

Entropy and the Absolute Rate of Chemical Reactions. II. Unimolecular Reactions

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mate $\omega_e x_e$ so obtained being then used to calculate ω_e :

$$\omega_e = \omega_1 + \omega_e x_e / 2. \quad (30)$$

A second approximation can then be made if desired. In most cases, however, the second approximation is only about 0.2 cm^{-1} lower than the first approximation and the calculated values are rarely that accurate. (Compare columns 4 and 5 of Table I.) They are especially inaccurate for highly excited states and for states having r_e , not very different from r_{12} .

CALCULATION OF $\omega_e x_e$ AND OTHER CONSTANTS FROM ω_1 , a AND $(C' - C)$

As already pointed out, $(C' - C)$ is not in general equal to the dissociation energy, for any assumed value of a . Taking $a = 4.0$ however, one can obtain approximate $(C' - C)$ values by Eq. (6) and from these by Eqs. (16) and (29) $\omega_e x_e$ may be calculated. As in the computation

of this quantity from ω_1 and r_e , one can use ω_1 in place of ω_e for a rough calculation, later, if desired, using ω_e obtained by means of Eq. (30).

Values of $\omega_e x_e$ obtained in this way are given in col. 6 of Table I for comparison with the experimental values in col. 4.

Knowing $\omega_e x_e$ and ω_e , one can of course then calculate r_e , B_e , α , etc., assuming $a = 6.0$ and $r_{12} = 1.46$, if these are not already known.

POTENTIAL CURVES FOR LARGE VALUES OF r

Comparison of the experimental values of $\omega_e y_e$ and D_e with those calculated indicates a closer agreement, when r is much larger than r_e , if a is taken as 4.0 than if it is given a higher value. To obtain the equation of a potential curve conforming reasonably well to the actual curve for r large, it is suggested that one use this smaller value of a and Eqs. (6), (16) and (17) to obtain a' , C and C' from the dissociation energy (if known) and ω_e (or ω_1).

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Entropy and the Absolute Rate of Chemical Reactions. II. Unimolecular Reactions

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In this paper the considerations of the previous paper have been developed further and compared with the theory of reaction rates as formulated in terms of a specifically defined activated complex by Eyring. The theory has been applied to a discussion of various unimolecular reactions. A number of cases have been treated by considering the reverse bimolecular or trimolecular association and discussing the extent to which rotational degrees of freedom must be frozen out in order for the associations to occur. Other cases have been treated by the activated complex method, which involves discussion of the number of free rotations and the frequency of the vibrations in the com-

plex. It has been shown that it is possible to account for the rates of a considerable number of unimolecular reactions by making reasonable assumptions and that there is a considerable class of unimolecular reactions which conform to what is designated as the "hypothesis of exact orientation," the only necessary assumption being that the rotational degrees of freedom of the fragments which recombine in the reverse reaction must be frozen out just sufficiently so that they correspond as regards their entropy terms to the resulting vibrational degrees of freedom of the molecule formed.

1. GENERAL CONSIDERATIONS

IN a recent paper² (referred to hereafter as Part I) we have developed a method for the discussion of the rates of reactions which do not

involve any change in the electronic states of the system. Since the publication of Part I, there has appeared an interesting paper by Eyring³ in which the same problem is treated by a method which has many features in common with our procedure, though the viewpoint and the termi-

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² O. K. Rice and Gershinowitz, J. Chem. Phys. 2, 853 (1934).

³ Eyring, J. Chem. Phys. 3, 107 (1935).

nology are different. Before proceeding with the treatment of unimolecular reactions we shall attempt to correlate the two points of view. We shall then, in our applications, borrow freely from both of them, according to expediency, and we shall find that we are thus led to conclusions of interest.

It has been usual in the treatment of bimolecular reactions to consider a collision factor and a steric factor. If we consider a reaction of the type $M_2 + M_3 \rightleftharpoons M_1$, then, speaking very roughly, we may say that when association occurs the six translational degrees of freedom of M_2 and M_3 go over, on association, into three degrees of freedom of translation, two degrees of freedom of rotation, corresponding roughly to rotations about axes of the molecule M_1 perpendicular to the bond of M_1 which breaks in the reverse reaction, and one degree of freedom of vibration, which may be roughly described as being directed along the bond which breaks. The "A-factor" for the rates of reaction of the unimolecular reaction⁴ were considered in Part I to be broken into two factors. If A_1 is the "A-factor" for the unimolecular reaction and A_2 for the bimolecular reaction, then we write

$$A_1 = A_1' A_1'', \text{ and } A_2 = A_2' A_2'', \quad (1)$$

where A_1' and A_2' , the "collision factors," contain entropy terms which have to do only with the above-mentioned degrees of freedom, while A_1'' and A_2'' take into account the effect of the other degrees of freedom. We finally arrived at the following expressions for A_1' and A_2' :

$$A_1' = ekT/hE_1', \quad (2a)$$

$$A_2' = e(B_1 C_1' / B_2 B_3) kT/h. \quad (2b)$$

In expressions of this sort we mean by the B 's, C 's and E 's antilogarithms of entropy terms for translation, rotation and vibration, respectively, the subscripts indicating the particular molecule.

⁴ The rate of reaction for the unimolecular reaction is written in the form $A_1 \exp(-\epsilon_a/kT)$, where ϵ_a is the energy of activation according to the definition of Tolman (*Statistical Mechanics* (Chemical Catalog Co., 1927), p. 261-2). This is the value obtained by plotting the logarithm of the rate constant against the reciprocal of the absolute temperature. The theoretical value of A_1 is not independent of temperature but may, for comparison with experiment, be evaluated for the middle of the experimental range of temperatures, as noted in the following paper.

