

259. *Considerations concerning the Mechanism of Chemical Reactions.*

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THE object of this paper is to attempt to bring certain unco-ordinated results of chemical kinetics into relation with one another. These results will first be stated and numbered for future reference.

(1) Unimolecular reactions depend upon activation of molecules by collision and a subsequent rearrangement of the activation energy inside the molecule. To account for the fact that the reaction is of the first order at higher pressures, the probability of decomposition of the activated molecule is assumed to be small, deactivation by a second collision usually occurring (for references, see Hinshelwood, "Kinetics of Chemical Change," 3rd edtn., Oxford, 1933).

(2) Many degrees of freedom may contribute to the activation energy (*idem, ibid.*). If only one internal vibration could so contribute (or, in general, energy in two square terms), the activation rate would be  $Ze^{-E/RT}$ , but when  $n$  square terms contribute this must be multiplied by a factor of the order  $(E/RT)^{n-1}/\frac{1}{2}n - 1$ , which may become very great. Thus if we write the reaction rate as  $PZe^{-E/RT}$ ,  $\bar{P}$  often has a value from  $10^2$  to  $10^5$ . It will be convenient to use two new terms. We will call a molecule *preactivated* when it has received so much energy that it can decompose after a suitable internal redistribution of this energy, and *critically activated* when it possesses enough energy in a vital bond or bonds to ensure that it will decompose within the next vibration period. For a unimolecular reaction, then, we may say that  $P$  tends to be large because there are so many ways in which the molecule can be preactivated, though it tends to be reduced by the relatively small chance that preactivation becomes critical before the next collision.

(3) Unimolecular reactions are often sensitive to homogeneous catalysts such as iodine. Certain generalisations have emerged from the study of these reactions (Bairstow and Hinshelwood, *Proc. Roy. Soc.*, 1933, *A*, **142**, 77). The activation energy is almost invariably lower than that of the uncatalysed reaction, and usually the number of degrees of freedom which have to be invoked to account for the activation rate is much smaller. Quite often, indeed, the rate is given by the simple expression  $Ze^{-E/RT}$ , where  $Z$  is the number of collisions between catalyst and reactant. This means that preactivation becomes critical immediately; *i.e.*, that the catalyst puts the activation energy directly into the vital part of the molecule. As typical examples may be quoted: (*a*) iodine molecules catalyse the decompositions of aldehydes and ethers; (*b*) halogen atoms catalyse that of nitrous oxide (Musgrave and Hinshelwood, *ibid.*, 1932, **137**, 25); (*c*) nitric oxide that of chloral and of acetaldehyde (unpublished experiments of Verhoek); (*d*) oxygen

that of acetaldehyde (Letort, *Compt. rend.*, 1933, **197**, 1042). There must be a strong specific action between catalyst and reactant, or the activation energy would not be so markedly reduced. But another factor is of importance: in (a) the iodine is highly polarisable and the reactants possess dipoles in the vital part of the molecule; in (b) the catalyst has a free valency; in (c) it has an odd electron; and in (d) the oxygen is itself magnetic, and also gives rise to some concurrent oxidation of the reactant, during which chain reactions may introduce free radicals into the system. These various conditions are precisely those likely to favour highly specific energy transfers. The important condition for the transfer of vibrational energy on collision is a strong mutual distortion of the potential energy curves of the colliding molecules (Franck and Eucken, *Z. physikal. Chem.*, 1933, *B*, **20**, 460). Dipoles, free charges, and unsaturated valencies provide the conditions for such distortion.

(4) The study of certain reactions has shown the existence of qualitatively distinct types of activated state, or, rather, of preactivated state. This provides additional evidence that internal energy changes of the kind necessary for chemical change sometimes require longer time intervals than those between collisions at moderate pressures (Hinshelwood, Fletcher, Verhoek, and Winkler, *Proc. Roy. Soc.*, 1934, *A*, **146**, 327).

(5) For bimolecular reactions in solution (for references, see Hinshelwood and Legard, this vol., p. 587) the factor  $P$  in the expression  $PZe^{-E/RT}$  is sometimes of the order unity, and sometimes as small as  $10^{-6}$ — $10^{-8}$ .

