

A REVIEW OF PHOTOCHEMISTRY

W. ALBERT NOYES, JR., AND LOUIS S. KASSEL

Photochemistry is one branch of the study of the effects of radiations on chemical reactions. Studies of the effects of various types of radiation have received a great deal of attention and in recent years a comprehensive theory of the chemical effects of alpha and beta particles has permitted a general correlation of most of the important data.¹ Unfortunately, while Photochemistry may be said to be much older than its fellows, it is at present in a far more unsatisfactory state.

The Radiation Hypothesis of Chemical Action² has brought the subject of Photochemistry into prominence during the past few years. It is not the purpose of this paper to discuss the Radiation Hypothesis, but we would like to show something of the developments in the field of Photochemistry and to present some of the hypotheses advanced to interpret the data obtained. The subject is so vast and its ramifications so numerous that it is necessary to limit the field very carefully. For this reason no mention will be made of studies relative to photographic processes and little attention will be given to the hydrogen-chlorine reaction. This reaction has probably received more attention

¹ See Lind, *The Chemical Effects of Alpha Particles and Electrons*, The Chemical Catalog Company, 1921 and for more recent work a series of articles by Lind and his coworkers in the *Journal of the American Chemical Society*.

² Trautz, "Sitzungsber. Heidelberger Akad. Wissenschaft," **1917**; Lewis, *Trans. Faraday Soc.*, **17**, 573 (1922) (This article presents a brief statement of Lewis' viewpoint. Many other articles have been published, principally in the *Journal of the Chemical Society (London)*); Perrin, *Annales de Physique*, **11**, 5 (1919). Many other authors have discussed the Radiation Hypothesis critically. Perhaps the most interesting and significant recent articles on the subject are by Tolman, *J. Amer. Chem. Soc.*, **42**, 2506 (1920); **45**, 2285 (1923); **47**, 1524 (1925); **47**, 2652 (1925) and by Lewis and Smith, *ibid.*, **47**, 1508 (1925). Harned (*Journ. Franklin Institute*, **196**, 181 (1923)) has given an excellent review of the subject.

than any other single photochemical reaction. Nevertheless this reaction, which seemed to be relatively simple at the time the first studies were made, has proved to be very complex. A great deal has been learned, but there are still many points of disagreement among the various workers. Marshall³ has given a very complete and satisfactory review of the work on this particular reaction.

There are many reasons why the subject of Photochemistry is in such an unsatisfactory state. In general, data on the kinetics of reactions are very difficult of interpretation. It is only recently that the effects of even minute traces of impurities have been recognized. Perhaps the work of Baker⁴ on extremely dry liquids has served to bring this matter to general attention more than any other single piece of work. It would seem that many chemical reactions take place only in the presence of some catalyst, i.e., either the walls of the vessel or traces of moisture or some small amount of foreign substance whose existence is frequently ignored. The most notable exceptions seem to be the decomposition of nitrogen pentoxide which has been studied by Daniels and his coworkers⁵ and the decomposition of sulfuryl chloride which has been studied by Smith.⁶ The decomposition of nitrogen pentoxide has been found to be a monomolecular reaction and the specific reaction rate is found to be constant over a wide range of concentrations. By far the great majority of reactions do not behave in such a simple fashion. Many authors have arrived at conclusions with regard to the mechanisms of certain reactions by means of studies of chemical kinetics. It would seem advisable to regard most of these conclusions with a great deal of skepticism. It is always advisable to present some picture of the mechanism of a reaction if it is possible, since the human mind is so con-

³ Marshall, *Trans. Amer. Electrochem. Soc.*, Preprint for meeting held April 22, 1926.

⁴ Baker, *Phil. Trans.*, **79A**, 583 (1888); *J. Chem. Soc.*, **65**, 611 (1893); **81**, 400 (1902); **91**, 1862 (1907), **101**, 2339 (1912); **121**, 568 (1922).

⁵ Daniels and Johnston, *J. Amer. Chem. Soc.*, **43**, 53 (1921); **47**, 1602 (1925); Hirst has obtained results agreeing with those of Daniels, *J. Chem. Soc.*, **127**, 657 (1925).

⁶ Smith, *J. Amer. Chem. Soc.*, **47**, 1862 (1925).

stituted that it must have a picture as a working basis. The formation of pictures serves a useful purpose in stimulating research and the criticism and consequent rearrangement of these pictures will continue to lead to many valuable conclusions. Far too frequently, however, authors have been led to form pictures and then to seek an interpretation of all data obtained subsequently in terms of these pictures, thereby overlooking many important points. It must be borne in mind that several different pictures will usually interpret a given set of data with equal exactness.

In general the application of thermodynamics to photochemical reactions has reached only a very elementary stage. Einstein⁷ has derived the law of Photochemical Equivalence and the quantum theory has given a means of applying energy relationships to photochemical reactions. This subject has been well treated in other reviews.⁸ Most of the applications of quantum theory to photochemical reactions have been based on postulations of "activated" states. The exact nature of the activated state is usually unknown, but it is assumed that the difference in energy between the activated molecule and the normal molecule can be calculated from the wave length of light absorbed.⁹ However it would seem that the postulation of a single definite activated state and the calculation of the energy of activation is not justified in many cases. As an example we may cite the photochemical decomposition of solutions of oxalic acid. Oxalic acid presents an absorption band¹⁰ which apparently begins between 3000 and 3500 Å and it is well known that solutions of oxalic acid are decomposed by the ultra-violet radiation in sunlight¹¹ and that the amount of decomposition is a function of the quantity of energy absorbed. If it is assumed that a certain "activated state" is necessary as a preliminary to the decomposition of oxalic acid

⁷ Einstein, *Ann. Physik*, **37**, 832 (1912).

⁸ Harned, *loc. cit.* ref. 2; Dushman, *A Treatise of Physical Chemistry*, edited by H. S. Taylor, D. Van Nostrand Company, 1924.

⁹ See Tolman, *J. Amer. Chem. Soc.*, **42**, 2506 (1920) for a discussion of this matter.

¹⁰ Hantzsch and Scharf, *Ber.*, **46**, 3570 (1913).