These antilogarithms are subsequently referred to simply as entropy factors. If a letter is unprimed, it includes all of the degrees of freedom of the particular kind which occur in the whole molecule. Primes (single or double, respectively) indicate that only those degrees of freedom which occur in the collision factor, or only those which occur in the steric factor, are to be included. The number of degrees of freedom to be included in any given entropy factor is generally easily seen and the B 's, C 's and E 's may be evaluated from expressions like Eqs. (5), (6) and (7) of Part I. In particular, we may note that

$$E_1' = x(e^x - 1)^{-1} - \ln(1 - e^{-x}),$$

where $x = h\nu_1/kT$, in which ν_1 is the frequency of the vibration along the bond which breaks in the unimolecular reaction.

For the "steric factors," A_1'' and A_2'' , we set down in Part I (Eqs. (11)) the following *provisional* expressions (we again use the symbol \doteq to mean "equals provisionally"):

$$A_1'' \doteq (C_1'' E_1'')^{-1}, \quad (3a)$$

$$A_2'' \doteq (C_2 E_2 C_3 E_3)^{-1}. \quad (3b)$$

These provisional expressions are based on the assumption that, for the degrees of freedom involved, only one quantum state is available for reaction;⁵ in other words, all these degrees of freedom must be completely frozen out in order for reaction to occur. Since this is obviously too stringent a condition on these degrees of freedom we must correct (3a) and (3b) by such entropy factors as will account for the number of states actually available for reaction. Now the vibrations of M_2 and M_3 on combination will go over into vibrations of M_1 with approximately the

⁵ They do assume that, if there is spin degeneracy in the electronic and nuclear states, all these degenerate states are equally available for reaction, and that the degeneracy is the same for M_1 and for the system M_2 plus M_3 . This may not always be true but we may in general assume that spin does not affect the probability of a decomposition, so that (3a) will always hold. As noted in footnote 13 of Part I, however, the spin state may affect the possibility of association, since the relative orientations of the spins of M_2 and M_3 will determine whether they will attract or repel each other. So, in general, if the association involves free radicals, or systems not in S states, (3b) will not hold, but needs to be multiplied by a constant factor. This, however, will not affect considerations of the present paper, as we are interested in the unimolecular decomposition, to which (3a) applies.

same entropy. If we make the usual assumption that all vibrational states of M_2 and M_3 are equally available for reaction, we multiply (3a) and (3b) through by E_2E_3 which will approximately cancel part of E_1'' . Some of the rotations of M_2 and M_3 correspond to free rotations within M_1 or to the rotation of M_1 about an axis approximately parallel to the bond which breaks; these rotations of M_1 are included in C_1'' . It is reasonable to suppose that all states of these rotations of M_2 and M_3 are equally available for reaction and that the entropy expressions approximately cancel C_1'' , when (3a) is multiplied through by the proper factor. The other rotations of M_2 and M_3 go over into vibrations of M_1 and one cannot say *a priori* to what extent these rotations will have to be frozen out in order for reaction to occur, but it is reasonable to suppose that they will not have to be frozen out beyond what corresponds to the entropy of the vibrations which they are going to form⁶ and this is what we shall mean, hereafter, by saying that certain rotations are frozen out. Under these circumstances we must multiply (3a) and (3b) by a factor which will just cancel the remaining portions of E_1'' and we get, approximately at least,

$$A_1'' = 1. \quad (4)$$

Eq. (4) may be said to be the condition for the greatest possible freezing out of rotations of M_1 and M_2 (hereafter described as "exact orientation"). It is to be noted that this is what follows from the assumption that *all* states included in A_1'' are equally available for decomposition of M_1 . As might be expected, under these conditions the expression for the rate reduces essentially to that obtained by Rodebush.⁷

If not all rotations have to be frozen out we get the more general expression

$$A_1'' = C_2'''C_3'''/E_1''', \quad (5)$$

where C_2''' and C_3''' represent the entropy ex-

pressions for those rotations which are not frozen out and E_1''' the entropy expression for the corresponding vibrations. Of course, this is an idealized expression and varying extents of freezing out of the rotations may be necessary for reaction.

Certain considerations, to be discussed below in connection with our treatment of the alkyl azo-compounds, lead us to believe that when these compounds decompose the two alkyl groups leave the nitrogens simultaneously. This leads us to inquire as to the formulation of our theory for the case where the reverse reaction is trimolecular. Another type of trimolecular reaction has already been considered by Gershinowitz and Eyring⁸ and, as a matter of fact, no new principles beyond what have been discussed above are required.

To fix the ideas we shall consider specifically the case of azomethane, as generalization to other cases, particularly the other azo-compounds, is readily made. We start with the same provisional equation for the unimolecular decomposition,

$$A_1 \doteq (B_1C_1E_1)^{-1}kT/h \quad (6)$$

that was used in Part I (Eq. (9a)), collision and steric factors being included together. In the unimolecular reaction we must in this situation have three translational degrees of freedom, two rotational, and *four* vibrational going over into *nine*⁹ translational degrees of freedom. It seems reasonable to include all these degrees of freedom in what may be called a collision factor. In getting the collision factor for the bimolecular reaction we assumed that in the reverse unimolecular reaction all states of the rotational degrees of freedom included in C_1' were available for reaction, and multiplied the provisional Eq. (6) through by the corresponding entropy factors. To take care of the vibration which was converted

⁸ Gershinowitz and Eyring, submitted to J. Am. Chem. Soc.

