

# CHEMICAL ACTIVATION BY LIGHT AND BY IONIZING AGENTS

## INTRODUCTION TO SYMPOSIUM ON RADIATION<sup>1</sup>

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In recent years much light has been shed on the subject of chemical kinetics from quite varied sources—partly classical and partly new. As a whole the subject does not reveal itself as a simple one. Much of the progress that has been made is of orientative character and most details yet remain to be worked out and fitted to general schemes. Nevertheless it is perhaps not too much to claim that we begin to get an outline of the underlying principles of chemical activation from the least to the most energetic types. The working out of a complete mechanism is a special problem for each reaction, and there seems to be no end to the variations that are encountered.

As indicated in its title, the object of the present Symposium was to consider mainly the more vigorous types of activation, as they are represented in the phenomena of ionization, on the one hand, in the complete removal of an electron from one of the reactant molecules or, on the other hand, in photochemical excitation as represented in the orbital shift of an electron, sometimes followed by dissociation.

Although only part of the papers presented at the Symposium are contained in this issue of CHEMICAL REVIEWS, reference will be made to some of the others, which have been published elsewhere. Also, for the sake of completeness, certain phases of the less vigorous types of reactions as represented in homogeneous thermal reactions will be discussed as an introduction to the

<sup>1</sup> This Symposium on Radiation was held under the auspices of the Division of Physical and Inorganic Chemistry at the Minneapolis meeting of the American Chemical Society, September 10–11, 1930.

present status of chemical kinetics. Chain mechanism may be initiated by either type of activation, and hence is appropriately considered. The comparison of temperature coefficients of velocity in the various cases is also illuminating.

The greatest difference between thermal reactions and photochemical or ionochemical ones is in the quantity of energy involved in the primary activation process. In thermal reactions the heats of activation are from 21,000 to 58,000 calories for second order reactions, while for first order reactions they extend over about the same range, 24,700 to 68,500 calories, or in both cases from 1 to 3 electron-volts; while in activation involving electron shift or removal, the energy is 5 to 15 electron-volts. In bimolecular thermal reaction this critical energy increment above the average energy content may be distributed presumably in any proportion between the two colliding molecules, principally in the form of kinetic energy. The molecules which react directly in this way have been found to be of a rather simple character, that is, possessing a limited number of atoms and a correspondingly small number of degrees of freedom to withstand shock and to store energy in a latent form.

Unimolecular reaction, on the other hand, is exhibited by more complex molecules with a large number of degrees of freedom in which activation energy is accumulated (or lost) by successive collisions and stored for the critical condition of dissociation or change. It is not quite so obvious why the heat of activation should be of the same order for this type of activation as for the bimolecular type (1). However, the difficulty of explaining the mode of activation in unimolecular reaction has been largely overcome by Lindemann's suggestion of successive accumulation and storage, so that there is no direct relation between rate of storage and rate of reaction as long as most of the stored energy leaks away by the reverse process of deactivation.

In any case we are no longer under the necessity of resorting to the radiation hypothesis to account for unimolecular reaction. In this connection it is interesting to have the most recent views of F. Perrin (p. 232), who points out that although activation and fluorescence are in general opposing influences, yet, according to

the principles of microscopic reversibility of equilibrium, where one exists the other must be possible; and since fluorescence in the infra-red region is rare or unknown, energy of activation by collision ought to be especially available.

The conception of chain mechanism, originally proposed by Bodenstein in the case of the photochemical interaction of hydrogen and chlorine has proved highly useful, and in more recent times is being extended to thermal reactions on the one hand and to ionic<sup>2</sup> ones on the other. Semenoff has used thermally initiated chains and the breaking of chains to distinguish a type of explosion different from the ordinary thermal type, which is characterized by its dependence on the size and shape of the vessel, thus giving a spatial reality to the chain conception.

Chain mechanism has been successfully used to establish reaction mechanism involving intermediate processes. The two outstanding examples of chain mechanism in photochemical reactions are the syntheses of hydrogen chloride and of phosgene. In the former we still have two possible types of chain reaction to decide between,—the material chain of Nernst on the one hand, which assumes the production of Cl atoms which are used and regenerated in each cycle, and the energy chain of Bodenstein which assumes that only the heat of reaction is passed on by collision from freshly formed "hot" molecules to activate the reactants. The selectivity which this latter mechanism requires in the presence of foreign or product molecules begins to appear possible through the resonance relations of wave mechanics. Such a selectivity of transfer also appears necessary in chain reactions in solution, to avoid the problem of deactivation by the solvent.