¹¹ See, for example, Bongiovanni, *Gazz. chim. ital.*, **46**, 127 (1916).

and that the difference in energy between the normal molecule and the activated molecule can be calculated from the position of the absorption band, then we are apparently forced to conclude that the activated state of oxalic acid in the presence of uranyl salts is different from the activated state in solutions of pure oxalic acid, for solutions of oxalic acid containing uranyl salts are decomposed by visible light to a slight extent.¹² There is, of course, the possibility that the activated state in both cases is the same and that absorption of light by the uranyl sulfate may cause a subsequent activation (by collisions of the second kind) of the oxalic acid molecules which have an energy content greater than the average. The uranyl sulfate would merely act as a holder of the energy until an oxalic acid molecule of the proper energy content was able to absorb it. In many cases it would seem doubtful whether an energy of activation can be calculated directly from the wave length of the absorption band. For many reactions the number of molecules reacting per quantum absorbed is a decided function of the wave length and it would seem that in many cases the amount of substance reacting is proportional to the amount of energy absorbed.¹³ This is in contradiction to Einstein's law, which would tell us that every quantum absorbed should have the same effect as any other quantum and that therefore the amount of substance reacting per calorie of energy absorbed should be greater at the longer wave lengths. It may be answered with reason that the conditions postulated by Einstein probably have not been fulfilled for any photochemical reaction studied and that Einstein's law should be applied only to the primary process, presumably the process of activation. Thus as the next logical step we would find it necessary to postulate a series of activated states, or perhaps a gradual variation in the energy content of the absorbing molecules, in such a way that the probability of reaction divided by the probability

¹² Mathews and Dewey, *Jour. Phys. Chem.*, **17**, 211 (1913); Landau, *Compt. rend.*, **156**, 1894 (1913); Anderson and Robinson, *Jour. Amer. Chem. Soc.*, **47**, 718 (1925).

¹³ See, for example, Bowen, *Phil. Mag.*, **50**, 879 (1925); *Trans. Far. Soc.*, 1926 (advanced proof).

of return to the unactivated state without reaction would be a function of the energy absorbed and would be greater for the shorter wave lengths. If this is the case one should expect a certain amount of fluorescence and consequent light scattering for the longer wave lengths absorbed, or at least an increase in temperature of the system, which fluorescence and increase in temperature would be less noticeable as one proceeded to the shorter wave lengths. Certain reactions have been studied and data obtained which might be said to agree with such assumptions, but we may safely say that statements of this sort rest on doubtful experimental evidence.

There have been many attempts to classify photochemical reactions. The classification proposed by Bodenstein¹⁴ seems to be quite logical. His classification is based on the Einstein law of photochemical equivalence. He classifies the reactions into primary and secondary, depending on whether the reactions obey Einstein's law or not. For primary photochemical reactions the number of molecules reacting per quantum is either unity or some small whole number, within the experimental error. As we have mentioned above, probably no reaction studied has been carried out under the conditions postulated by Einstein. For primary photochemical reactions, therefore, we may consider that each quantum absorbed leads to an activated molecule and that the probability of reaction after activation is one. If any other small whole number of molecules is found to react per quantum absorbed, it is possible to postulate collisions between activated products and unactivated molecules or between activated molecules and unactivated molecules in such a way that energy is transferred or that both molecules entering into collision react. Measurements of light intensity are difficult to carry out and in particular is it difficult to get an exact measure of the amount of light absorbed in a photochemical process, making due allowance for scattering and for absorption by the walls of the container. In addition it must be remembered that we are dealing with large numbers of molecules and that at best any

¹⁴ Bodenstein, *Z. physik. Chem.*, **85**, 333 (1913).

data obtained will be of a statistical character. Thus if the probability of reaction after activation were not unity, but when a molecule did react a chain were started involving activation by the products, it would be possible to find an agreement with Einstein's law. In this same manner it would be possible to explain a deviation from the law, while an agreement might be fortuitous. In fact there seems to be some evidence that an activated molecule will not decompose or react spontaneously but that it will only do so upon collision with a second molecule. This would make a reaction which apparently behaves as a reaction of the first order really a second order reaction. Some evidence has been obtained on this point by studying certain gas reactions at pressures so low that the duration of the activated state is of the same order of magnitude as the mean time between collisions. Under such conditions the order of the reaction should be higher than at higher pressures. The decomposition of nitrogen pentoxide in the dark apparently does not deviate from a first order equation even at very low pressures.¹⁵

Secondary photochemical reactions are those which exhibit a wide deviation from Einstein's law, many molecules reacting per quantum absorbed. Here again we must bear in mind that we are dealing with final reactions and not with the activating process. It would seem necessary to postulate chain mechanisms of some sort to account for reactions of this type.

As would be expected, those reactions which proceed with a large decrease in free energy belong in the class of secondary photochemical reactions, while those reactions which proceed with a slight negative free energy or a positive free energy fall in the class of primary light reactions. However this generalization can only be made when conditions are such that a deviation from Einstein's law is permitted. Marshall¹⁶ has shown that monatomic hydrogen is capable of initiating the reaction between hydrogen and chlorine and that the yield per hydrogen atom is a function of the pressure, being greater at higher pressures. He has also investigated the photochemical reaction between hydro-

¹⁵ Daniels, *J. Amer. Chem. Soc.*, **47**, 1602 (1925).

¹⁶ Marshall, *J. Phys. Chem.*, **29**, 842 (1925).

gen and chlorine at low pressures¹⁷ and has found that the yield of hydrogen chloride molecules per quantum is twenty at a pressure of 0.001 cm. and increases to over 25000 at a pressure of 6.0 cm. Thus while we have given the rule that those reactions which involve a large decrease in free energy would probably be secondary photochemical reactions, we must qualify our statement and add that conditions must be such that some sort of chain mechanism can take place. We can now explain the effect of inhibitors as being due to action in stopping the chain, while the effect of the reduced pressure would be to decrease the probability of collision between an activated and an unactivated molecule during the duration of the activation.

Other classifications of photochemical reactions have been proposed. Schidlof¹⁸ has put all photochemical reactions into three groups as follows: (1) Exoenergetic reactions. An increase in frequency displaces the equilibrium in the same direction as an increase in temperature for exothermic reactions. (2) Endoenergetic reactions. The effect of change in frequency is the reverse of the above. (3) Reactions for which energy is neither taken up or given out. For these reactions the equilibrium would be independent of the frequency and radiation may act simply as a catalyst. Unfortunately, while this classification obviously has much in common with the classification of Bodenstein, very few measurements have been made of the effect of radiation on equilibria. There is no doubt that such an effect does exist as evidenced by the fact that reactions may be made to proceed in both directions by a proper choice of wave length and of other conditions. For example, Warburg has found that maleic acid may be converted into fumaric and vice versa.¹⁹ The rate of change of fumaric into maleic is more rapid than from maleic into fumaric and the effects of various wave lengths are not identical.

Plotnikov²⁰ has classified photochemical reactions according to

¹⁷ Marshall, *ibid.*, **29**, 1453 (1925).