⁶ Compare Part I, p. 860.

⁷ Rodebush, J. Chem. Phys. **1**, 440 (1933). If $kT \gg h\nu$, then in the case of exact orientation A_1 becomes equal to ν , in which case it is like Rodebush's expression. A similar result was also obtained by Polanyi and Wigner, Zeits. f. physik. Chemie, Haber Band, 439 (1928). The latter authors also gave a comparison of experiment and theory. In the following pages we shall give a more detailed comparison of the theory with a number of gas phase unimolecular reactions. See also Rodebush, J. Am. Chem. Soc. **45**, 606 (1923).

⁹ Two of these vibrational degrees of freedom are the carbon-nitrogen stretching vibrations, while two will be bending vibrations of the carbon-nitrogen skeleton. Of the degrees of freedom not included in the collision factor, the rotations of the methyl group will correspond in part to free rotations in the azomethane molecule and in part to carbon-hydrogen bending vibrations, while corresponding to the rotation of the nitrogen will be the other skeletal bending vibration and the rotation about the long axis of the kinked chain.

into a translation we multiplied through by e . In this case we multiply through by the entropy factors for the two rotations and for three of the vibrations; the fourth vibration (one of the valence vibrations of the row of two carbon and two nitrogen atoms) we again take care of by multiplying through by e . The fact, that in this case some of the entropy factors by which we multiply our expression go with vibrations rather than rotations, corresponds to the necessity that in an effective triple collision there be a pretty exact lining up of the molecules; some of the translations must be frozen out to vibrations rather than merely to rotations. Only one of the vibrations is taken care of by the factor, e , because, although two bonds are broken, the two alkyl groups must leave together, since the breaking of the bonds is presumably accompanied by a simultaneous rearrangement of the nitrogen to give a triple bond, it being this rearrangement which allows the breaking of the *two* bonds with an activation energy of only 40,000–50,000 calories. As the motion of one of the alkyls is thus definitely related to that of the other, only one "normal" coordinate is actually connected with the breaking of the bond.

The result of the above considerations is that the collision factor, for the *unimolecular* reaction comes out to have the same form as before, and is given by Eq. (2a). Likewise it may be shown that the steric factor is equal to 1 for exact orientation and otherwise is given by an equation just like Eq. (5), except that the numerator contains three factors, one for each of the combining molecules or radicals, so that we have

$$A_1'' = C_2''' C_3''' C_4''' / E_1''' \quad (7)$$

We thus have to consider the possibility that in the reverse of the azomethane decomposition neither of the methyl radicals has to be oriented.

So far we have examined the reaction by considering the initial and final states of the system. Sometimes it is better to investigate the state of an intermediate condition, an "activation complex." Such a procedure was used in Part I in the discussion of the ethylene-hydrogen reaction and has been formulated more definitely and generally by Eyring. If we consider the system to be represented by a phase point (in the coordinate space) traveling along a potential energy surface,

then, in general, reaction may be said to take place when the point passes over a saddle point on the potential energy surface. Eyring defines the "activated complex" as the state of the system just at the top of the saddle point. The activated complex differs from the molecule M_1 and also from the pair of molecules M_2 and M_3 and, in general, we may expect its properties to be intermediate between the properties of the two systems, M_1 and $M_2 + M_3$. Rotations of M_2 and M_3 which are going to be frozen out on association will presumably have already become vibrations but these vibrations will be expected to be of very low frequency so that their entropy factors will be of the same order of magnitude as those of rotations. Looking at the situation from the point of view of the reverse reaction this would mean that certain of the vibrations of M_1 have to all intents and purposes become rotations in the activated complex. To calculate the rate of reaction one calculates the equilibrium concentration of the activated complex and multiplies by the proper absolute time factor. This may be done by multiplying the provisional rates of reaction of Part I (Eqs. (9)) by the proper entropy factors for the activation complex, such entropy factors being set up on the theoretically unjustifiable but probably practically justifiable assumption that normal coordinates for the activation complex can be found.

The method of the activated complex assumes that equilibrium is completely established all along the path as the system approaches the activated state. It may be, however, if the reaction is proceeding in that direction in which degrees of freedom are becoming loosened or "melting" that equilibrium will not be established in these degrees of freedom clear to the top point of the saddle; then the activation complex will be the system at the last point where equilibrium is established (this, of course, being an approximate statement, based on the assumption that this "last point" may be definitely defined). If this is true, then in the reverse reaction, in which degrees of freedom are being frozen out, some systems will cross over the saddle and later be forced back because of the action of the other degrees of freedom. This may really mean that the potential energy surface is more complicated than a simple saddle, which would not be sur-

prising, since it is a multidimensional affair. It might be possible to effect such a change of variables that the activation complex could always be located at the top of a saddle, but the situation defies visualization. In any event, we can treat Eyring's definition of the activated complex, which has the advantage of definiteness and concreteness, as the norm from which an activated complex in nature may differ by much or little. Whether it is advantageous to use the idea of the activated complex or not will depend in large degree on how closely the actual case conforms to this normal definition of the complex.