(6) The majority of the reactions where  $P$  approaches unity involve a charged ion (*idem, ibid.*), many being of the type  $XY + Z^- = XZ + Y^-$ .

(7) In esterification reactions (*idem, ibid.*), if the hydrion replaces an undissociated acid molecule as a catalyst,  $P$  increases by about  $10^4$ , attaining a value of *ca.*  $10^{-2}$  for the reaction between benzoic acid, methyl alcohol, and hydrion (in methyl-alcoholic solution). In the acetone-iodine reaction (Smith, J., 1934, 1744), with the hydrion as catalyst,  $P$  is 0.15; with the charged propionate and acetate ions the values are respectively about one-half and one-third of this, and for undissociated acid catalysts the values are much smaller, 26 times smaller for dichloroacetic acid, and over a 1000 times smaller for acetic acid.

*Unimolecular and Bimolecular Reactions.*—We will consider first the contrast between the large values of  $P$  for unimolecular reactions and the small values for certain bimolecular reactions. Some time ago it was suggested (J., 1933, 1357) that forbidden transitions might play a part in the reactions with very small values of  $P$ . Since experimental investigation seems, on the whole, to give a definitely negative answer to this suggestion (Hinshelwood and Legard, *loc. cit.*), it is necessary to see what other resources can account for.

To ensure that other factors are as nearly as possible equal, it will be convenient to consider a unimolecular forward reaction with  $P$  much greater than unity and a bimolecular reverse reaction with  $P$  much smaller than unity. Such an example would be the dissociation of a quaternary ammonium salt. Salts of this type undergo unimolecular decompositions with  $P$  of the order  $10^3$  or greater, whereas the formation of quaternary ammonium salts is a bimolecular reaction with  $P$  of the order  $10^{-7}$ .

We will try to express formally the principal factors determining the rate of reaction in one or other direction.\* In both cases activation is by collision, and, unless there is a chain reaction, the rate of reaction cannot be greater than the possible rate of activation. The rate of preactivation, in the sense defined above, is  $Z \cdot f(E, n) \cdot e^{-E/RT}$ ,  $Z$  being the collision number,  $E$  the energy concerned in the preactivation process, and  $n$  the number of square terms involved. The maximum rate at which preactivation can become critical is  $Z \cdot f(E, n) \cdot e^{-E/RT} \cdot \alpha/\beta$ , where  $\alpha$  is the rate at which energy can find its way into the right place in the molecule, on the assumption that no deactivation occurs, and  $\beta$  is the rate at which the preactivation of the molecules is destroyed again, either by collision in

\* The method of approach adopted here must, if properly applied, lead to the same results as the "transition state" method of Evans and Polanyi, Eyring, and others, though considerable apparent differences exist between the two methods.

the case of a unimolecular reaction, or by separation of the partners in the case of a bimolecular reaction.

The nature of  $\alpha$  and  $\beta$  can be seen from the following simple considerations. In the *unimolecular* reaction, let  $k_1c^2$  be the rate at which normal molecules, concentration  $c$ , become activated by collision. Let  $a$  be the stationary concentration of activated molecules, and let the latter suffer decomposition at a rate  $k_3a$ , and deactivation by collision with normal molecules at a rate  $k_2ca$ . Then we have, as usual,  $k_1c^2 - k_2ca - k_3a = 0$ ; whence, rate of reaction =  $k_3a = k_3k_1c^2/(k_3 + k_2c)$ , which, when  $c$  is great enough for the reaction to be of the first order, is  $(k_3k_1/k_2)c$ . Thus the rate depends upon the ratio of  $k_3$  to  $k_2$ . In the *bimolecular* reaction the rate of activation will be  $k_1c_1c_2$ . We think of the colliding molecules as united in a temporary complex, which either separates into its partners at a rate  $k_2x$ , where  $x$  is the stationary concentration of the complex, or undergoes spontaneous re-arrangement into the reaction products at rate  $k_3x$ . Then  $k_1c_1c_2 - k_2x - k_3x = 0$ ; whence rate of reaction =  $k_3x = k_3k_1c_1c_2/(k_2 + k_3)$ . If there is any difficulty about the change from the preactivated to the critically activated state, then  $k_2$  is great compared with  $k_3$ , and we have once more: rate =  $k_1c_1c_2 \cdot k_3/k_2$ , the ratio  $k_3/k_2$  determining the reaction velocity.  $\alpha$  and  $\beta$  are written in the general formula instead of  $k_3$  and  $k_2$  so that the concentration terms can be omitted.