¹⁸ Schidlof, *Arch. sci. phys. nat.*, **37**, 493 (1914).

¹⁹ Warburg, *Sitzb. kgl. preuss. Akad.*, **1919**, 960.

²⁰ Plotnikov, *Z. physik. Chem.*, **78**, 573 (1911).

their temperature coefficients. He has given three classifications for which the factors for change in reaction rate with a ten degree rise in temperature are 1.04 ± 0.03 , 1.20 ± 0.03 and 1.39 ± 0.03 . Plotnikov's original idea seemed to be that the electron configurations of the reacting substances determined the nature of the photochemical effect and therefore the temperature coefficient of their photochemical reactions. Thus he found that the temperature coefficients of several reactions involving the addition of iodine were the same as for several reactions involving the addition of bromine, i.e., an increase in reaction rate of about 1.4 times for a ten degree rise in temperature. Tolman²¹ has considered the problem of the temperature coefficients of photochemical reactions in detail. He concludes that when the temperature coefficient is unity that the average energy of the molecules which enter into reaction is practically the same as the average energy of all the molecules. This means that the average molecule has as good a chance of picking up a quantum and reacting as any molecule in a quantum state far removed from the average. It is thus easy to interpret the temperature coefficient which Plotnikov has found for one class of reactions. With regard to the other classes Tolman finds that there is no theoretical reason why the temperature coefficient should have any particular value other than unity. If the temperature coefficient is not unity, the chance that a given molecule will be able to pick up a quantum and react will depend on the particular quantum state in which it finds itself. Tolman suggests a possible effect of the decrease in viscosity of water which might account for the temperature coefficient 1.20.

We will divide the following discussion into several parts. The first part will consist of a study of photochemical reactions from the standpoint of their active wave lengths, with a presentation of some of the ideas relative to active states and the application of thermodynamics. It would be obviously impossible and equally inadvisable to mention all of the photochemical reactions studied. The recent report of the Chemical Society²² has

²¹ Tolman, *J. Amer. Chem. Soc.*, **45**, 2285 (1923).

²² Allmand, *Annual Reports on the Progress of Chemistry*, **22**, 333 (1926).

covered the field of photochemistry from 1913 to 1925 in a very thorough manner. As a consequence, in part II we will limit ourselves to a few reactions which may be cited as examples.

PART I

Before starting on a discussion of photochemical reactions from the standpoint of wave length, we might mention possible methods of calculating the wave length which should be active for a given reaction. The simple equation of the Radiation Hypothesis

$$\frac{d \ln k}{dT} = \frac{N h \nu}{RT^2}$$

was proposed by Trautz, Lewis and Perrin.²³ The frequency of the active radiation is represented by ν , k is the specific reaction rate for the dark reaction, h is Planck's constant and N is Avogadro's number. This equation has been tested with great care by Daniels and Johnston²⁴ and has been discussed critically by various authors. Other authors have attempted to apply this equation²⁵ and we must admit that the evidence in favor of its applicability is rather unsatisfactory. For most reactions the temperature coefficient is such that a wave length in the near infra-red should be active. So far little work has been done on the chemical effects of the infra-red, but the results indicate that in very few if any cases does the infra-red exert any effect. Daniels²⁶ and Taylor²⁷ have studied the effect of infra-red radiation on the decomposition of nitrogen pentoxide and both have come to the conclusion that the infra-red is without any noticeable effect.

²³ Loc. cit., ref. 2.

²⁴ Daniels and Johnston, *J. Amer. Chem. Soc.*, **43**, 72 (1921).

²⁵ Taylor and Lewis, *ibid.*, **46**, 1606 (1924).

Capper and Marsh, *ibid.*, **47**, 2847 (1925).

Noyes and Kouperman, *ibid.*, **45**, 1398 (1923); Wobbe and Noyes (to be published in the near future).

Griffith and Shutt, *J. Chem. Soc.*, **119**, 1948 (1921).

Norrish and Rideal, *ibid.*, **125**, 2070 (1924).

Smith, *J. Amer. Chem. Soc.*, **47**, 1862 (1925).

²⁶ Daniels, *J. Amer. Chem. Soc.*, **48**, 607 (1926).

²⁷ Taylor, *ibid.*, **48**, 577 (1926).

Since we must eliminate the above simple equation as a means of calculating the active wave length, we may next inquire into the relation between absorption spectra and active wave lengths. We have not time in this review to enter into a detailed consideration of the various types of spectra. We may roughly divide spectra into band spectra and line spectra. Band spectra should be divided into many sub-groups. Nearly all substances possess absorption spectra in the infra-red. Some of these band systems have been accurately studied. There may be simple rotation bands. For the derivation of a formula to fit rotational bands it is assumed that $2 \pi M = m h$, where M is the impulse moment and is equal to the moment of inertia around the principal axis multiplied by the angular velocity, h is Planck's constant and m is a whole number. If I is the moment of inertia around the principal axis and ω is the angular velocity, then

$$I \omega = \frac{m h}{2 \pi}, E_{kin} = \frac{h^2}{8 \pi^2 I} m^2$$

If we put $B = \frac{h}{8 \pi^2 I}$ then if we imagine that a molecule absorbed light in such a manner that the value of m is changed to m' , the frequency will be given by

$$\nu = B (m'^2 - m^2)$$

This would be the simple formula for a pure rotation spectrum. Bands of this type would fall in the far infra-red.

In addition to simple increase in kinetic energy of rotation by absorption of infra-red radiation there may be an increase in the energy of vibration of the atoms with respect to each other. If the vibrations are those of a simple harmonic oscillator, the vibrations may be taken as of such a nature that the energy is some multiple of a simple quantum $h \nu_0$. If n' is the quantum number of the oscillation at the beginning and n is the quantum number at the end then the change in energy will be $h(n' - n) \nu_0$ and the change in wave number $(n' - n) \nu_0$. Combining with the

previous formula for rotation spectrum we find that the wave numbers should be represented by a formula of the type

$$\nu = (n' - n)\nu_0 + B(m'^2 - m^2)$$

There should be a series of bands of this type in the infra-red.