One case in which we believe it advantageous to use the concept of freezing out of degrees of freedom rather than the concept of the activated complex is the case of exact orientation, discussed above, a case which we shall see seems to be frequently realized experimentally. From the activated complex point of view exact orientation follows if the activated complex has the same frequencies and moments of inertia as the molecule M_1 , except in the degree of freedom in which dissociation is taking place. It seems likely, however, if we insist on the normal definition of an activated complex, that we should actually expect the complex to be much more loosely bound than this would indicate. Furthermore, this case often occurs when we should expect the activation energy of the bimolecular association to be zero. If this is true, the height and position of the saddle point may depend strongly on the angular momentum of M_1 and M_2 with respect to each other, which complicates the situation. In this case, the concept of the freezing out of degrees of freedom therefore seems preferable.

On the other hand, in cases where the degrees of the freedom before and after reaction are not easily correlated, it may be necessary to consider some kind of a complex. This we found to be the case in the ethylene-hydrogen reaction and it is necessary in the study of bimolecular and trimolecular reactions, which are not associations. In the case of some of the unimolecular reactions which we shall treat below, namely the decompositions of the tertiary alcohols, the isomerization of cyclopropane and the decomposition of certain esters, we have used essentially the idea of the activated complex but the two points of view are so nearly interchangeable that we use freely, in

discussing the same reaction, any of the expressions, "the state of the activated complex," "the number of degrees of freedom frozen out," "the number of quantum states from which reaction can occur," etc.

2. THE DECOMPOSITIONS OF THE ALKYL IODIDES

Ogg¹⁰ has found that methyl, ethyl and *n*-propyl iodides decompose in the neighborhood of 600°K according to the mechanism $RI \rightarrow R + I$, with rate constants given, respectively, by $3.93 \times 10^{12} \exp(-43,000/RT)$, $1.82 \times 10^{13} \exp(-43,000/RT)$, and $2.80 \times 10^{13} \exp(-43,000/RT)$ sec.⁻¹.

The evaluation of Eq. (2a), assuming that E_1' involves a frequency of the order of 500 cm⁻¹, the frequency which is associated with an iodine atom,¹¹ gives the same value of A_1' for all the iodides at 600°K, namely 1.45×10^{13} . This agrees within the limits of error with the experimental values of A_1 and suggests that exact orientation of the alkyl radicals is necessary for recombination. The value for methyl iodide is, indeed, a little small. It may well be that the recombination of methyl radicals and iodine atoms cannot take place at every collision because of difficulty in the transfer of translational to vibrational energy; if this be so the reverse reaction will take place correspondingly more slowly.

3. THE DECOMPOSITION OF ALKYL NITRITES

Steacie and Shaw¹² have studied the rates of decomposition of methyl and ethyl nitrites at around 200°C. Allowing for the fact that these reactions probably involve a chain of two,^{12b} the rates for the initial process, in which, probably, an NO molecule splits off, may be written as $0.92 \times 10^{13} \exp(-36,400/RT)$ and $7.0 \times 10^{13} \exp(-37,700/RT)$ sec.⁻¹, respectively. Making the assumption that exact orientation is required for the reverse reaction, thus setting $A_1 = A_1'$, and using Eq. (2a) (calculating E_1' from the assumption that an NO vibration of frequency near 1500

¹⁰ Ogg, J. Am. Chem. Soc. **56**, 526 (1934).

¹¹ Kohlrausch, *Zeit. f. Elektrochemie*, (a) **40**, 429 (1934); (b) *Der Smekal-Raman Effekt* (Springer, 1931), p. 154.

¹² (a) Steacie and Shaw, J. Chem. Phys. **2**, 345 (1934); Proc. Roy. Soc. **A146**, 388 (1934). See also (b) F. O. Rice and Rodowskas, J. Am. Chem. Soc. **57**, 350 (1935).

cm^{-1} is involved¹³) we find that A_1 for both reactions comes out to be 2.4×10^{13} . This is probably equal to the observed values within the limit of error, although the difference between values for methyl and ethyl nitrites seems rather large to be all error and it is a little difficult to account for as large a difference.

4. THE DECOMPOSITION OF THE TERTIARY ALCOHOLS

The splitting off of water from tertiary butyl and tertiary amyl alcohols has been studied by Schultz and Kistiakowsky,¹⁴ who find the reaction rates to be given by $4.8 \times 10^{14} \exp(-65,500/RT)$ and $3.3 \times 10^{13} \exp(-60,000/RT)$ sec^{-1} at around 500°C . In this case we may assume that the primary reaction involves a shift of a hydrogen atom from a carbon atom to the oxygen. Such a reaction involves, essentially, the breaking of a bond, but not the formation of two separate bodies, at least in the primary reaction. If we start with the provisional Eq. (6) and assume that all the translational, vibrational and rotational levels are equally available for reaction, except that the vibration directly connected with the bond which breaks is to be taken care of in the usual way by multiplication by e , we get for the case of the tertiary butyl alcohol $A_1 = 3A_1'$ where A_1' is given by Eq. (2a), the term E_1' involving a single carbon hydrogen stretching vibration of about¹¹ 3000 cm^{-1} . The factor 3 is introduced because there are three methyl radicals which can give a hydrogen to the oxygen, it being assumed that one of the hydrogens on any given methyl is always in a position where it can go over to the oxygen and that the hydrogen on the oxygen does not get in the way. It might, perhaps, be expected that there should be some freezing out of the rotations of the methyl and the hydroxyl radicals but, on the other hand, it might well be that this would be unnecessary if there were a small amount of energy of activation in other degrees of freedom than the particular one which "breaks." In any event, on the basis of these assumptions, we find $A_1 = 1.2 \times 10^{14}$ which is still somewhat less than the experimental value, but the greater experimental value may be

due to some loosening of the bending vibrations of the active hydrogen when it is in the activated condition.

