

# RATE CONSTANTS OF REACTIONS OF ATOMS AND RADICALS AS DERIVED FROM DIFFERENT SOURCES

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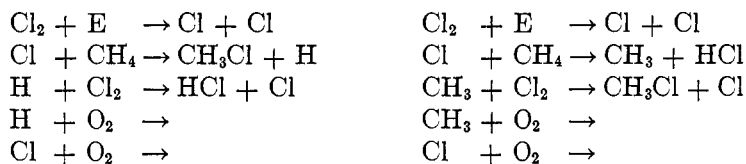
Almost all photochemical reactions are of the type which have come to be called complex. For example, at present we know of no reaction which may be described as a bimolecular process in which the activated reactant is produced by absorption of radiation rather than by thermal excitation. We may go further and make the statement that, with not more than one or two exceptions, all of the photoreactions which have been studied take place through the intermediate formation of atoms and radicals. Once formed, these react just as though we could produce them in a stable condition and introduce them into a reaction vessel. Since these processes are thus thermal in nature, it is not surprising to find the same ones occurring not only in different photoreactions but also in various thermal reactions. Those radical reactions which are common to several different over-all reactions of course take on added interest and importance.

The individual steps which consist of reactions of atoms and radicals may of course be classed as uni-, bi-, or tri-molecular, and each have their appropriate specific reaction constants. The value of these (either absolute or relative) may often be obtained from a kinetic study of a complex reaction in which they are involved. The difficulties in such a procedure are many. Often it is not known whether the steps postulated in the mechanism actually occur or not. Too frequently it is possible to write down two (or more) entirely different series of steps, both (or all) of which are in agreement with experiment. Direct determination of the transient existence of the radical intermediaries in reactions is at present practically impossible. Much has been said of the spectroscopic method in this connection, but this does not give us much more assurance than to prove the general fact that radicals may exist. To obtain emission spectra of these radicals a large amount of surplus energy is needed, which cannot usually be obtained under the conditions imposed. In fact this method may be misleading. For example, the presence of OH bands in the flame of burning hydrogen has led some to believe that this radical occurs in the photoreactions involving hydrogen and oxygen, which fact, because of other

evidence, I for one do not believe to be true. However, a recent paper of Oldenberg's has given a method of obtaining evidence of radicals through absorption spectra under high dispersion. This is a yet unexplored possibility which might in some cases yield the desired result.

But we should like to know definitely what radicals occur in a given process and what the specific rate constants of their various reactions are. Very often if we knew the values of the rate constants of even some of the possible reactions we should be able to write the actual steps, know what radicals were involved, and have no doubts as to the validity of the mechanism.

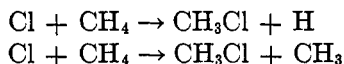
The photochlorination of methane illustrates this very nicely. The over-all reaction rate shows a dependence (7) on methane, oxygen, and chlorine concentrations which makes it seem certain that the reaction occurs through an atom or radical intermediate similar to that of the Nernst chain mechanism for the hydrogen-chlorine reaction. There are, however, two quite different mechanisms which give the dependence found experimentally, one involving hydrogen atoms as the chain carrier and the other involving methyl groups:



Both of these give the rate as follows:

$$\frac{d(\text{HCl})}{dt} = \frac{K[\text{CH}_4][\text{Cl}_2]}{k[\text{O}_2] + [\text{Cl}_2]}$$

in good agreement with experiment if  $k$  be put equal to unity. Thus the whole question of which of the two postulated mechanisms is valid depends upon the relative rates of the two reactions of chlorine atoms and methane:



A knowledge of these two reaction rates would allow us to choose between the two over-all mechanisms, even though we should not know the values of the rate constants of the other steps in the process. When we are faced with a dilemma of this type the obvious solution would seem to be to attempt to discover these needed values from some other source. In the present example this has not been found possible, but there are cases which should lend themselves to this type of solution.

Since hydrogen atoms occur in so many of the photoreactions which have been studied, it is quite natural to find the same processes involving these atoms appearing in different reactions. Here it is quite possible to obtain values of the same reaction constant from different sources, and in some cases a fair agreement may be found. However, extremely serious discrepancies exist which should claim our attention. The ideal coördination of the reaction constant values should be obtained by basing the values of the reaction constants involving hydrogen atoms upon some well established, or easily determined constant. In attempting to do this in connection with some recent results on hydrogen iodide photooxidation rather startling difficulties are observed. Let us take a simple example,—the photodissociation of hydrogen iodide. The physicist has already informed us that the first process is dissociation of the molecule by the light quantum:



What possible reactions may then occur?