If we now consider the visible and ultra-violet bands it is necessary to consider another type of change in addition to rotation of the molecule and vibration of the atoms, namely electron displacements. The formula which fits this type of band is even more empirical than the formulae for bands in the infra-red. This formula is of the type

$$\nu = A(n, n') \pm 2B(n')m + C(n, n')m^2 + \dots$$

where

$$A(n, n') = \nu_0 + B(n') + n'\nu_0' (1 - n'x') - n\nu_0 (1 - nx) + \dots$$

$$B(n') = \frac{1}{8\pi^2 I'} - \alpha'n', \quad B(n) = \frac{1}{8\pi^2 I} - \alpha n.$$

$$C(n, n') = B(n') - B(n)$$

ν_0 is a term which depends on the electron displacement, m is a whole number, n and n' are whole numbers, I is the moment of inertia of the molecule after absorption and I' is the moment of inertia before absorption. Thus the formula contains three quantum numbers, n , n' and m and nine arbitrary constants ν_0 , ν_0' , x , x' , I , I' , α , α' . Unfortunately this is the type of band photochemists are most interested in studying. No satisfactory picture has yet been given of the rearrangements of the electron systems of molecules upon absorption. Consequently, while it is probably possible to calculate the change in energy of a molecule upon absorption of a given wave length, it is not possible to make any definite prediction as to the photochemical activity of a particular band. It would seem that more studies should be carried out using monochromatic light and substances whose band spectra have been thoroughly investigated.

Many substance in solution present what is called commonly "end absorption." This term means that absorption begins in the visible or near ultra-violet and continues down to the

shortest wave length studied, which is usually about the limit of the ordinary quartz spectrograph. This type of absorption is found for most substances in aqueous solution. Very rarely have instruments of sufficient dispersion been used in this type of work to permit developing the fine structure of these bands. Henri²⁸ has carried out many studies of the absorption spectra of organic substances and for certain ones, notably benzene and benzene derivatives, has been able to apply formulae of the type mentioned above.

The main conclusion we can draw from this brief discussion is that simple increase in rotation or in atomic vibration is not sufficient to produce the effects observed in photochemistry. It is necessary to use wave lengths whose effects on the molecule can best be interpreted by postulating changes in the electron system. The exact nature of the effects on the electron system are not known, although some idea of the difference in energy can be obtained.

In addition to band spectra line spectra are frequently observed as absorption spectra. In general it may be said that only monatomic gases (the rare gases and the metals) present well defined line absorption spectra. The polyatomic gases and practically all substances in solution present absorption spectra of the type discussed in the preceding paragraphs. We may take the Bohr atom as a basis for presenting a picture of the nature of line absorption spectra without going into detail as to the applicability or non-applicability of this atom-model to other fields. All atoms are supposed to have a certain arrangement of their planetary electrons when they are in the normal state. When energy is absorbed the arrangement of these electrons is changed. We are here concerned only with the outermost or valence electrons. If we designate the normal position of one of these electrons as "one," then when the atom absorbs energy the electron is changed to some other position further removed from the nucleus which we may call "two" or "three" or etc. If the electron were already in position "two" upon absorption it could

²⁸ Henri, *Etudes de Photochimie*, Gauthier-Villars et Cie, 1919; *La Structure des Molecules*, 1925.

go to position "three" or "four," etc. As a result the normal atom would only absorb in such a way that the electron would be removed from position "one" to some other state and the other lines observed in the emission spectrum and ascribed to the return of the electron from some state to state "two" would only be obtained in the absorption spectrum at high light intensities.

In general very little work has been done in photochemistry involving monatomic gases directly. Most of those monatomic gases which react at all react quite rapidly, and there would seem little possibility of determining accurately the effect of line absorption of this type. As a result of the researches of Cario and Franck,²⁹ however, it has been shown that mercury vapor may absorb light of wave length 2537, which corresponds to the first line in a series of the type mentioned above, and may transmit the energy upon collision to hydrogen or to other molecules. In the case of hydrogen the result is apparently dissociation and the monatomic hydrogen formed may react subsequently with molecules which will not react normally with diatomic hydrogen. There is some evidence that mercury in the first resonance state forms a hydride upon collision with a hydrogen molecule.³⁰ Whatever the mechanism of the process, hydrogen is made available for reactions for which ordinary hydrogen is not active. Cario and Franck studied the reaction of this monatomic hydrogen with certain metal oxides. Dickinson³¹ has studied the formation of water vapor from hydrogen and oxygen at 45°, Mitchell³² has studied this same reaction in some detail and has also studied the effect of the addition of an inert gas like argon. Taylor and Marshall³³ have carried out a series of reactions (with ethylene, oxygen, carbon monoxide and nitrous oxide). Noyes³⁴ has found that traces of ammonia are formed from nitrogen and hydrogen at the boiling point of mercury. It was not

²⁹ Cario and Franck, *Z. Physik*, **11**, 161 (1922); Franck, *ibid.*, **24**, 450 (1923).

³⁰ Compton and Turner, *Phil. Mag.*, **48**, 360 (1924).

³¹ Dickinson, *Proc. Nat. Acad. Sci.*, **10**, 409 (1924).

³² Mitchell, *ibid.*, **11**, 458 (1925).

³³ Taylor and Marshall, *J. Phys. Chem.*, **29**, 1140 (1925). See also Taylor, *Trans. Far. Soc.*, 1926 (Report of meeting held October 1, 1925).

³⁴ Noyes, *J., Amer. Chem. Soc.*, **47**, 1003 (1925).

definitely shown in this case, however, that there had been no effect either by multiple collision or by the silica walls on the nitrogen, since the pressure and temperature were higher than had been used by the other authors. Taylor³⁵ has shown that no ammonia is formed at lower temperatures. Recently Hirst³⁵ has studied a series of reactions in the presence of a mercury surface and radiation from a quartz mercury arc lamp. He finds that both ammonia and hydrazine are formed from hydrogen and nitrogen. Hirst is inclined to the view that the surface plays an important part in the reactions as carried out. In this connection it is of interest to point out some work by Franck and Grotrian³⁶ on the absorption band at 2540 Å of mercury vapor. Olson and Meyers³⁷ have studied the hydrogenation and polymerization of ethylene. They find that the initial rate of reaction is proportional to the square root of the hydrogen pressure. This they ascribe to the slow rate of diffusion of the monatomic hydrogen away from the proximity of the window of the reaction vessel, where most of the radiation would be absorbed. The work of Mitchell³² is in agreement with this assumption since he found that the presence of argon decreased the reaction rate.

As a result of these studies we may conclude that activation by collisions of this type may play a very important rôle in photochemistry and we may have here the explanation of the remarkable effect, in certain instances, of very small amounts of impurity.

We may summarize briefly the conclusions which may be drawn from this preliminary discussion. A great deal of the data in photochemistry is unreliable due to faulty technique and many of the conclusions should be regarded as empirical, no satisfactory explanation having been found. Certain reactions have been studied with sufficient detail to permit the postulation of mechanisms, but usually several mechanisms will prove equally satisfactory. In addition to the ordinary difficulties involved in the studies on kinetics of reactions, we have the difficulty of isolation

³⁵ Hirst, Proc. Camb. Phil. Soc., **23**, 162 (1926).