The case of tertiary amyl alcohol is somewhat different, inasmuch as the end hydrogens of the ethyl group are differently situated than the others. It is possible for them to come closer to the oxygen than the other hydrogens and this probably accounts for the lower activation energy and higher overall reaction rate.^{14a} The fact that the A_1 value is lower is probably due to the fact that there is free rotation of the ethyl radical and that this free rotation has to be frozen out in the most favorable position for reaction to take place. If this degree of freedom has to be completely frozen out the value of the A_1 factor for the reaction of these hydrogens would be about 90-fold smaller than the value for reaction from a single methyl radical, namely $4.0 \times 10^{13}/90$ or 4.4×10^{11} . The actual value with which this is to be compared is not the experimental value for *t*-amyl alcohol. We must rather take the experimental rate constants for *t*-amyl alcohol and subtract from them 8/9 of the values of the rate constants for *t*-butyl alcohol (*t*-amyl alcohol has 8 hydrogens in positions similar to the 9 hydrogens on the methyl groups of *t*-butyl alcohol). An approximate result is obtained if we note that around the middle of the range of temperatures over which *t*-amyl alcohol was investigated 8/9 of the rate of decomposition of *t*-butyl alcohol constitutes about 38 percent of the rate of decomposition of *t*-amyl alcohol. We may therefore conjecture that the true energy of activation of the part of *t*-amyl alcohol decomposition which we are interested in should differ 38/62 more from the energy of activation of *t*-butyl alcohol than the observed difference. This lowers the activation energy by 3400 calories and will make the true value of A_1 become $3.3 \times 10^{13} \times 0.62 \times \exp(-3400/RT) = 2.3 \times 10^{12}$. This is somewhat larger than calculated but this is not unexpected inasmuch as complete freezing out of the rotation of the ethyl radical should not be necessary for reaction. Although the calculations agree reasonably well with the experimental results in this case, per-

¹³ Kohlrausch, reference 11b, p. 188.

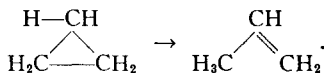
¹⁴ Schultz and Kistiakowsky, J. Am. Chem. Soc. **56**, 395 (1934).

^{14a} The mechanism assumed here implies either the immediately subsequent shift of a second hydrogen atom or the formation of dimethyl cyclopropane. It would thus be of interest to ascertain whether any of the latter substance were present in the reaction products.

haps too much emphasis should not be placed on this fact, on account of the possibility of fairly large errors in the activation energies. We have felt however, that the above calculations should be presented as they may serve as predictions of what may be expected to occur in the splitting out of HCl from tertiary chlorides. Such reactions are now being studied by Kistiakowsky and Brearley.

5. THE ISOMERIZATION OF CYCLOPROPANE

This reaction has been studied around 500°C by Chambers and Kistiakowsky¹⁵ who find for the rate constant $1.48 \times 10^{15} \exp(-65,000/RT)$ sec.⁻¹. Chambers and Kistiakowsky have discussed two possible mechanisms for this reaction. The first mechanism involves the breaking of a carbon-carbon bond and a subsequent rearrangement, consisting in the shift of a hydrogen atom. Although the reverse of this reaction is not an association, but another unimolecular reaction, we should expect it to proceed like a reaction requiring exact orientation; if, namely, we make the assumption that all states of the molecule are equally available for reaction we see that A_1 should be equal to $3A_1'$ as given by Eq. (2a) with ν_1' equal to 1000 cm⁻¹, the frequency of a carbon-carbon stretching vibration,¹¹ the factor 3 being introduced because there are three bonds which can break. This yields $A_1 = 8.1 \times 10^{13}$ and it is seen that it is much too small. Chambers and Kistiakowsky also suggested that the mechanism might consist in the jumping of a hydrogen from one carbon to an adjacent one with simultaneous formation of a double bond,



In this case, we naturally assume that A_1 is equal to $12A_1'$, as given by Eq. (2a), with ν_1' equal to a carbon-hydrogen frequency, the factor 12 being introduced because there are six hydrogen atoms and each one can go to either of two carbon atoms. It is not certain whether this would be a stretching or bending¹⁶ frequency; we assume it to be the latter, which can only cause A_1

to have too small a value. This assumption gives $A_1 = 3.9 \times 10^{14}$, probably agreeing with experiment within the limit of error; in any event, the difference could easily be accounted for by a slight loosening of the frequencies in the activation complex. This, we believe, is evidence in favor of the hydrogen shift mechanism, though one must be cautious in drawing conclusions on the basis of such grounds as these. It may be well to remark that one cannot exclude the assumption that a carbon-carbon bond breaks first, equilibrium being established between the activated molecules thus formed and the normal molecules, and that the subsequent rearrangement is the rate determining step. At first sight it would appear that the rate for this mechanism would be too large, for one would naturally assume that the intermediate would have free rotations, which would mean that its entropy would be large and its concentration correspondingly great. However, if these free rotations must be frozen out again before the rearrangement can take place, the same rate will result as with the direct shift of the hydrogen. With this condition imposed the difference between the two mechanisms in which the hydrogen shift is the rate-determining step becomes in a sense trivial.

