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Bimolecular Association Reactions.*

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By means of classical vibration theory a method is developed for estimating the mean lifetimes of the unstable molecules formed by the reaction of two polyatomic radicals. It is shown that these lifetimes are usually long in comparison with the time between collisions, except for the very simplest radicals. Approximate lifetimes for a number of these unstable molecules are given. From these values the orders of the corresponding association reactions may be predicted.

INTRODUCTION

BIMOLECULAR association reactions play an important rôle in the kinetics of homogeneous gas reactions, especially in chain reactions, the whole kinetics of which often depend on whether a chain breaking association reaction is of the second or third order. Direct experimental evidence of the order of these reactions is difficult to obtain, and is usually complicated by side reactions.

The explanation of why these reactions are sometimes second order and sometimes third order was originated by Herzfeld¹ and developed by a number of others.² It is now generally accepted that a molecule formed by the association of two radicals can only exceptionally lose its energy of formation as radiation, or convert any appreciable part of it into rotational energy or energy of electronic excitation. All the energy of formation is therefore present as vibrational energy, and unless the molecule is deactivated by collision with another molecule it will eventually redissociate. If the "mean life" of the new molecule is long compared with the mean time between collisions (about 10^{-11} sec.) the reaction is of the second order, while if the "mean life" is short, the reaction is of the third order.

Rosen³ has computed the mean life of a linear triatomic molecule by quantum-mechanical methods. His method, however, is so complicated that it is very difficult to apply. It therefore seems better to give up the use of

quantum mechanics and treat the problem classically. The results will, of course, be only approximate, but even a knowledge of the orders of magnitude of the mean lives of these molecules is of great value.

GENERAL THEORY

In order to specify the positions of the atoms of the new molecule we shall use a set of coordinates x_0, x_1, \dots, x_n , of which x_0 is the displacement from equilibrium of the bond just formed, and the remaining coordinates are the displacements of the other bonds and bond angles. Now for the theory of small vibrations of the molecule certain "normal" coordinates are introduced. These may be defined in terms of the x_i by a set of equations

$$\xi_i = \sum_j a_{ij} x_j \quad (i=0, 1, \dots, n), \quad (1)$$

which may be solved for the x_i :

$$x_i = \sum_j b_{ij} \xi_j \quad (i=0, 1, \dots, n). \quad (2)$$

The motion of the system is then represented at any time when all the x_i are small by

$$\xi_i = \xi_i^0 \cos \vartheta_i \quad (3)$$

or

$$x_i = \sum_j b_{ij} \xi_j^0 \cos \vartheta_j, \quad (4)$$

where the ξ_i^0 are constants determined by the initial conditions and ϑ_i is of the form

$$\vartheta_i = 2\pi\nu_i t + \epsilon_i, \quad (5)$$

where ν_i is the frequency and ϵ_i is the initial phase of the i th mode of vibration.

Eqs. (3), (4) and (5) describe the motion of the molecule only insofar as the forces acting are harmonic, i.e., as long as the x_i are so small that

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¹ Herzfeld, *Zeits. f. Physik* 8, 132 (1922).

² Cf. Kassel, *Kinetics of Homogeneous Gas Reactions* (Chemical Catalog Co., 1932), Chapter III.

³ Rosen, *J. Chem. Phys.* 1, 319 (1933).

the potential energy can be expressed in the form $V = \sum_i \frac{1}{2} k_i x_i^2$. In Fig. 1 is shown the actual form of the potential energy of one of the bonds. Instead of following the parabola $V = \frac{1}{2} k x^2$ (shown as a dotted line) the potential energy approaches the limiting value D as x becomes large. After the point M is reached the restoring force decreases instead of increasing, and consequently the acceleration produced is smaller.

If we compare the motions of two systems, one with the harmonic potential $OMA'B'C'$ and one with the potential $OMABC$, we find that there are many corresponding features. If, for example, the two systems are started at O with the same velocity, and the first system reaches its maximum displacement at A' , the maximum displacement of the second system is at the corresponding point A . Upon returning to O the systems will again be moving with the same velocity, but on the other hand the times taken for the two vibrations will not be the same, that of the vibration from O to A' to O being shorter than that from O to A to O .