³⁶ Franck and Grotrian, Z. tech. Physik, **3**, 194 (1922).

³⁷ Olson and Meyers, J. Amer. Chem. Soc., **48**, 389 (1926).

of the effective wave length, the determination of the exact amount of radiation absorbed and the possibility that the entire effect may be due to small amounts of impurity. We have discussed the various general types of absorption spectra and have arrived at the general conclusion that some rearrangement of the electron systems of the molecules entering into reaction is necessary. The extremely interesting work which was started by Cario and Franck has thrown open a new method of attack on photochemical problems and we may look for new important results along this line in the future. In passing we may mention some calculations by Volmar³⁸ on the effective wave length necessary for the decomposition of certain organic compounds. By postulating dissociation as the activation process and assuming certain values for the energy necessary to break the various bonds, he is apparently able to calculate with some degree of success the wave lengths which will cause certain reactions to occur. The agreement is better than the accuracy of the data used in the calculations would warrant, although his calculations may prove of importance.

In what follows we have chosen certain photochemical reactions as typical and have presented a rather full discussion of the work on them. This list is by no means complete, nor is our selection necessarily the best that could be made. Allmand²² has covered the field in a very thorough and admirable manner and we would refer the reader to his summary should information of a more general nature be desired. We hope merely to show what conclusions have been reached with regard to typical photochemical reactions and to show something of the trend which photochemistry has taken. There are, of course, an enormous number of qualitative photochemical studies, particularly on organic reactions. These studies have consisted, usually, in exposing various systems to the sun's rays and determining after a given length of time what has happened. These studies may have some practical, but they have very little theoretical interest.

³⁸ Volmar, *Compt. rend.*, **178**, 697 (1924).

PART II. TYPICAL PHOTOCHEMICAL REACTIONS

A. The decomposition of ozone

The decomposition of ozone, both thermally and photochemically, has been the subject of a number of investigations during the last twenty-five years. The thermal decomposition of partially ozonized oxygen has been studied by Warburg,³⁹ Clement,⁴⁰ Perman and Greaves,⁴¹ Jahn,⁴² and Chapman and Jones.⁴³ These workers all agree that in the absence of a catalyst the reaction is second order with respect to the ozone concentration. Jahn found that the presence of oxygen retarded the decomposition, while Chapman and Jones found that it had little effect. Clement measured the reaction rate at thirteen temperatures between 80° and 250°; from this data he arrives at the equation

$$\log k = - 5700/T + 14.939$$

The results of Warburg and of Perman and Greaves, which are less extensive, are in approximate agreement with this equation.

Perman and Greaves also investigated the effect of increasing the wall surface by adding glass tubing or glass wool; they found that the reaction took place largely on the surface, and that in the presence of a porous substance such as pipestems it became first order. Clarke and Chapman,⁴⁴ however, consider the reaction to proceed almost entirely in the gas phase. The results of Perman and Greaves may possibly be explained by imperfect drying of the glass wool, or by the presence of other impurities in it.

The photochemical decomposition was first investigated in ultra-violet light by Regener⁴⁵ and von Baur.⁴⁶ Both found the

³⁹ Warburg, *Ann. Physik*, **9**, 1286 (1902).

⁴⁰ Clement, *ibid.*, **14**, 341 (1904).

⁴¹ Perman and Greaves, *Proc. Roy. Soc.*, **80A**, 353 (1908).

⁴² Jahn, *Z. anorg. Chem.*, **48**, 260 (1906).

⁴³ Chapman and Jones, *J. Chem. Soc.*, **97**, 2463, (1910).

⁴⁴ Clarke and Chapman, *J. Chem. Soc.*, **93**, 1638 (1908).

⁴⁵ Regener, *Ann. Physik*, **20**, 1033 (1906).

⁴⁶ von Baur, *ibid.*, **33**, 598 (1910).

reaction to be of the first order in the ozone concentration. Weigert⁴⁷ found that for very thin layers the apparent order increased, reaching, in his experiments, 1.4 at a thickness of 5 mm. In the same paper Weigert postulates the photo-formation of "active centers" which cause chemical decomposition in some catalytic manner. On this basis he explains the observation of von Baur that the addition of an inactive gas retards the action; he suggests that the effect is to hinder diffusion of the active centers, thus decreasing their effectiveness.

Griffith and Shutt⁴⁸ have worked on the decomposition of ozone by visible light, using a set of Eastman color filters. They find two active regions, 5100–6150 Å and 6700–7600 Å. The methods they used are not capable of much accuracy and the limits of these regions are only approximate. Comparison of their results with the visible light absorption of ozone, as determined by Chappuis,⁴⁹ Schoene,⁵⁰ Liveing and Dewar⁵¹ and Ladenburg and Lehmann⁵² indicate that the photochemical efficiency of visible light is determined primarily by its absorption coefficient, since the two regions which are active photochemically are the only regions of visible absorption. Unfortunately, nothing is known about the quantum efficiency of visible light for this reaction.

The photochemical reaction has been studied in the presence of various other gases. Von Baur⁴⁶ found that upon replacing the oxygen in the mixture by an inactive gas the reaction was accelerated. Griffith and Shutt⁵³ and Weigert and Bohm,⁵⁴ the former using visible light, the latter ultra-violet, both find a specific acceleration due to hydrogen, much greater than for other gases. The study of this reaction is complicated by the simultaneous water formation and the results are little more than qualitative. There have been three explanations suggested for this hydrogen

⁴⁷ Weigert, *Z. physik. Chem.*, **80**, 78 (1912).

⁴⁸ Griffith and Shutt, *J. Chem. Soc.*, **119**, 1948 (1922).

⁴⁹ Chappuis, *Compt. rend.*, **91**, 985 (1880); **94**, 858 (1882).

⁵⁰ Schoene, *J. Russ. Chem. Soc.*, **2**, 250 (1884); *J. Chem. Soc.*, **48**, 713 (1885).

⁵¹ Liveing and Dewar, *Proc. Roy. Soc.*, **46**, 222 (1889).

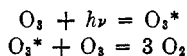
⁵² Ladenburg and Lehmann, *Verh. physik. Ges.*, **8**, 125 (1906).

⁵³ Griffith and Shutt, *J. Chem. Soc.*, **123**, 2752 (1923).