Assuming that the rate-determining step is the shift of a hydrogen atom, it will be of interest to consider the reverse reaction, namely, the formation of cyclopropane from propylene. In propylene a free rotation of a methyl group with entropy term C_2'' , let us say, takes the place of a carbon-hydrogen bending vibration with entropy factor E_1'' , while a rotational entropy factor C_2' takes the place of the rotational entropy factor C_1 of the cyclopropane. We shall neglect changes in the vibrational frequencies and assume that $C_2'/C_1 = 6$, since 6 is the symmetry number of cyclopropane. A consideration of the relation between rate constants of direct and reverse reactions and equilibrium constant then shows us at once that the relation between A_2 , the "A-factor" for the *propylene* isomerization, and the factor A_1 for isopropane should be given by

$$A_2/A_1 = (C_1/C_2')(E_1''/C_2'') = E_1''/6C_2''.$$

Suppose now that we should assume that in the isomerization of propylene one of the hydrogen

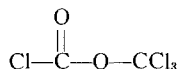
¹⁵ Chambers and Kistiakowsky, J. Am. Chem. Soc. **56**, 399 (1934).

¹⁶ Kohlrausch, reference 11a, and reference 11b, p. 206.

atoms on the methyl group is always in a position to react, as we have done in the decomposition of the tertiary alcohols; suppose, in fact, that all states of the molecule are equally available for reaction; we then find that A_2 will be given by an expression like (2a), namely ekT/hE_2' , where E_2' involves, probably, a carbon-hydrogen bending vibration. But we have already assumed $A_1 = 12ekT/hE_1'$ where $E_1' = E_2'$. Hence we should have $A_2/A_1 = E_1''/6C_2'' = 1/12$, or $E_1''/C_2'' = 1/2$. Actual calculation of E_1''/C_2'' (remembering that the free rotation of a methyl involves a symmetry number of 3) gives 0.14. This shows that the assumptions we have made regarding A_1 and A_2 are not quite consistent with each other (and as cyclopropane is undoubtedly a stiffer structure than propylene the discrepancy is actually a little greater than this). In view of the roughly approximate nature of these considerations such a difference is not unexpected. Assuming that the estimate of A_2 is correct, we get for A_1 the value 1.5×10^{15} , a result which is in closer agreement with experiment than the value originally obtained.

6. THE DECOMPOSITION OF TRICHLOROMETHYL CHLOROFORMATE

The decomposition of trichloromethyl chloroformate,



to give two molecules of phosgene, which according to Ramsperger and Waddington¹⁷ has a rate constant given by $1.4 \times 10^{13} \exp(-41,500/RT)$ sec.⁻¹ at around 300°C, is undoubtedly similar to the isomerization of cyclopropane, inasmuch as it must involve the transfer of a chlorine atom from one carbon atom to the other. While the O—C Cl₃ group can presumably rotate freely about the other carbon-oxygen bond this will not change the relative position of the chlorines with respect to the other carbon atom and if we assume that one chlorine is always in a position to react, then the reaction consists essentially in the breaking of a carbon-chlorine bond, followed by the breaking of a carbon-

oxygen bond, and the formation of another carbon-chlorine bond. In the latter processes some vibrational frequencies change to rotational but it seems reasonable to suppose that these rotational frequencies would have to be frozen out for recombination to occur. If we assume that the breaking of the carbon-chlorine bond is the rate determining step, which seems likely, as it would appear that the chlorine is the active atom in the decomposition, then A_1 should be equal to A_1' , as given by Eq. (2a), with E_1' calculated on the assumption that it involves a carbon-chlorine stretching frequency of about¹¹ 700 cm⁻¹. The value of A_1 thus obtained is 1.9×10^{13} , in good agreement with the experimental value.

7. THE DECOMPOSITIONS OF CERTAIN ESTERS

Coffin¹⁸ has studied the decompositions of ethylidene diacetate, ethylidene dipropionate and butylidene diacetate at temperatures somewhat above 200°C and found the A_1 factors to be, respectively, 2.0×10^{10} , 2.5×10^{10} and 3.2×10^{10} . Contrasted to the values generally obtained from the hypothesis of exact orientation, $2-3 \times 10^{13}$, these seem at first sight very low. However, it seems probable that the reaction goes, as shown in Fig. 1, through an activated complex in which three degrees of freedom of free rotation which can normally occur in the ester (about three of the bonds shown dotted in the activated complex) have become frozen out into vibrations. As we have stated above, the hypothesis of exact orientation gives the same result as assuming that, except for the bond that breaks, the activated complex is entirely similar to the decomposing molecule; in this case, in which three rotational degrees of freedom have become vibrations in the complex, the result will be obtained by multiplying the rate to be expected for exact orientation by E_0/C_1''' where E_0 is the entropy expression for the vibrations in the complex and C_1''' is the entropy expression for the rotations frozen out. Now it is very difficult to make an estimate of C_1''' for these cases, as we do not know enough about the dynamics of such complicated molecules. It is obvious, however, that the moments of inertia involved will be large and a rough estimate for ethylidene diacetate indicates

¹⁷ Ramsperger and Waddington, J. Am. Chem. Soc. 55, 214 (1933).

¹⁸ Coffin, Can. J. Research 5, 636 (1931); 6, 417 (1932).

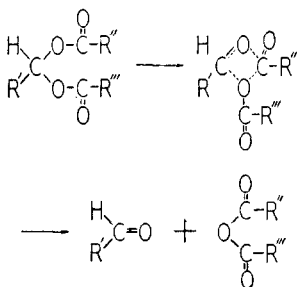


FIG. 1. The decomposition of esters like ethylidene diacetate. *Erratum:* An H-C and an R'-C bonding line were unintentionally omitted in the activated complex.