Finally, we multiply by a factor  $G_1G_2$ , which expresses the condition for a correct geometrical orientation of the two molecules. Roughly,  $G_1$  and  $G_2$  may be considered to be the fractions of the two molecular surfaces which can come into contact with any useful effect. Thus for the maximum reaction rates we have  $G_1G_2Z \cdot f(E,n)\alpha/\beta \cdot e^{-E/RT}$ , and  $P$  will be  $G_1G_2 \cdot f(E,n)\alpha/\beta$ .

In the unimolecular reaction,  $G_1G_2$  will be unity, since preactivation is not concerned with reactive groups, and the energy may go anywhere. When  $n$  is considerable,  $f(E,n)$  may be great—values of about  $10^4$  are not uncommon;  $\alpha/\beta$  depends upon the ratio of the time between preactivating and deactivating collisions to the average time required for the redistribution of energy in the undisturbed molecule to give a state of critical activation. In general, it will be less than unity, but need not be enormously less, since the order of unimolecular gas reactions often changes at quite moderate pressures, showing that the time required for energy rearrangement can become comparable with that between collisions. Thus,  $P$  can be very great. Turning now to the bimolecular reaction,  $G_1$  and  $G_2$  will both be less than unity, since the reactive groups must be properly orientated. The next factor is very important: the duration of a collision is small, and thus  $\alpha/\beta$  will be many times smaller than for a unimolecular reaction, since  $\alpha$  may be of the same order for the two types, while  $\beta$  for the bimolecular is to  $\beta$  for the unimolecular as the time between collisions is to the duration of a collision. ( $\alpha$  will be the rate at which the preactivation of the collision complex would become critical if the partners did not separate again.) This difference in the time factor can account for differences of many powers of ten between the values of  $P$  for the two types of reaction. If we look on the process by which the preactivation energy becomes critical as the redistribution of energy inside a collision complex, then the life of this complex is very important, and any factors which tend to lengthen it increase the probability of reaction enormously. If there is no complex formation in the definite chemical sense, then the time during which the molecules are in close enough contact for energy changes to occur with any efficiency may easily be as small as, say, one-tenth of the time which a freely moving molecule takes to traverse a molecular diameter. The ratio of this time to the average time between collisions at ordinary pressures is  $10^{-4}$  or less. Thus the chance of critical activation is small, unless it occurs at the very moment of impact. This demands the fulfilment of special conditions which allow the energy to be put just in the right place without the need for redistribution. These special conditions, combined with the geometrical factors,  $G_1$  and  $G_2$ , may account for the very small values of  $P$  sometimes found.

The possibility that special conditions favouring specific energy transfers may be necessary, brings us to the connexion between the facts just discussed and the other set referred to in Section (3) above.

*Efficiency of Activating Collisions.*—It is well known that different degrees of freedom in molecules can be excited with very varying facility (cf. Franck and Eucken, *loc. cit.*).

This does not conflict with the principles of thermodynamics, since the energy is lost with corresponding ease or difficulty. The excitation of a degree of freedom in the collision complex may, on the one hand, prove to be rarely successful, or, on the other, it may happen whenever the necessary energy is available. The question arising is whether some of the reactions where  $P$  is small are characterised by conditions such that collisions which will critically activate the collision complex occur very rarely in comparison with collisions which put the energy in the wrong place. As we have seen, energy in the wrong place has not time to be redistributed, as it can be in a unimolecular reaction. At this point, it seems that we may come one stage nearer to understanding the problem if we bring into relation the two sets of facts referred to in Sections (3) and (7) above. It seems possible, for example, that the superiority of the charged catalysts is partly due to a mechanism analogous to that by which iodine and nitric oxide are enabled in homogeneous gas reactions to communicate energy of activation in such an effective way that it immediately counts as critical activation energy. In other words, the special quality of reactions involving an ion becomes one case of the general ability of ions, atoms, free radicals, molecules with odd electrons, or easily polarisable substances to take part in specific energy transfers. In comparing a series of catalysts, two factors must be taken into account: first, the lowering of the activation energy which the catalyst causes, and secondly, the ease with which activation of the right part of the molecule occurs, under the influence of the collision. The two factors will not be uncorrelated. That catalyst which causes the greatest weakening of the critical bond must do so in virtue of a specific force acting precisely on that part of the molecule which contains the reactive system. This specific action is of the kind which facilitates the transfer of energy, on collision, to that same part of the molecule.