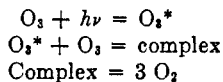
⁵⁴ Weigert and Bohm, *Z. Physik. Chem.*, **90**, 194, 223 (1915).

catalysis. Weigert and Bohm proposed local heating due to the reaction $O_3 + H_2 = H_2O + O_2$. Griffith and Shutt suggest catalysis due to the water formed; Warburg⁵⁵ found this effect to exist, when ultra-violet light is used, but his work shows it to be insufficient in magnitude to account for the whole acceleration observed. Hence Griffith and Shutt⁵³ reject this explanation and propose activation of the ozone by collision with activated water molecules, formed by $H_2 + O = H_2O^*$ or $H_2 + O_3 = H_2O^* + O_2$. Both of these reactions are considerably exothermic.

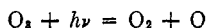
Recent work on the effect of various inert or inactive gases on the decomposition is considered by Griffith and McKeown.⁵⁶ On the basis of the catalytic effect of such gases they reject the mechanism previously given by Griffith and MacWillie⁵⁷ for the visible light reaction:



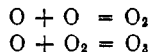
They propose instead



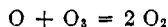
By postulating such an intermediate product, they are able to explain the catalytic effect of inert gases as due to their action in decomposing the complex into O_2 . Griffith and McKeown criticize the mechanism given by Warburg⁵⁵ for the ultra-violet reaction for its failure to explain this catalysis. This mechanism is



followed by



or



⁵⁵ Warburg, Sitzungsber. Preuss. Akad., **1913**, 644.

⁵⁶ Griffith and McKeown, J. Chem. Soc., **127**, 2086 (1925).

⁵⁷ Griffith and MacWillie, *ibid.*, **123**, 2767 (1923).

When the mixture $O_3 - O_2 - Cl_2$ is studied, more satisfactory results are obtained. Here the decomposition takes place in blue light, and the chlorine is left unchanged. Weigert⁵⁸ showed the reaction velocity to be proportional only to the amount of light absorbed and Bonhoeffer,⁵⁹ using the mercury line 4360 and the group at 4060, confirmed the results of Weigert and showed that, for pressures of O_3 greater than 0.5 mm. of mercury, two molecules of ozone are decomposed per quantum absorbed. The Einstein law is thus verified for this reaction.

Bonhoeffer found, at the same time, that if bromine replaces chlorine as a sensitizer, the quantum efficiency rises from two to thirty-one.

Weigert⁶⁰ has discussed the photochemical chlorine reactions, and especially the ozone decomposition, in considerable detail. He points out the large effect of small amounts of matter on the final distribution of the light energy absorbed. In the presence of traces of water, this energy becomes transformed into heat (the Budde effect) while in the presence of traces of O_3 it is changed into chemical energy. Weigert compares the photo-sensitization of O_3 by chlorine with the dissociation of hydrogen by mercury vapor which is absorbing its resonance radiation. He calculates that, for these two reactions, when the pressures of H_2 on the one hand and of O_3 on the other are just large enough to have no further effect on the reaction, that layers of the two reacting mixtures which absorb the same amount of light contain about equal numbers of molecules of the two reactants. In the Cario-Franck activation of H_2 , it is exceedingly probable that the first collision of an activated Hg atom will be with a hydrogen molecule; for the ozone chlorine mixture, however, an activated molecule of chlorine must, on the average, undergo 1000 collisions before striking an ozone molecule. This has led Bonhoeffer,⁵⁹ Noddack,⁶¹ Grüss⁶² and others to assume that an activated molecule may pass unchanged through collisions with an inactive one.

⁵⁸ Weigert, *Z. Elektrochem.*, **14**, 591 (1908).

⁵⁹ Bonhoeffer, *Z. Physik*, **13**, 94 (1923).

⁶⁰ Weigert, *Z. physikal. Chem.*, **106**, 407 (1923).

⁶¹ Noddack, *Z. Elektrochem.*, **27**, 359 (1921); *Physik. Zeit.*, **21**, 602 (1922).

⁶² Grüss, *Z. Elektrochem.*, **29**, 144 (1923).

Weigert points out that, by destroying the mechanism that has been given for transformation of radiation into random kinetic energy, i.e., heat, this hypothesis would greatly diminish the value of the entire concept of energy transfer during collisions. He postulates instead a weak resonance radiation for chlorine and finds confirmation for this idea in the observation of Halban and Siedentopf⁶³ that while wet and dry chlorine have the same absorption, only the wet shows the Budde effect. This idea has been criticized by Allmand,⁶⁴ who realizes the difficulties involved in the long life for activated molecules, but does not consider Weigert's idea more plausible.

Finally mention must be made of an attempt by W. C. McC. Lewis⁶⁵ to apply the simple radiation hypothesis to the ozone decomposition. The work of Clement⁴⁰ and others on the thermal decomposition, mentioned previously, indicates a heat of activation of 26,000 calories. Lewis takes half of this as the heat of activation of a single molecule; this does not seem to be justified unless every molecule of ozone that takes part in the reaction must be activated, which is not in accord with most of the mechanisms which have been suggested. The wave length corresponding to 13,000 calories is 21,700 Å, that to 26,000 calories is 10,850 Å. O₃ has an absorption band at about 47,500 Å^{66,67}. Then, according to Lewis, two quanta of this long wave length are absorbed to produce activation. Lewis considers also the higher stages of activation corresponding to frequencies that are known to be effective. Thus, it is probable that O₂ is dissociated by light of wave length 1850, to which corresponds E_{O₂} = 151,000 calories. The heat of formation of ozone is not accurately known, but is about 35,000 calories^{68,69}. Then, if E_{O₃} is the energy necessary for the reaction O₃ = O₂ + O, the equation

$$- 35000 = E_{O_3} - 1/2 E_{O_2}$$

⁶³ Halban and Siedentopf, *Z. Elektrochem.*, **23**, 499 (1923).

⁶⁴ Allmand, *Trans. Far. Soc.*, report of meeting held Oct. 1, 1925.

⁶⁵ W. C. McC. Lewis, *Trans. Far. Soc.*, **17**, 373 (1922).

⁶⁶ Warburg and Leithauser, *Ann. Physik*, **28**, 313 (1909).

⁶⁷ Angstrom, *Arkiv für Matematik (Stockholm)*, **1**, 347, 395 (1904).

⁶⁸ Meulen, *Rec. trav. chim.*, **2**, 69 (1883).

⁶⁹ Kailan and Jahn, *Z. anorg. Chem.*, **68**, 243 (1910).

may be written. Whence $E_{O_3} = 40,500$ calories. This corresponds to 7000 \AA and is doubtless in better agreement with the results of Griffith and Shutt on visible light decomposition than the accuracy of the data warrant. Lewis also explains the ultra-violet decomposition by a similar sort of calculation. Many other cases are known where discrepancies between active frequencies and those calculated from temperature coefficients may be explained by such calculations as these. In practically every case, however, the frequency calculated directly from the temperature coefficient corresponds to a region in the infra-red that is not active photochemically, frequently one that is not even absorbed.