C_1''' will probably be of the order of 10^6 . Since E_0/C_1''' must be of the order of 10^{-3} , we see that E_0 must be around 10^3 , which would make the vibrations involved of the order of 90 to 100 cm^{-1} . Since the complex is undoubtedly very loosely bound and 100 cm^{-1} is not far below the lower bending frequencies in complex molecules, this does not seem at all unreasonable. As the moments of inertia of the other esters are undoubtedly larger than those for ethylidene diacetate it might be expected that the A_1 's would decrease rather than increase, but it is also very probable that in these cases the complex would have still lower frequencies, which might about cancel the other effect.

8. THE DECOMPOSITIONS OF THE AZO-COMPOUNDS

We shall next consider the decompositions of azomethane¹⁹ and azoisopropane,²⁰ which go in the neighborhood of 570°K . The respective rate constants are given²¹ by $3.1 \times 10^{16} \exp(-52,440/RT)$ and $5.7 \times 10^{13} \exp(-40,900/RT)\text{ sec}^{-1}$.

Assuming that the frequency involved in Eq. (2a) is of the order of magnitude of carbon-nitrogen stretching vibrations, namely²² 1000 cm^{-1} , we get $A_1 = 2.4 \times 10^{13}$ for both azomethane and azoisopropane if we use the hypothesis of exact orientation. This agrees within the limits of error with azoisopropane.

The rate of reaction of azomethane, however, is much faster than we would expect from the

hypothesis of exact orientation. Let us, therefore, attempt to calculate A_1'' from Eq. (5), assuming that the methyl radical on combination with the $\text{CH}_3\text{-N=N-}$ radical, does not need to be oriented at all. The moments of inertia of the methyl radical (assuming tetrahedral angles are preserved and that the carbon atom is at the center of gravity) are 5.17×10^{-40} and 3.24×10^{-40} , the latter representing two degrees of freedom. The entropy term corresponding to the larger of the above moments is the one which will cancel against the entropy due to the free rotation of the methyl radical in azomethane. We can, therefore, write in this case

$$A_1'' = \pi^{-1}(8\pi^3 e I''' kT/h^2)/E_1''',$$

where $I''' = 3.24 \times 10^{-40}$; the factor π^{-1} is included (see Part I, Eqs. (7b)) because in the process of fixation of the methyl radical it ceases to rotate as a separate body and E_1''' contains the entropy due to the two vibrations corresponding to the two rotations. These vibrations are presumably of the carbon-hydrogen bending type, and are approximately¹⁶ 1400 cm^{-1} . We thus get $A_1'' = 87$, giving $A_1 = A_1' A_1'' = 2.4 \times 10^{13} \times 87 = 2.1 \times 10^{15}$. When we double this to allow for the possibility that either methyl can leave, it is still seven-fold too low, as compared to the experimental value. The uncertainties are probably sufficiently great so that this interpretation of the azomethane reaction cannot be excluded on these grounds alone. Nevertheless, other considerations point to it as being rather improbable. Thus, it is obvious from the discussion in §1 that to be consistent with the above picture the activated complex must have the rotations of the methyl group fully excited. In this case there is probably no saddle point in the potential energy when the relative angular momentum of the fragments is zero and so one might have some justification in claiming that the fragments produced in the decomposition actually constitute the activated complex, and in this state the methyl does rotate freely. It does, nevertheless, hardly seem reasonable that the methyl group could be as loosely bound as this at the last point at which it is possible to transfer energy from one degree of freedom to any other of the whole system²³ and,

¹⁹ Ramsperger, J. Am. Chem. Soc. **49**, 912, 1495 (1927).

²⁰ Ramsperger, J. Am. Chem. Soc. **50**, 714 (1928).

²¹ Kassel, *Kinetics of Homogeneous Gas Reactions* (The Chemical Catalog Co., 1932) pp. 192, 196.

²² Kohlrausch, reference 11b.

²³ See the discussion, last part of §1.

in any event, this surely seems not to be the case with the isopropyl compound.

However (though we still have to account for the difference between azomethane and azoisopropane), if we should be willing to admit that the reverse of the decomposition of azomethane is trimolecular, the large value of A_1 would seem less surprising since the effect would then be divided between two methyl radicals. There is, as a matter of fact, other evidence, which has been discussed by Ramsperger,²⁴ in favor of the supposition that the reverse reactions of the decompositions of the azo-compounds are trimolecular. The rate of decomposition of methylazoisopropane²⁴ is given by the expression²⁵ $2.80 \times 10^{15} \exp(-47,480/RT)$ sec.⁻¹ and it will be noted that both the energy of activation and A_1 have intermediate values with respect to the other azo-compounds. This suggests that there are certain energies of activation and certain contributions to A_1 , which are characteristic of the splitting off of methyl and isopropyl groups, respectively, and that these are independent of the compound.

