GASEOUS UNIMOLECULAR REACTIONS

G. B. KISTIAKOWSKY

Mallinckrodt Chemical Laboratory, Harvard University, Cambridge, Massachusetts

Received May 15, 1935

It is now universally recognized that the source of activation of molecules in thermal unimolecular reactions is their collisions, and not the absorption of radiation as had been frequently proposed in the past. Lindemann (14), more than ten years ago advanced a plausible explanation of how the rate of this type of reaction can be of the first order despite the fact that the process is inherently due to molecular collisions, the frequency of which is proportional to the square of the gas pressure. He assumed that reaction follows activation with some delay, and that in the meantime the activated molecules—which are none other than the energy-rich molecules of the Maxwell-Boltzmann distribution—can lose their energy on other collisions. Clearly, so long as the activation and deactivation rates are much faster than reaction, the number of activated molecules will be the equilibrium number, that is, a constant fraction of the total number.

Since, furthermore, the reaction is supposed to take place spontaneously, in a manner similar to radioactive decompositions, a constant fraction of activated molecules will react and an overall first-order rate will result. As the pressure of the reactant gas is lowered more and more, the rates of activation and deactivation decrease proportionally to the number of molecular collisions, thus as the square of the pressure. The reaction then consumes an ever greater fraction of activated molecules, depressing their concentration below the equilibrium value and consequently lowering the reaction rate below the value predicted from the first-order rate equation. Finally, when on further lowering of the pressure the average time between activating and deactivating collisions has become much longer than the average time between activation and reaction, essentially all activated molecules undergo reaction and the reaction rate becomes equal to the rate of activation, that is, becomes of the second order.

In the years following Lindemann's suggestion his theory was not generally accepted, mainly because the rate of the then well-studied nitrogen pentoxide decomposition remained of the first order down to such low pressures (1 mm. and below) that the rate of activating molecular collisions seemed to be inadequate to explain the maintenance of the equilibrium concentration of activated molecules. This difficulty was removed by Hinshelwood (7) and Lindemann, who pointed out that very much faster rates of activation result statistically if it is assumed that energy contained in several internal degrees of freedom of the molecule contributes to the activation. In earlier calculations, on the other hand, it was usually assumed that only one degree of freedom is involved in the process of activation. As the theory was being formulated, Hinshelwood succeeded in finding gaseous unimolecular reactions showing the desired falling-off of the first-order rate constant at lower pressures and thus a positive proof of the theory seemed to have been obtained. Considerable doubts exist at the present time concerning the real mechanism of reactions then studied by Hinshelwood, but other unimolecular reactions are known, owing chiefly to the work of Ramsperger, which are free from serious objections and which demonstrate the essential correctness of the Lindemann-Hinshelwood theory.

This theory received very essential improvement in the hands of O. K. Rice and Ramsperger (25) and of Kassel (8), who incorporated in it the idea that while energy contained in different parts of the molecule may contribute to activation, in order that reaction may occur a minimum energy of activation must become concentrated in the reacting part of the molecule. This concept leads to the idea that the greater the total amount of energy in a molecule, the greater is the chance that a given minimum amount (the "activation energy" of Arrhenius) will, as the result of statistical fluctuations, concentrate in a given bond of the molecule. Accordingly, activated molecules must have different reactivities; in other words, the average times between activation and reaction must be different for molecules with different amounts of energy in excess of the minimum required amount. These improvements change somewhat the quantitative dependence of the rate on pressure and temperature, but leave the essential features of the original theory intact. In those few cases where the dependence of the rate on pressure has been accurately studied, a quantitative agreement with the Rice-Kassel theories has been obtained.

Quite naturally, the development of a satisfactory theory was followed by active experimental work, and in recent years quite a number of gaseous decompositions involving large molecules have been interpreted as of unimolecular type. It is indeed quite probable that unimolecular processes play an important part in these reactions; but on the other hand, owing to a great extent to the work of F. O. Rice, it is being recognized now that in many such reactions—particularly those occurring at higher temperatures—secondary processes are quite complex, completely obscuring the kinetics of the primary step and leading to the establishment of reaction chains. As has been shown by Rice and Herzfeld (23), such reaction chains in organic decompositions can readily lead to kinetic expressions superficially similar to those of unimolecular reactions. It is therefore necessary to exercise some caution in selecting from the list of known reactions those which should be used as examples of unimolecular processes. Table 1 represents one such selection.