In conclusion of the discussion of ozone decomposition, it must be mentioned that any complete theory of this reaction must explain the markedly different effects of chlorine and bromine on the decomposition. So far as we know, this has not been even attempted.

B. The decomposition of nitrogen pentoxide

The decomposition of nitrogen pentoxide is the only reaction known which certainly proceeds as a homogeneous, uncatalyzed first order gas reaction. The thermal reaction has been studied by Daniels and his co-workers,⁵ by Tolman and White⁷⁰ and by Hirst.⁵ It has been established by all of these workers that the reaction proceeds with a velocity dependent only upon the temperature. The velocity is the same in almost pure N_2O_5 as it is in the presence of large quantities of the decomposition products, N_2O_5 , NO_2 and O_2 . Indeed, dilution with 1000 parts of oxygen or nitrogen does not alter the specific reaction rate. It was thought at one time that the reaction was auto-catalytic, being affected by NO_2 , but this idea has been completely disproved.

This reaction, then, is particularly suitable for testing those theories which seek to connect the energy of activation, as calculated from the temperature coefficient of the reaction rate, with the photochemically active frequencies. The wave length cor-

⁷⁰ Tolman and White, J. Amer. Chem. Soc., **47**, 1240 (1925).

responding to the active frequency ν , calculated from the simple equation

$$\frac{d \ln k}{dT} = \frac{Nh\nu}{RT^2}$$

is 1.16μ . The work of Warburg and Leithauser⁷¹ shows that nitrogen pentoxide does not absorb light of this wave length, but does have bands at 3.39 and 5.81μ . This led Lewis⁷² to postulate that the activation occurs through absorption of five quanta corresponding to 5.81μ or more probably of three corresponding to 3.39μ . Either of these processes would give the proper energy. The work of Daniels and Johnston⁵ has shown the originally calculated frequency, corresponding to 1.16μ , to be inactive photochemically while more recently both Daniels²⁶ and Taylor²⁷ have shown that pure nitrogen pentoxide is unaffected by any infra-red radiation. Indeed, the longest wave length at which any photochemical activity has been observed is 4600 \AA ⁵ and for that the presence of NO_2 is necessary.

In view of the remarkable constancy of the specific reaction rate for this decomposition, not only in the gaseous phase but in solution,⁷³ it seems hardly possible that molecular collisions have anything to do with the reaction. The simple radiation theory is certainly not capable of explaining it. Indeed, if there is any frequency of radiation that is responsible for the thermal reaction, it is hard to see in what part of the spectrum it can lie. The infra-red waves longer than 8μ would hardly have enough energy to be effective. Between 8μ and $460 \text{ m}\mu$ the light has been shown to be without effect. Blue light is active in the presence of NO_2 , but it has been shown that this substance does not affect the thermal reaction and hence this is not the active region; certainly ultra-violet light is not present in sufficient density in the thermal radiation at ordinary temperatures to account for the observed rate of reaction, unless reaction chains are set up; but this last supposition is very unlikely in view of the constancy of the specific reaction rate for widely varying pressures.

⁷¹ Warburg and Leithauser, *Ann. Physik*, **28**, 313 (1909).

⁷² Lewis, *Trans. Far. Soc.*, **17**, 585 (1922).

⁷³ Lueck, *J. Amer. Chem. Soc.*, **44**, 757 (1922).

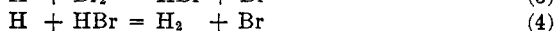
Similar results are obtained from a study of other reactions.⁷⁵ It is now certain that the original, so-called simple radiation hypothesis must be abandoned. Furthermore, in spite of the extensions which have been suggested by Lewis and Smith, Tolman² and others, it is still far from clear how thermal reactions are to be explained as basically photochemical. It is only the apparently greater difficulties^{2, 74} that an explanation on the basis of molecular collisions must overcome, which encourage further efforts to improve upon the radiation hypothesis.

C. The decomposition and formation of hydrogen bromide

The thermal formation of hydrogen bromide from its elements was studied by Bodenstein and Lind⁷⁵ who found that between 200° and 300° the rate of reaction was given by the equation.

$$\frac{d[2 \text{ HBr}]}{dt} = \frac{k [\text{H}_2] \sqrt{[\text{Br}_2]}}{m + \frac{[2 \text{ HBr}]}{[\text{Br}_2]}}$$

The fact that the bromine concentration appears as a square root was supposed by them to indicate that bromine atoms were necessary for the reaction. The inhibiting effect of the hydrogen bromide formed was not understood at the time. Somewhat later, Christiansen,⁷⁶ Polanyi,⁷⁷ and Herzfeld⁷⁸ proposed explanations for this action. The essential part of the three explanations is the same:



The reactions (1) and (5) together maintain a concentration of bromine atoms which is always proportional to the square root of the bromine concentration, since the other reactions, (2), (3),

⁷⁴ Christiansen and Kramers, *Z. physik. Chem.*, **104**, 451 (1923).

⁷⁵ Bodenstein and Lind, *Z. physik. Chem.*, **57**, 168 (1906).

⁷⁶ Christiansen, *Dansk. Vid. Math. Phys. Med.*, **1**, 14 (1919).

⁷⁷ Polanyi, *Z. Elektrochem.*, **26**, 50 (1920).

⁷⁸ Herzfeld, *ibid.*, **25**, 301 (1919); *Ann. Physik*, **59**, 635 (1919).

and (4) do not reduce the number of bromine atoms; it seems that these authors neglect the effect of the reaction $2 \text{H} = \text{H}_2$. However, if either $[\text{Br}_2]$ or $[\text{HBr}]$ is large compared to $[\text{H}]$, this neglect would not introduce an appreciable error.

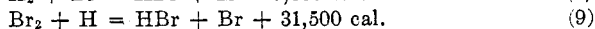
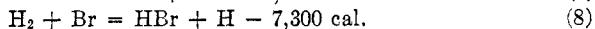
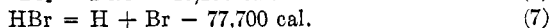
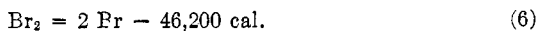
On the basis of the first five equations, an expression for the rate of reaction is found which is of the same form as that experimentally determined.