In phosgene synthesis a still more complicated case is presented in which even the mechanism seems to change with temperature. Prof. Bodenstein has presented the latest views in his paper on this subject (p. 225). A universal mechanism for the phosgene reaction has not yet been worked out, but such progress has been

<sup>2</sup> The discovery of the great excess of hydrogen chloride molecules formed over the number of *ions* under alpha radiation of  $H_2 + Cl_2$  mixture slightly antedated Bodenstein's photochemical work and was cited by him in support of his first "electron" chain mechanism.

made as to justify the hope of a definite solution in the near future.

The syntheses of HCl and of  $\text{COCl}_2$  have also been investigated under alpha radiation and have disclosed a complete parallelism with the photochemical processes. The first investigation of the  $\text{H}_2 + \text{Cl}_2$  reaction under alpha radiation by Bodenstein and Taylor disclosed a large excess of action over ionization ( $M/N = 4,000$ ) but nevertheless far below that in the photochemical reaction ( $M/h\nu = 10^5 - 10^6$ ), to be understood on account of variation in sensitivity. The work of Porter, Bardwell and Lind raised the  $M/N$  value to nearly four times the  $M/h\nu$  value as determined in a gas mixture of the same sensitivity, but the latest work of Lind and Livingston (2) reported in this Symposium shows that within experimental limits of error  $M/N = \frac{M}{h\nu}$ , for all sensitivities. The method of work did not permit of investigating the reaction mechanism with respect to other than equivalent concentrations of  $\text{Cl}_2$  and  $\text{H}_2$ . The work of Alyea and Lind (3) on phosgene synthesis under alpha radiation shows that the kinetics are identical with those found by Bodenstein and co-workers for its photochemical synthesis, both with respect to the rate, which is proportional to the square root of the intensity of radiation, and with respect to the concentrations of both CO and  $\text{Cl}_2$ . The chain length is also of the same order as under the influence of light and also subject to the same degree of inhibition by oxygen.

The equality of  $M/N$  and  $M/h\nu$  extends also to the non-chain types of reaction, of which about a half dozen cases have now been quantitatively investigated by means of both agents of activation. Each new reaction investigated or each increase in accuracy for old ones establishes this equality more firmly and brings us face to face with the problem of a mechanism to provide a step that will lead to a common course from that point on. It is to be remembered how different the agents are, one an atomic particle of high velocity with a universal ionizing power toward all atoms and molecules in proportion to the two-thirds power of the concentration of their orbital electrons, while the photochemi-

cal agent is highly specific, dependent on its wave length, toward absorption by and action on different atoms and molecules. The primary activation step consists then of ionization, or the removal of an electron in one case, and of the orbital displacement in the other. It is not immediately apparent why the two types should lead to the same kind and amount of reaction, but it is clear that they may do so.

In the ionic reaction it has proved useful to assume that the molecular ions of one of the reactants collects by electro-dynamic induction other neutral molecules into a positive (or sometimes negative) cluster, which undergoes chemical reaction upon final electrical neutralization (return of the electron). From the known rate of ion recombination, it may be calculated that a large number of collisions of neutral molecules with an ion would take place before its neutralization occurs. It has been suggested (4) that even in the case of the excited state, its duration and electrical moment would be sufficient to account for "photochemical clustering", which would then furnish a common basis for the ionic- and photo-chemical types of reaction. The main objection to the clustering hypothesis is that we have no definite knowledge of the actual existence of such ion clusters and certainly none of the photochemical ones. But we do know that as many as twenty acetylene molecules condense per ion pair into a solid polymer, presumably of high molecular weight, and it appears easier to assume that this collecting action proceeds under an electrical attraction, rather than by some step process after that attraction has been removed.