In describing the actual motion it is therefore convenient to introduce a new set of variables \bar{x}_i , which are related to the x_i by the equation

$$\frac{1}{2} k \bar{x}^2 = V(x),$$

i.e., in such a way that the \bar{x} of the point A is the x of the corresponding point A' . As long as the displacements are small, the x 's and the \bar{x} 's are the same. In the same way we may introduce a set of variables $\bar{\xi}_i$ which are the same functions of the \bar{x}_i as the ξ_i are of the x_i .

If we consider a single vibration in terms of its \bar{x} we find that the motion may be expressed again by the equation $\bar{x} = \bar{x}^0 \cos \vartheta_i$, i.e., the motion still lies between the limits $\bar{x} = \bar{x}^0$ and $\bar{x} = -\bar{x}^0$,

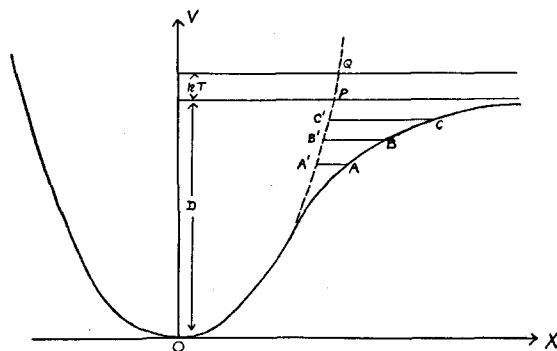


FIG. 1.

but because of the anharmonicity of the potential the angle ϑ no longer increases linearly with the time, but instead with a more complicated function of the time. The same conclusion holds true (at least to a first approximation⁴) in the coupled vibrations of molecules: Eqs. (3) and (4) still are good if we replace the x 's and ξ 's by the \bar{x} 's and $\bar{\xi}$'s, but Eq. (5) is no longer valid.

The values of the $\bar{\xi}_i^0$ must be calculated from the initial conditions. We assume that initially the molecule is at rest except for a motion of the coordinate x_0 , which we assume to be decreasing in such a way that the energy of relative motion of the two colliding radicals is kT . In terms of the \bar{x}_0 this is equivalent to the motion of a harmonic system started at rest ($\dot{\bar{x}}_i = 0$) and with all the $\bar{x}_i = 0$ except \bar{x}_0 , to which we give such a value that the total energy is $D + kT$. In terms of Fig. 1 this corresponds to a motion from rest at the point Q , or $\bar{x}_0 = [2(D + kT)/k_0]^{\frac{1}{2}}$.

The condition $\dot{\bar{x}}_i = 0$ requires that $d(\cos \vartheta_i)/dt = 0$, i.e. that $\vartheta_i = 0$, $\cos \vartheta_i = 1$, and $\bar{\xi}_i = \bar{\xi}_i^0$. Putting the given values of the \bar{x}_i into (1) then gives

$$\bar{\xi}_i^0 = a_{i0} [2(D + kT)/k_0]^{\frac{1}{2}}. \quad (6)$$

The motion of the new bond is then found by putting this into (4) (with $i = 0$)

$$\bar{x}_0 = [2(D + kT)/k_0]^{\frac{1}{2}} \sum_j a_{j0} b_{0j} \cos \vartheta_j. \quad (7)$$

Dissociation will take place when \bar{x}_0 becomes greater than $(2D/k_0)^{\frac{1}{2}}$, that is, when the potential energy of the bond becomes greater than D . The condition for this is

$$\sum_j a_{j0} b_{0j} \cos \vartheta_j > [D/(D + kT)]^{\frac{1}{2}}. \quad (8)$$

Since kT is usually small compared to D this may be put into the simpler form

$$\sum_j a_{j0} b_{0j} \cos \vartheta_j > 1 - kT/2D. \quad (9)$$

Among the terms on the left of this equation some will vanish because the product $a_{j0} b_{0j}$ vanishes. The values of the corresponding ϑ_j are immaterial. Since $\sum_j a_{j0} b_{0j} = 1$ and $kT/2D$ is usually small, the remaining cosines must have values near unity for (9) to be satisfied, i.e., the values of the ϑ_i must be near 0 after subtraction of an appropriate multiple of 2π . If there remain

⁴ The basis for this statement is a series of numerical integrations of equations of motion of simple molecules.

