (1935).
(20) PEARSON: J. Chem. Soc. **1934**, 1718; **1935**, 1151.
(21) RICE, F. O.: Trans. Faraday Soc. **30**, 166 (1934).
(22) RODEBUSH AND KLINGELHOFER: J. Am. Chem. Soc. **55**, 130 (1933).
(23) Symposium on Photochemistry: see Trans. Faraday Soc. **21**, 438 (1925).
(24) TERENIN: J. Chem. Physics **3**, 436 (1935).
(25) WEST: J. Am. Chem. Soc. **57**, 1931 (1935).
(26) WEYDE AND FRANKENBERGER: Trans. Faraday Soc. **28**, 561 (1931).