If it were known *a priori* that reactions 3, 4, 5, and 6 were slow compared to reaction 2, we should have full knowledge that only reactions 1, 2, and 4 were involved, as is found experimentally. There are theoretical bases for this result. The last three are association reactions and reaction 3 is highly endothermic. But if we were to attempt to find accurate values for the rate constants there would be considerable difficulty. Certainly from the above reaction nothing quantitative can be learned of these values. If, however, iodine vapor be present in the system we may determine the relative values of the two reactions  $\text{H} + \text{HI}$  and  $\text{H} + \text{I}_2$ , since by a study of the inhibiting effect of iodine the ratio of the two constants may be obtained. This has been done by Bonhoeffer and Farkas, who found

$$\frac{k_{\text{H}+\text{I}_2}}{k_{\text{H}+\text{HI}}} = 100$$

The value of  $k_{\text{H}+\text{I}_2}$  is not known experimentally, but may be calculated on the rather reasonable assumption that the reaction goes on every collision.

It is now also possible to compare the two constants  $k_{\text{H}+\text{HI}}$  and

$k_{\text{H}+\text{O}_2+\text{M}}$  by illuminating mixtures of hydrogen iodide and oxygen. From this may be obtained the ratio (3, 5)

$$\frac{k_{\text{H}+\text{O}_2+\text{M}}}{k_{\text{H}+\text{I}_2}}$$

and if the  $k_{\text{H}+\text{I}_2}$  be computed on the basis of reaction on every collision a value of  $k_{\text{H}+\text{O}_2+\text{M}}$  is obtained. Such a value has also been calculated roughly by Bodenstein (2, 4) from data on the hydrogen-chlorine reaction and found to agree with that as obtained above.

In spite of this agreement, and because the standard of  $k_{\text{H}+\text{I}_2}$  used is perhaps a shaky one, it is obviously worthwhile to seek a more certain, and an experimentally determined constant to which to refer our values. Farkas and Sachsse (6) have furnished us with a value of the ratio

$$\frac{k_{\text{H}+\text{O}_2}}{k_{\text{H}+\text{H}+\text{H}_2}}$$

which allows of comparison with perhaps the most logical of the reaction constant standards for reactions involving hydrogen atoms, the recombination process. This has been the subject of work by Smallwood (9), Steiner (10), Senftleben (8), Farkas and Sachsse (6), and Amdur (1). However, the results are sadly conflicting. Smallwood and Amdur find that the recombination occurs through a three atom process, while Steiner and Farkas and Sachsse find that the molecule is the more efficient third body. The result of this is that Steiner gives for  $k_{\text{H}+\text{H}+\text{H}_2} = 1 \times 10^{16}$  cc.<sup>2</sup> mole<sup>-2</sup> sec.<sup>-1</sup> and Smallwood  $3 \times 10^{14}$ . Farkas and Sachsse, using a competitive reaction method involving ortho-para hydrogen conversion, obtain  $3 \times 10^{16}$ . As we have said, the latter also determined by the same method the relative values of  $k_{\text{H}+\text{H}+\text{H}_2}$  and  $k_{\text{H}+\text{O}+\text{H}_2}$ . Since the relative values of  $k_{\text{H}+\text{HI}}$  and  $k_{\text{H}+\text{O}_2+\text{M}}$  are known from the effect of oxygen on the hydrogen iodide decomposition, it is possible to compare the validity of choosing  $k_{\text{H}+\text{I}_2}$  as a standard with that of the constant of atom recombination. The result is highly unsatisfactory, no matter which value of the atom recombination constant is used. The discrepancy varies from a factor of 100 in the case of Farkas and Sachsse to  $10^4$  for Smallwood's value. Certain reasons for some difference can be seen, but such large ones are not easy to explain.

In conclusion, it should be emphasized that the accurate determination of these and other atom and radical reaction constants seems to be one of the most pressing and profitable fields for future efforts. It might even be said, perhaps too optimistically, that a correlation of such constants would have the same relation to the photochemistry of the gaseous state that the accurate atomic weight determinations had to all of chemistry.

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## DISCUSSION

DR. R. A. OGG, JR. (Stanford University): Aside from the disagreement among various investigators as to the velocity of hydrogen atom recombination, it appears that the discrepancy pointed out by Professor Bates is readily explained. In essence, the ratios

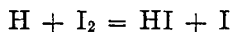
$$\frac{k_{\text{H}+\text{I}_2}}{k_{\text{H}+\text{HI}}}, \frac{k_{\text{H}+\text{HI}}}{k_{\text{H}+\text{O}+\text{M}}}, \text{ and } \frac{k_{\text{H}+\text{O}+\text{M}}}{k_{\text{H}+\text{H}+\text{M}}}$$

have been determined experimentally. The product of these three gives the ratio

$$\frac{k_{\text{H}+\text{I}_2}}{k_{\text{H}+\text{H}+\text{M}}}$$

If this ratio and the measured value of  $K_{\text{H}+\text{H}+\text{M}}$  be multiplied, a *calculated* value of  $K_{\text{H}+\text{I}_2}$  is found which is *smaller* than that based on the assumption of reaction occurring at every collision. The simplest inference to be drawn from the discrepancy is that the assumption of reaction on every collision between H and I<sub>2</sub> is unwarranted, and that this reaction actually requires a finite, although doubtless small, activation energy. This conclusion seems the more reasonable, in view of the fact that the closely related reaction  $\text{H} + \text{Br}_2$  apparently requires an activation energy of some 3000 calories per mole. (Kassel, L. S.: Kinetics of Homogeneous Gas Reactions. The Chemical Catalog Co., New York (1932)). The observed discrepancy could actually be used to estimate the activation energy for  $\text{H} + \text{I}_2$ , but the uncertainty in the value of  $k_{\text{H}+\text{H}+\text{M}}$  would be reflected in a corresponding uncertainty of this activation energy.