The photochemical formation of hydrobromic acid has been studied by Bodenstein and Lütkemeyer.⁷⁹ Here the velocity follows the equation

$$\frac{d [2 \text{HBr}]}{dt} = \frac{k [\text{H}_2] \sqrt{I}}{m + \frac{[2 \text{HBr}]}{[\text{Br}_2]}}$$

where I is the amount of light energy absorbed. The constant k is not necessarily independent of the spectral region considered. The rate of formation of bromine atoms by light is doubtless proportional to the amount of light absorbed, for constant wavelength; if this is the case, the concentration of bromine atoms in the steady state will be proportional to the square root of the amount of light absorbed. This makes it seem probable that the initial photochemical reaction is the dissociation of bromine and that the succeeding steps are the same as in the thermal reaction.

This dissociation mechanism for photochemical reactions has been considered by Nernst,⁸⁰ Noddack, and by Warburg.⁸¹ Bowen⁸² has attempted to develop a complete theory of the photochemistry of the hydrogen halides on the basis of such a picture. Thus from the heats of dissociation of hydrogen (which he takes as 85,000 calories) and of Br_2 (46,200 calories) and the heat of formation of hydrogen bromide he writes



⁷⁹ Bodenstein and Lütkemeyer, *Z. physik. Chem.*, **114**, 208 (1924).

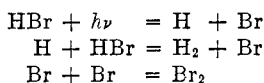
⁸⁰ Nernst, *Z. Elektrochem.*, **24**, 355 (1918). Nernst and Noddack, *Sitz. Preuss. Wiss.*, **110** (1923).

⁸¹ Warburg, *ibid.*, **1916**, 300, 314.

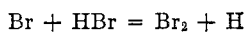
⁸² Bowen, *J. Chem. Soc.*, **125**, 1233 (1924).

The energy necessary to dissociate bromine corresponds to 6100 Å; since this wave length is absorbed by bromine, Bowen considers that it must be the photochemical threshold for the formation of hydrogen bromide. Bowen then supposes that reaction (8) in spite of its slightly endothermic character, can occasionally occur; when it does, (9) may also take place. Since (8) is endothermic, it would be probably favored by increase in temperature; this is apparently the case since the photochemical reaction has the high temperature coefficient of 1.5.⁷⁹ The quantum efficiency is certainly very low at room temperature.⁸³ The reaction has been studied up to about 250°. Lind⁸⁴ working at that temperature, reports an efficiency still less than one. His work, however, does not seem to have been very extensive.

On the basis of equation (7), Bowen predicts a photochemical threshold at 3630 Å for the photolysis of hydrogen bromide. Hydrogen bromide does not absorb at this wave length. This reaction has been studied by Warburg⁸⁵ at the wave lengths 2090 and 2530. The quantum efficiency in both cases was 2.0 within the experimental error. Warburg has proposed for this reaction the mechanism



The reaction



can not take place, since it occurs with the absorption of about 30,000 calories. Bowen has proposed the same mechanism.

Bowen has applied this same type of mechanism to the photochemistry of HCl and HI. The results are in reasonably good agreement with experiment. There are two objections to which the theory is open. One is that the experimental values for the heats of dissociation, particularly of hydrogen and of chlorine, are

⁸³ Pusch, *Z. Elektrochem.*, **24**, 336 (1918).

⁸⁴ Lind, *J. Phys. Chem.*, **28**, 55 (1924).

⁸⁵ Warburg, *Sitsb. Preuss. Akad. Wiss.*, **1916**, 314.

not known with any accuracy; the other is the possibility that the application of thermodynamics in this way to atomic processes is not justified. This latter suggestion has been made by many writers.

Coehn and Stuckardt⁸⁵ have studied both the formation and the decomposition of hydrogen bromide in quartz, in uvial and in glass vessels. They find that when light is used with a short wave limit of 2200, there is complete decomposition of the HBr; for a short wave limit of 3000 there is no decomposition and the formation is eventually complete, though the reaction is very slow. For intermediate wave lengths, about 2540, there is an equilibrium set up; in their particular experiments this equilibrium corresponded to about twenty per cent decomposition. This is in good agreement with the fact that HBr begins to absorb about 2640 Å.

There would be no particular reason for believing that the mechanism of the HBr formation is based upon a dissociation of bromine into atoms, were it not for the work of Bodenstein and Lind. Their results indicate fairly definitely that the thermal reaction takes place as a result of dissociation and they seem to show that the photochemical reaction takes place in the same way. There would seem to be no definite proof that this is the mechanism. For the decomposition, there is no reason for favoring the dissociation mechanism. Warburg has shown that it does not disagree with the facts, but it would be easy to explain the same results by means of a primary photochemical process consisting of activation.

D. The photochemical reactions of solids

With the exception of work on the silver halides with special reference to photographic processes, very little work has been done on the photochemistry of solid bodies. The problem of measuring the amount of light absorbed is, of course, a very difficult one to solve.

⁸⁵ Coehn and Stuckardt, *Z. physik. Chem.*, **91**, 722 (1916).

Renz⁸⁷ has worked on the darkening of thallos chloride and the reactions of cerium dioxide. These studies seem to have led to very little of a definite nature.

Bružs⁸⁸ has studied the thermal decomposition of a series of carbonates (ferrous, lead, cobalt, zinc, and mercurous). The variations in the critical increments for these decompositions are quite large, although the average is about 80,000 calories and Bružs concludes that this value is characteristic of the carbonate ion. This would correspond to a wave length of about 3600 Å. Schaefer and Schubert⁸⁹ have found that carbonates exhibit characteristic absorption at 6.5, 11.5 and 14.5 μ .⁹⁰

Berthelot and Gaudechon⁹¹ have studied both the thermal and photochemical decomposition of oxalic acid. They postulate that oxalic acid gives carbon dioxide and formic acid and that long waves change the latter into carbon monoxide and water and short waves into carbon dioxide and hydrogen. Noyes and Kouperman and Wobbe and Noyes²⁵ find that the wave length calculated from the critical increment does not agree with the wave length which makes the anhydrous solid decompose. The presence of water apparently accelerates the reaction considerably.

⁸⁷ Renz, *Helvetica Chim. Acta*, **2**, 704 (1919); *Zeit. anorg. allgem. Chem.*, **110**, 153 (1920).

⁸⁸ Bružs, *J. Phys. Chem.*, **30**, 680 (1926).

⁸⁹ Schaefer and Schubert, *Ann. Physik*, **50**, 283 (1916).

⁹⁰ There would seem to be a mistake in the footnote of the article by Bružs (page 693). The critical increment as calculated from the three wave lengths together would be 8,800 calories (not 89,000). This is one-tenth of the value found from the thermal decomposition.

⁹¹ Berthelot and Gaudechon, *Compt. rend.*, **158**, 1791 (1914).