If this supposition is true, then the activation energy necessary for removal of a methyl radical is greater than that necessary to remove an isopropyl. One is inclined to believe that this excess of energy is connected in some way with the large value of A_1 for azomethane and, indeed, on closer consideration, it seems very likely that this is the case. This can be understood better by a discussion of the reverse reaction. Since the moment of inertia of a methyl radical is small, the hydrogens will be rotating around rather rapidly, and if the methyls approach the nitrogen with just average energy, the hydrogens will get in the way, and except in very rare instances may be expected to prevent the carbon atoms from forming bonds. The reason for this is that the repulsive forces acting between the hydrogens and the nitrogen, will transmit enough momentum to the methyl radical to cause it to reverse its direction. However, if the methyl radical is going fast enough, this is less likely to happen. The force between the hydrogens and the nitrogen will ultimately be dissipated in causing vibrations of the hydrogens or, still more likely, since they have lower fre-

quencies, to the bending vibrations of the molecule, and the hydrogens will simply be dragged in, so to speak, with the relatively heavy carbon atom. It does thus appear likely that some additional energy will be required for the trimolecular association reaction to take place if the recombining groups have small moments of inertia, the large A_1 value being accounted for because it does not much matter what the rotational state of the methyl radical is, so long as it has sufficient translational energy. In the case of the reverse unimolecular reaction we must assume that it is correspondingly difficult for the methyls to leave, unless they have some additional energy, or have the possibility of getting the requisite energy from other degrees of freedom.

Since the moments of inertia of the isopropyl radical are all large, it will be seen that no effect, such as we have assumed to be operative in the case of the methyl radical, is to be expected. The rotation will be relatively slower and it will be difficult for the carbon atom which forms the bond to drag along equally heavy atoms if the orientation is not correct. The difference between methyl and isopropyl radicals is thus to be expected and it is seen that methylazoisopropane, which has one methyl and one isopropyl radical, should be intermediate in all respects to the other two azo-compounds, as is observed.

In the case of azoethane, which D. V. Sickman and O. K. Rice are now attempting to prepare, we have to consider the recombination of ethyl radicals. An ethyl radical has four degrees of freedom of rotation (including one internal free rotation), two of them having large moments of inertia due to rotation of carbon atoms, and the two have small moments of inertia due to rotation of hydrogen atoms. On recombination it will be seen that one of each kind of rotation will be frozen out so that we may well expect that the kinetics of azoethane will be intermediate between azomethane and azoisopropane. A consideration of the rotations which must be frozen out in the case of azo-*n*-propane, indicates that it will behave more like azoethane than azoisopropane. The fact there are no rotations possible which involve hydrogen and at the same time affect the carbon atom which is actually combining or breaking a bond may be a general cause of the abnormal activity of isopropyl radicals in organic reactions

²⁴ Ramsperger, J. Am. Chem. Soc. **51**, 2134 (1929). See especially p. 2141.

²⁵ Reference 21, p. 199.

which involve removal of the radical, since it apparently gives a lower energy of activation, which is not completely counterbalanced by the lower value of A_1 .

As hexadeuterozomethane will no doubt be prepared in the next dozen years we may make a remark regarding what it may do according to the theory outlined, for there is the possibility, though not the certainty, of a very striking result being obtained. It may, namely, be the case that the rotation of the trideuteromethyl radical will be sufficiently slow so that the anomalies of the methyl radical will not be evident; if this is true, then hexadeuterozomethane will resemble the azoisopropane in its kinetics rather than azomethane. In any event, experiments with hexadeuterozomethane will certainly be of great interest.

9. CONCLUSION

There are a number of other unimolecular reactions and for some of them the constant A_1 has anomalously low values. This may be because the decomposition involves an electronic transition; in any event it is likely that the mechanism must differ in a fundamental way from that discussed in this paper.²⁶ The A_1 values for methyl azide and ethyl azide,²⁷ 3.02×10^{15} and 2.00×10^{14} ,

²⁶ It may be of interest in this connection to note that in many of these cases, for example, the decompositions of nitryl chloride (Schumacher and Sprenger, *Zeits. f. physik. Chemie* **B12**, 115 (1931)) and dimethyltriazenes (Ramsperger and Leermakers, *J. Am. Chem. Soc.* **53**, 2061 (1931)) and the isomerization of dimethyl maleate (Nelles and Kistiakowsky, *J. Am. Chem. Soc.* **54**, 2208 (1932)), the effective number of degrees of freedom calculated on the basis of the Rice-Ramsperger-Kassel theory is smaller than expected from the structure of the molecule.

²⁷ Leermakers, *J. Am. Chem. Soc.* **55**, 2719, 3098 (1933).

are perhaps a little high, but the reaction products are so complex as to make it difficult to speculate as to the initial process and there may, indeed, be short chains involved. The relative A_1 values and the relative activation energies (43,500 and 39,740, respectively) suggest that possibly something similar to what we have postulated for the azo-compounds is involved. The A_1 value for the decomposition of paracetaldehyde²⁸ 1.3×10^{15} may be rather high but this reaction has rather peculiar characteristics^{28b} and may be of a complex nature. The values for parabutyraldehydes²⁹ are also a little high. We should also remark that the reverse reactions to the bimolecular associations considered in Part I must have rather large A_1 values in view of the small number of rotations apparently frozen out when the associations occur.

Other reactions might be discussed, but our aim has not been to exhaust the possibilities but to give a sufficient discussion to show that there are a considerable number of unimolecular reactions which may be explained on the basis of the hypothesis of "exact orientation" and to illustrate the value of the point of view which has been developed in previous articles. It will be evident that no philosopher's stone has been discovered which will explain all reactions but we believe that we now have at hand a valuable means for classifying reactions and guiding our speculations about them.

We wish to acknowledge our indebtedness to Professor Henry Eyring for helpful discussions with one of us (H. G.).

²⁸ (a) Coffin, *Can. J. Research* **7**, 75 (1932); (b) Coffin and Geddes, *ibid.* **11**, 180 (1934).

²⁹ Coffin, *Can. J. Research* **9**, 603 (1933).