This idea can be extended to reactions which we do not ordinarily call catalytic. If we recognise that collisions vary very widely in their efficiency for certain types of energy transfer, then correspondingly wide variations in the factor  $P$  may be expected. The term  $f(E,n)$  will, in fact, contain an extra specific constant. Small values of  $P$  will appear when, for any reason, the mutual influences of the molecules are such as to favour chemically unsuitable energy transfers in the activating collisions. The difference in the value of  $P$  found for bromides and iodides in their reactions with tertiary bases (see following paper) may be an example of the varying operation of such effects. The facts mentioned under (6) should also be considered in this connexion.

*Relations between P and E.*—(a) With a series of related reactions, we may have a constant  $P$  and a variable  $E$ . An example of the approximate realisation of this condition is provided by the reactions of a series of aromatic amines with substituted benzoyl chlorides (Williams and Hinshelwood, J., 1934, 1079). The structural relations of the molecules in the immediate vicinity of the reactive groups are the same for all the reactions of the series, and the effect of the substituents is mainly to modify the various bond strengths. In other words, the passage from preactivation to critical activation involves qualitatively similar processes in each reaction of the series. Thus, only the  $e^{-E/RT}$  factor is very seriously altered.

(b) Another case arises, and is exemplified to some extent in the series of esterification reactions: there is a fairly well marked tendency for  $P$  to increase as  $E$  increases (Hinshelwood and Legard, *loc. cit.*; compare also, for unimolecular reactions in solution, Moelwyn-Hughes, "Kinetics of Reactions in Solution," Oxford, 1933, p. 168). The increase of  $P$  may be due to the fact that a very highly activated molecule would be so dislocated that delicately adjusted orientation is no longer necessary, as it is when  $E$  is small. Another contributing factor may be the greater closeness of vibrational levels in a highly excited molecule. This will make the quantum conditions for critical activation easier to satisfy, and so increase the frequency of its occurrence, and thus raise the value of  $P$ . Yet another factor must be taken into account: the structural and polar changes which have occurred in passing from the faster to the slower reaction may be such as to render direct critical activation almost impossible. Reaction can now take place only when the molecule is preactivated to such an enormous extent that  $\alpha$  is increased to something comparable with  $\beta$ . The participation of more degrees of freedom, with

consequent increase of  $P$ , now becomes possible. (The participation of internal degrees of freedom in bimolecular reactions is impossible according to the views of Evans and Polanyi, although it is not clear that exceptional cases are excluded by their arguments.)

(*c*) The third case is where there is a change of catalyst and  $P$  alone varies, or varies to a more important extent than  $E$  (cf. Smith, *loc. cit.*). This is the case to which the considerations advanced earlier in this paper apply, and according to the view there expressed, the effect depends upon the action of the catalyst in favouring the specific energy transfers necessary for direct critical activation.

Combinations of these various types of behaviour may occur. Furthermore, different catalysts alter the activation energy to varying extents, and since those which produce the greatest lowering can most easily effect specific energy transfers (because they will most distort the potential-energy curves of the reactive groups), we might expect, in special cases, a correlation between a small value of  $E$  and a large value of  $P$ . Thus, by a combination of this effect with that discussed under (*b*), one might encounter cases where  $P$  showed a minimum for a certain value of  $E$  in a series of reactions.

It is not profitable to discuss this matter in further detail until more experimental evidence is available, but with regard to the type of evidence required, one conclusion may safely be drawn from the foregoing. Just as the testing of the quantum-mechanical hypothesis indicated experiments upon the influence of polar substituents, and upon reactions involving proton movements, so the further investigation of the ideas discussed in these notes requires experiments upon the relations of  $P$  and  $E$  for series of reactions in which the structural types of the reacting molecules are varied over as wide a range as possible.

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