DR. LOUIS S. KASSEL (U. S. Bureau of Mines, Pittsburgh): The calculation actually made by Eyring for the reaction

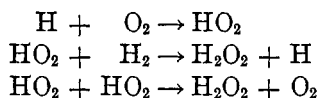


applies only when the atom approaches along the axis of the molecule. For other directions of approach a small activation energy is a conceivable result of the as yet unmade calculation. Should such a result be found, theory would give a steric factor which might be of the order of  $10^{-1}$ .

PROFESSOR BATES: In reply to the remarks of Drs. Ogg and Kassel, it perhaps can be said that Dr. Kassel's remark is really an answer to Dr. Ogg's explanation. We might expect a small steric or activation energy factor to produce a discrepancy of an order of magnitude, but not one which apparently has a possible minimum value of about 300-fold. The fact that  $H + Br_2$  has an activation energy of 3000 calories does not insure that  $H + I_2$  have one. In fact, calculations which give  $H + Br_2$  this value yield a value of zero for  $H + I_2$ .

PROFESSOR J. FRANCK (Johns Hopkins University): Could I have detailed information about the reaction between hydrogen and oxygen? I should like to know how far chain reaction in this case plays a rôle.

PROFESSOR BATES: The mechanism which I believe to be the correct one is



The reasons which lead to this conviction are too many and too long to be presented here, but are set forth in a paper published in the Journal of Chemical Physics in 1933.

PROFESSOR W. H. RODEBUSH (University of Illinois): I do not believe that the data in the literature on the recombination of hydrogen atoms are reliable. I feel that we have a method for the measurement of atom combination developed to a point where it should be possible to determine the rate of recombination of hydrogen atoms accurately.

DR. J. A. LEERMAKERS (Eastman Kodak Co., Rochester) (communicated): In connection with Dr. Bates' remarks, it seems to me worth while to mention a reaction for which a mechanism has been derived which has found support from three independent sets of measurements. I refer to the decomposition of acetaldehyde. Rice and Herzberg first postulated a chain mechanism which involved methyl radicals for the purely thermal decomposition of acetaldehyde. Hinshelwood and coworkers were responsible for the measurements which were made on the pure vapor. Allen and Sickman later sensitized the acetaldehyde reaction by thermally decomposing azomethane, which has been shown to give methyl radicals, in a system containing both azomethane and acetaldehyde; the mechanism of Rice and Herzberg was found to fit the experimental facts entirely satisfactorily. I studied the kinetics of the photolysis of acetaldehyde at

moderately high temperatures, and found that the original mechanism of Rice and Herzberg, with insignificant changes, accounted for the experimental data.

These three series of measurements, the purely thermal, the thermally sensitized, and the photochemically sensitized decomposition of acetaldehyde, tie together so well that it seems highly probable that the single mechanism is correct.

There are numerous experiments of the type I have mentioned which can be made on the decompositions of organic compounds, and I feel that such studies will lead to a very definite understanding of the mechanism of such reactions. At least such studies will automatically eliminate from consideration many mechanisms which fit one set of facts alone.

DR. OGG (communicated): From Professor Bates' last remarks it would appear that the assumption of a zero activation energy for  $\text{H} + \text{I}_2$  rests solely upon the calculations of Eyring. The discrepancy is therefore between the results of these calculations and of experiment. Since the inception of the London-Eyring-Polanyi treatment of adiabatic reactions it has become increasingly clear that this treatment, while undoubtedly correct in principle, involves such serious approximation that absolute values of the calculated activation energies are not reliable to within several thousand calories per mole. Hence Eyring's calculated "zero activation energy" for the reactions  $\text{H} + \text{Cl}_2$ ,  $\text{H} + \text{Br}_2$ , and  $\text{H} + \text{I}_2$  is to be interpreted as indicating the respective activation energies to be small, but not necessarily zero. It is of interest to note that for each of these reactions the experimentally determined velocity suggests an activation energy of the order of 2000 to 3000 calories per mole,—the experimental evidence in the case of  $\text{H} + \text{I}_2$  being that offered by Professor Bates himself. It is the writer's opinion that no adiabatic reaction proceeds without inertia, and the above evidence supports this view. It is of interest to contrast the above reactions with those of sodium atoms and halogens,  $\text{Na} + \text{Cl}_2$ ,  $\text{Na} + \text{Br}_2$ , and  $\text{Na} + \text{I}_2$ . These latter reactions have been definitely proved to require a negligibly small activation energy, and it is believed that this fact arises from the non-adiabatic mechanism which obtains, as contrasted to the adiabatic mechanism of the hydrogen atom-halogen reactions.