TABLE 1

Some unimolecular reactions. $k = Ae^{-\frac{E}{RT}}$ *sec.*$^{-1}$

REACTING SUBSTANCE	REFERENCE	E	A	NUMBER OF CLASSICAL OSCILLATORS PARTICIPATING IN ACTIVATION
Decomposition reactions				
N_2O	(15)	53,000	4.2×10^{9}	1
F_2O	(11)	39,000	$> 10^{12}$	3
N_2O_4	(26)	13,900	8.0×10^{14}	10 ?
N_2O_5	(6)	24,590	3.8×10^{13}	15 ?
$ClCOOCCl_3$	(22)	41,500	1.4×10^{13}	7
CH_3N_3	(12)	43,500	3.0×10^{15}	13
$C_2H_5N_3$	(13)	39,700	2.0×10^{14}	14
CH_3NNCH_3	(18)	52,400	3.1×10^{16}	12
$CH_3NNC_3H_7$	(20)	47,500	2.8×10^{15}	16
$C_3H_7NNC_3H_7$	(19)	40,900	5.7×10^{13}	>25
$CH_3N_3HCH_3$	(21)	33,800	4.0×10^{11}	7
CH_3I	(17)	43,000	3.9×10^{12}	7
C_2H_5I	(17)	43,000	1.8×10^{13}	9
C_3H_7I	(17)	43,000	2.8×10^{13}	>10
CH_3NO_2	(28)	36,400	9.0×10^{12}	>12
$C_2H_5NO_2$	(28)	37,700	7.0×10^{13}	>12
$CH_3CH(OOCCH_3)_2$	(2)	32,900	2.0×10^{10}	?
$CH_3CH(OOCC_2H_5)_2$	(3)	32,900	2.5×10^{10}	?
$C_3H_7CH(OOCCH_3)_2$	(3)	32,900	3.2×10^{10}	?
$(CH_3)_3COH$	(27)	65,500	4.8×10^{14}	19
$(CH_3)_2(C_2H_5)COH$	(27)	60,000	3.3×10^{13}	?
$(C_2H_4O)_3$	(4)	44,200	1.3×10^{15}	?
$(n\text{-}C_4H_8O)_3$	(5)	42,000	2.4×10^{14}	?
$(\text{iso-}C_4H_8O)_3$	(5)	42,000	2.8×10^{14}	?
Isomerizations				
Cyclopropane	(1)	65,000	1.5×10^{15}	12
2-Methyl maleic ester	(16)	26,500	6.8×10^{5}	<1
cis-Methyl cinnamic ester	(10)	41,600	3.5×10^{10}	6
cis-Stilbene	(9)	42,800	6.0×10^{12}	>12
Pinene	(29)	43,700	1.3×10^{14}	?

The table is subdivided into two parts: decomposition and isomerization reactions. The first column gives the reacting substance, but for the sake of brevity the reaction products have not been included. In many instances they are more complex than would be strictly desirable from the point of view of the unimolecular mechanism, and it is necessary occasionally to assume that the primary unimolecular decomposition is followed by several secondary reactions, which are, however, of such a type as not to obscure the kinetics of the primary step.

The second column gives the activation energies of the reactions calculated from the temperature coefficients of the rate. It will be observed that in several instances these energies are considerably smaller than those usually associated with the strength of bonds supposed to be broken in the reactions, but this is not necessarily a severe criticism of the unimolecular mechanism. Thus, from photochemical work it is well known that in some processes of decomposition the fragments of the original molecule rearrange into more stable configurations, the energy thus set free being utilized in the process of severing the bonds.

A few of the reactions in the table have been studied with several homologues, and the general rule seems to be that the energy of activation remains essentially constant in each case. Exceptions to this have been observed with azides, azo compounds, and tertiary alcohols, and with *cis-trans* isomerizations. The first three reactions recently received a satisfactory explanation, in terms of the somewhat special properties of the methyl group, by Rice and Gershinowitz (24), while the last reaction is as yet not understood.

The next column gives the temperature independent factor of the first-order rate constant calculated for the limit of very high pressures of the reactant. In the theories of O. K. Rice and Ramsperger and of Kassel this factor, A, represents the intrinsic rate of reaction of activated molecules possessing a specified excess of energy over the necessary minimum, the rate being a prescribed, but an entirely reasonable, function of the excess energy. In the decomposition of F_2O it has not been possible to reach sufficiently high pressures to determine the limiting rate constant, and therefore only the lower limit of the constant A can be given; in the other reactions of table 1 the limiting rate has been almost realized experimentally.

The table shows quite considerable variations of the factor A from reaction to reaction and the older ideas that it could be set equal to 10^{13} or connected to the activation energy by the relation

$$A = \frac{E}{hN_{\mathrm{Av}}}$$

is seen to be only a rough approximation, although many reactions do possess *A* factors of this order of magnitude.

Some understanding of the causes of the wide variations of the *A* factor in many reactions has been gained recently by Rice and Gershinowitz (24). Upon considering the hypothetical equilibrium between the reactant molecule and its immediate decomposition products and the mechanism of the reverse (association) reaction, they conclude that when considerable "steric hindrance" or, to be more precise, a necessity for strict orientation exists in reforming the molecule from its products (as in the case of ethylidene diacetate and its homologues, for instance), the *A* factor of the forward reaction must be small and *vice versa*. Their calculations give very satisfactory agreement with experimental data and explain in particular why in a number of reactions involving the breaking-off of a methyl group, the *A* factor is so large; they suppose that in the instant of reaction a methyl group is capable of much freer motions in the molecule than a similar but larger group.

Connected with this is the larger activation energy usually observed with methyl compounds. This theory does not attempt to explain the exceptionally low *A* factors observed in a few reactions. That of the nitrous oxide decomposition, however, has been attributed to the occurrence of an electronic transition, an explanation strongly supported by the existing evidence. The isomerizations of maleic ester and of two other aliphatic double bond compounds (not given here), on the other hand, lack at present any satisfactory theory.

The last column of the table gives the number of vibrations in the molecule, supposed to have classical energy content for simplicity in treatment. This number must be assumed to contribute to the activation, if the pressure range where the falling-off of the rate constant has been found, is to be reconciled with the rate observed. The pressures at which falling-off becomes noticeable vary in different reactions from several atmospheres (nitrous oxide, F_2O, maleic ester) to pressures much lower than 1 mm. mercury (nitrogen pentoxide, azoisopropane, etc.). In the case of two molecules—nitrogen tetroxide and nitrogen pentoxide—the theory must be strained by assumption of large molecular diameters and excessive heat capacities if the observed rates are to be accounted for. In other cases the numbers found seem to be quite reasonable, and show in general the expected tendency to increase with increasing complexity of the molecule. However, too little is known on this subject to make possible extensive deductions.

Taken together, all these experimental observations leave no doubt that the present theories of unimolecular reactions are essentially correct and that they may need only minor improvements in the near future. Already, they furnish us with considerable information concerning the mechanics of molecular processes and should, when more experimental material is available, be of considerable help in the general study of molecular properties.

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