$q+1$ terms in (9) after discarding those which vanish, and if we expand the remaining cosines, retaining only the first two terms of the expansion, Eq. (9) reduces to

$$\vartheta_0^2/r_0^2 + \vartheta_1^2/r_1^2 + \cdots + \vartheta_q^2/r_q^2 < 1, \quad (10)$$

where we have put

$$r_i^2 = kT/a_{i0}b_{0i}D. \quad (11)$$

The physical significance of Eq. (10) is simply that dissociation will take place only if all of the modes of vibration are in phase at a time when the normal coordinate ξ_0 is at its maximum value, or nearly so. No great error will be introduced if we assume instead that Eq. (10) must be satisfied when this coordinate is exactly at its maximum value, i.e., when $\vartheta_0=0$. At this instant the condition (10) is

$$\vartheta_1^2/r_1^2 + \vartheta_2^2/r_2^2 + \cdots + \vartheta_q^2/r_q^2 < 1. \quad (12)$$

Since we know nothing of the values which the remaining ϑ_i have at such an instant, the only possible thing to do is to assume that all values of the ϑ_i are equally probable. The probability that Eq. (12) is satisfied is then the ratio of the volume of the q -dimensional ellipsoid determined by (12) to the volume $(2\pi)^q$ of the q -dimensional cube of allowed values for the ϑ_i . This ratio is given by⁵

$$r_1 r_2 \cdots r_q / 2^q \pi^{q/2} \Gamma(q+2/2). \quad (13)$$

The probable number, N , of vibrations before dissociation is the reciprocal of (13), which becomes, on substituting for the r 's and putting $a_{i0}b_{0i}=c_i^2$,

$$N = 2^q \pi^{q/2} \Gamma(q+2/2) (D/kT)^{q/2} c_1 c_2 \cdots c_q. \quad (14)$$

The mean life is then obtained by dividing this expression by the frequency, ν_0 , with which ϑ_0 vanishes:

$$\tau = N/\nu_0. \quad (15)$$

DETERMINATION OF THE c_i

Before Eq. (14) can be applied the quantities c_i must be determined. In view of the number of

⁵ This expression cannot be used when any of the r 's are greater than π , for then the ellipsoid projects beyond the cube. In such a case the expression for the probability would be much more complicated, but fortunately no such case has arisen in this work.

approximations which have already been made, the labor of the usual procedure for finding the normal coordinates of the molecule is hardly justified. A set of empirical rules has therefore been developed which gives estimates of the c_i which are as reliable as necessary for these purposes when the normal coordinates are not known exactly.

In a large number of molecules the number of possible interactions with the new bond is limited by the symmetry of the molecule. For example, if the molecule is linear, there is no tendency for the "bending" vibrations to couple with the vibrations along the axis. The two types of vibration are therefore completely distinct, and only the longitudinal vibrations need be considered.⁶

The best method of using the symmetry properties of the molecule is to introduce first a set of "symmetry coordinates."⁷ These symmetry coordinates are formed by taking linear combinations of the coordinates x_i corresponding to each type of vibration in such a way that the new coordinates form irreducible representations of the symmetry group of the molecule. Thus, for example, if the molecule being formed is CH_3Cl (symmetry C_{3v}), we combine the three C-H stretching coordinates into three new coordinates, one of which belongs to the representation A_1 , and two of which belong to the representation E . The C-Cl stretching coordinate is already a symmetry coordinate belonging to A_1 , and the five "bending" coordinates form one symmetry coordinate belonging to A_1 , and four belonging to E .

The c_i^2 we wish to determine are essentially the fractions of the normal coordinates which make up the bond being formed. By expressing the new bond in terms of these symmetry coordinates it is easy to find what fraction of the bond belongs to each representation of the group of the molecule. It only remains to divide these fractions among the various normal coordi-

⁶ This does not imply that there will be no bending of the newly formed molecule, for the motion of the molecules at the moment of collision will have components perpendicular to the axis. This motion, however, will have only the ordinary thermal energy, and in any case has no appreciable effect on the longitudinal vibrations.

⁷ For a complete account of the group-theoretical methods used here, cf. Rosenthal and Murphy, *Rev. Mod. Phys.* **8**, 317 (1936).

TABLE I.