The alternate view (5) is that dissociation into atoms and free radicals, or possibly activation without such dissociation, takes place in the primary step in both cases, to be followed then by the ordinary thermal behavior of the primary products. The question is really very much like the time-honored one of intermediate addition products versus primary dissociation. We have perhaps in the newer cases additional points of attack that will enable a definite decision, but up to the present they have not been sufficiently developed and we have only indirect evidence, some of which favors the one view and some the other. For

example, the fact that both the kinetics and the quantum yields indicate the identity of the mechanisms for the photo- and iono-reactions in the syntheses both of hydrogen chloride and of phosgene certainly appears to support the view of Taylor and Jones. On the other hand, when one has a straight reaction of polymerization as in the cases of acetylene, cyanogen etc., where there is little evidence of primary splitting and where the final products represent a much higher degree of association than in the initial state, one is forced to choose between ion clustering and some type of step reaction following ion recombination. One can assume that the heat of ion recombination becomes available for activation in some way, but must face the problem that this activation must be followed by a clustering process and without the aid of any electrical attraction, or else by step-wise accretion to a critical size, with no characteristics of chain mechanism exhibited, such as inhibition, variable yield etc. In the polymerization cases the choice appears to favor electrical clustering rather than the apparently more artificial step-mechanisms.

It is by no means impossible that the primary mechanism may be dissociation in some cases and clustering in others. Modern kinetics show us that the same reaction product may be arrived at in different ways.

Another common property of photo- and iono-chemical action is activation by means of sensitization through a non-reactant which receives the energy and imparts it to the reactant in a collision of the second kind. Owing to the selective nature of photochemical action, the sensitized reaction may represent the sole one occurring for a given wave length. But since no substance is transparent to alpha rays, the sensitized reaction in that case will not be exclusive but will always be added to the direct activation of the reactant. The sensitized fraction may, however, become very large where the concentration of reactant falls very low in comparison with that of the sensitizer.

In the ionochemical gaseous reactions one has a new principle entering,—namely, transfer by collision of positive charge to the component gas with lowest ionization potential. It has been found that even when the transfer is to a foreign inert gas, poly-

merization about the foreign ion occurs to the same degree as about a reactant one. This appears good evidence in favor of clustering about the foreign ion.

The advantage which alpha radiation has over other ionizing agents is that it can be produced by means of radon under such conditions, even at ordinary and higher pressures, that the total ionization is readily calculated. Therefore comparison of ionization and chemical action becomes possible, as expressed in the  $M/N$  ratio. In other modes of ionization, such as electrical discharge in gases and by means of cathode rays, it is not usually possible to calculate the ionization. The fact, however, that the nature of the products and of their proportions to each other—in a reaction yielding several products—are the same for the same gas both under alpha radiation and under electrical discharge, supports the view (6) that ionization is the primary step in both cases. Substantial progress has recently been made in calculating and measuring ionization also in electronically produced chemical action. Busse and Daniels (7) have passed a stream of cathode rays from a Coolidge tube through a thin window into oxygen where the ozone could be measured chemically; the ionization was calculated by receiving the cathode rays in a total absorption calorimeter to measure their total energy. By assuming the energy to have been primarily expended entirely in ionizing oxygen with an expenditure quantized by its known ionization-potential, a value of  $M_{O_3}/N$  ions was obtained which by its agreement with the alpha ray value demonstrated the reliability of the method.

In glow discharge at pressures of a few millimeters by suitable choice of electrode dimensions and separation, saturation is obtained so that the current flowing becomes a measure of the total ionization. Working under these conditions, Brewer (8) and his associates of the Fixed Nitrogen Laboratory have measured several gaseous reactions such as the syntheses of ammonia, of water and of nitrogen dioxide from their elements, and have found the same degree of equivalence between ionization and chemical action as was to be expected from the alpha ray results in the same cases. They propose a very clever and apparently

satisfactory interpretation,—namely, that the chemical action is due to the positive ions, while the electrical current is carried almost wholly by the free electrons due to their greater mobility. In saturation current the two are equal to each other, and therefore the amount of chemical action is equivalent to the current and independent of the gas pressure as long as the latter is kept within low limits where saturation is obtained. If the pressure is allowed to rise to values where recombination of ions in the gas phase exceeds discharge at the electrode, then chemical action associated with ion recombination will exceed the current equivalent. This is the usual case represented in all types of electrical discharge at atmospheric pressure, where the chemical action greatly exceeds the current equivalent.

In the general comparison of chemical action in gases under electrical discharge and under alpha radiation, it might be logically assumed that if action is due to ions and if the ions are of the same character in both cases the nature of the resulting chemical products should be the same. While this is true in general, as is shown by comparison of the results obtained for hydrocarbon gases by Lind and Bardwell for alpha radiation and by Lind and Glockler for electrical discharge, nevertheless unexplained exceptions are met. For example, polymerization of acetylene gives solid cuprene under alpha radiation, but according to Berthelot it gives a liquid product like benzene in silent discharge. To explain these differences it is to be remembered that even if the ions produced are of the same kind, their concentration, and hence their rate of recombination, is far greater in electrical discharge than can be produced with any attainable alpha radiation. Moreover, in electrical discharge there exists the possibility of the influence of the electrode either electrically or catalytically, especially if it be a metal. The concentration of ions may have a large influence since recombination is a second order reaction, so that if the concentration be a thousandfold greater in electrical discharge than in alpha radiation, the rate of recombination becomes a millionfold greater, hence the average life of an ion a millionfold less, which brings it into a region where there will be serious competition between premature ion neutralization—lead-



ing to lower molecular weight products—and complete cluster building. While, as explained, we can not calculate ionization in the higher ion concentrations, we may as a first approximation assume it to be proportional to the chemical action and may reverse the calculation. The formation of benzene, a lower polymer than cuprene, could then be understood as a result of premature ion neutralization. If this principle could be established firmly in a number of cases it would be a strong support of ion clustering versus dissociation or thermal activation as a result of ion recombination.

It is well known that many photochemical reactions exhibit very small temperature coefficients. The same is true of the ionochemical reactions to an even greater degree, and for the same general reason that the energy of the primary step of activation by excitation or by ionization so far exceeds the necessary energy for activation that additional thermal energy is not required and will not influence the rate. This general statement of principle requires extension. In chain mechanism where the primary photochemical or ionochemical step is succeeded by thermal steps, it is evident that temperature may have an influence, and correspondingly we find the chain syntheses of HCl and  $\text{COCl}_2$  exhibiting fairly large temperature coefficients (though much lower than those of purely thermal reactions). An additional proof of the identity of the chain mechanism of HCl synthesis by light and by alpha rays lies in the identity of the temperature coefficients for white light and for alpha rays. While this appears to contradict Tolman's principle that light of the longer wave length should exhibit the greater temperature coefficient, in reality it does not do so. An experiment of Lind and Livingston with monochromatic green light showed a somewhat higher coefficient than with white light and with alpha rays, but the proportion of green in the white source was so small that it cut but little figure in the over-all coefficient. It does mean, however, that it is inappropriate to choose a chain reaction to test the validity of Tolman's principle, because temperature can play a rôle in so many ways besides in the primary step with which one is solely concerned.

Regarding the temperature coefficient of radiochemical action in general; (1) temperature may, and sometimes does, affect directly the absorption of light of a given wave length by a given substance but not that of alpha rays; (2) temperature may and does affect the quantum efficiency of the primary activation step for light especially on the long wave length side of the critical value according to Tolman; this is not probable for ionization except at quite high temperature; (3) temperature may affect any succeeding step following the primary one; in chain reactions of several steps, each may be affected and some of them in opposite directions; the same would hold equally for the same chains initiated by ionization or by other agents. The temperature coefficient is therefore seen in complex cases to be made up of the algebraic sum of the coefficients of all steps. The fact that the coefficient of water synthesis by alpha rays is zero over a wide temperature range appears therefore to be evidence against the yield of four molecules per ion pair being accounted for by thermal processes succeeding primary ionization.

Further progress in photochemical and radiochemical effects on solids has been made (see p. 239). The primary effects do not appear to be of very different character from those observed for liquids and gases. But the opportunity for secondary effects and particularly for reverse reaction are profoundly modified by the rigidity of the solid system and its influence on diffusion of products and reactants. The result reported by Noyes (*loc. cit.*) that controlled electrons must have a voltage of 4.5 to 5.5 in order to decompose oxalic acid and that through the relation  $eV = h\nu$ , the effective wave length of light may be calculated and is experimentally found to lie near the threshold value, illustrates a direct application of quantum principles to radiochemical problems.

A very interesting region of photochemistry lies in the x-ray range, where but little quantitative work has been done. Here the energy quantum is so large that an electron is expelled with sufficient velocity to produce several thousand ion pairs in its small sphere of influence. We should therefore no longer expect equivalence between  $M$ , the reacting molecules, and number of

quanta  $h\nu$  in the Einstein sense as for smaller frequencies, but rather equivalence of  $M$  and the number of ion pairs  $N$  in the same way as in alpha ray reactions. Recent work by Clark, by Stenstrom (9) and by Fricke and Morse (10) has shown the latter to be the case.

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