REACTION	q	N	$\tau(\text{sec.})$
$\text{H} + \text{CN} \rightarrow \text{HCN}$	1	11	1.2×10^{-13}
$\text{Cl} + \text{CN} \rightarrow \text{ClCN}$	1	8	4.7×10^{-13}
$\text{Br} + \text{CN} \rightarrow \text{BrCN}$	1	6	4.5×10^{-13}
$\text{I} + \text{CN} \rightarrow \text{ICN}$	1	5	4.0×10^{-13}
$\text{O} + \text{CO} \rightarrow \text{CO}_2$	1	40	6.2×10^{-13}
$\text{CN} + \text{CN} \rightarrow (\text{CN})_2$	1	8	1.1×10^{-13}
$\text{H} + \text{OH} \rightarrow \text{H}_2\text{O}$	2	290	2.7×10^{-12}
$\text{H} + \text{O}_2 \rightarrow \text{HO}_2$	2	120	1.1×10^{-12}
$\text{H} + \text{CH}_3 \rightarrow \text{CH}_4$	2	290	3.2×10^{-12}
$\text{Cl} + \text{CH}_3 \rightarrow \text{CH}_3\text{Cl}$	2	73	4.4×10^{-12}
$\text{Br} + \text{CH}_3 \rightarrow \text{CH}_3\text{Br}$	2	61	4.3×10^{-12}
$\text{I} + \text{CH}_3 \rightarrow \text{CH}_3\text{I}$	2	45	3.6×10^{-12}
$\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$	2	73	2.4×10^{-12}
$\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2$	4	9×10^3	3×10^{-10}
$\text{CH}_3 + \text{OH} \rightarrow \text{CH}_3\text{OH}$	4	2×10^4	5.6×10^{-10}
$\text{H} + \text{CH}_2\text{Cl} \rightarrow \text{CH}_3\text{Cl}$	5	1×10^6	1.2×10^{-8}
$\text{NO}_2 + \text{NO}_2 \rightarrow \text{N}_2\text{O}_4$	10	8×10^7	5×10^{-6}
$\text{H} + \text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_6$	12	2×10^{14}	2.1
$\text{Cl} + \text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_5\text{Cl}$	12	1×10^{14}	6.3

nates belonging to the representations. To do this a simple empirical rule has been observed. Of the fraction of the bond belonging to any representation, each normal coordinate except the one arising principally from the symmetry coordinate in terms of which the new bond was first expressed takes 5 percent, the remainder belonging to the normal coordinate just mentioned. This rule has no theoretical justification, but gives in most cases an approximation good enough for the purposes of this paper.

For example, if we consider the reaction $\text{H} + \text{CH}_2\text{Cl}$ the bond x_0 is one of the C—H stretching coordinates, which, in terms of the symmetry coordinates already mentioned, is the sum of one coordinate belonging to A_1 and one belonging to E . We therefore assign one-half of the bond to each representation. In A_1 there are two other symmetry coordinates (the C—Cl stretching and a C—H bending) so we assign 5 percent of 0.5 or 0.025 to each, leaving 0.4

for the C—H stretching coordinate of this representation. In E we may have interaction with two types of C—H bendings, so we assign 5 percent of 0.5 or 0.025 to each of these, again leaving 0.4 to the C—H stretching. We have, therefore, the following set of c_i^2 :

$$c_0^2 = 0.4, \quad c_1^2 = 0.025, \quad c_2^2 = 0.025, \\ c_3^2 = 0.4, \quad c_4^2 = 0.025, \quad c_5^2 = 0.025.$$

This approximate method of finding the c_i is very rapid in practice, and in all the cases in which it has been checked against actual calculations of normal coordinates has proved to give fair agreement.

RESULTS

In Table I are shown the results of a number of calculations made by this method. In this table are given q , the number of vibrations interacting with the new bond, N , the number of vibrations before dissociation, and τ , the mean life of the molecule formed. These calculations have been made for a temperature of 300°K. From Eq. (14) it is seen that the mean life varies as the $-q/2$ power of T , so that the mean life for any other temperature can be obtained by multiplication of these values by $(300/T)^{q/2}$.

In many cases other reactions are possible than the simple association considered here. While these possibilities have not been considered in detail, it is evident that if the life of the associated molecule is long, conditions are favorable for such secondary reactions.

It is evident from Table I that the life of the associated molecule increases very rapidly with the value of q . It can be stated that in general a bimolecular association reaction will be of the second order, except those reactions in which the resultant molecule is of a very simple form.