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The Activation Energy of Unimolecular Reactions. II

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The modifications in our earlier paper by the above title, necessitated by recent work on the absolute rate of chemical reactions, are considered, and it is shown that the assumption that the fragments resulting from a unimolecular decomposition must be "exactly oriented" (in the sense of the preceding article) in order to be able to recombine is equivalent to the assumptions made by Kassel in his quantum theory of unimolecular reactions. The relation between the observed activation energy and the energy necessary to break the bond is discussed.

SOME revisions in our first article with the above title² are indicated by the results of the preceding paper on the absolute rates of chemical reactions. The conclusions in the former were based largely on the assumption that the reverse of a unimolecular reaction takes place without any energy of activation, provided this reverse reaction involves the recombination of free radicals. Now this assumption is essentially equivalent to the assumption that all energy states of the recombining radicals are equally available for reaction, and this is not consistent with the hypothesis of exact orientation, discussed in the preceding article, but is rather a hypothesis of no orientation. We are now, however, in a better position to find the relation between the energy of activation of a reaction and the energy necessary to break the bond. It is the purpose of this paper to discuss how this may be done and to consider again the nature and validity of the various quantum theories of unimolecular reaction.

It is usual to write the rate of a unimolecular reaction in the form

$$K = Ae^{-\epsilon_a/kT}, \quad (1)$$

where ϵ_a is the energy of activation per molecule, k is Boltzmann's constant, T the absolute temperature and A is a "constant." The usual method of obtaining ϵ_a is to plot $\ln K$ against $1/T$ and draw the best straight line through the experimental points. Since Tolman³ has shown that $k d \ln K/d(1/T)$ is equal to the difference

between the average energy of those molecules which react and the average energy of all the molecules, it is obvious that the experimental value of ϵ_a is equal to this difference of average energies, say for a temperature in the middle of the experimental range; theoretically we define it this way for all temperatures. But now from (1)

$$d \ln K/d(1/T) = d \ln A/d(1/T) - \epsilon_a/k - (1/kT)d\epsilon_a/d(1/T). \quad (2)$$

Since, by Tolman's relationship,

$$d \ln K/d(1/T) = -\epsilon_a/k, \quad (3)$$

we see that

$$k d \ln A/dT = (1/T)d\epsilon_a/dT, \quad (4)$$

the relation between ϵ_a and $k \ln A$ being thus just exactly like that between the average energy and the entropy of an ordinary thermodynamic system. This relationship has indeed been stated in work of La Mer.⁴ It must be noted, however, that A is not dimensionless, as would be expected if $\ln A$ were a true entropy term but it has the dimensions of reciprocal seconds.

In the case of a unimolecular reaction in which the reverse reaction requires exact orientation $A = ekT/hE_t'$, where E_t' is the antilogarithm of the entropy factor for the oscillation along the direction of the bond which breaks on reaction. The factor e which is introduced to take care of the effect of the bond which breaks is derived on the assumption that the temperature is high and at low temperatures should be replaced by a quantity, say e' , which is dependent on the temperature. We thus get, integrating Eq. (4)

¹ Parker Traveling Fellow of Harvard University.

² Gershinowitz and O. K. Rice, *J. Chem. Phys.* 2, 273 (1934).

³ Tolman, *Statistical Mechanics* (Chemical Catalog Co., 1927), pp. 261-2. See also footnote 11 of Ref. 2.

⁴ La Mer, *J. Chem. Phys.* 1, 289 (1933).

$$\epsilon_a = \epsilon_{a,0} - k \int_0^\infty T(d \ln E_1'/dT) dT \\ + k \int_0^\infty T(d \ln (e' kT/h)/dT) dT, \quad (5)$$

where $\epsilon_{a,0}$ is the activation energy at $^\circ\text{K}$. Now $k \int_0^\infty T(d \ln E_1'/dT)/dT$ is simply the average energy above the zero point of the oscillator involved in E_1' , while the last term of (5) is seen, from its origin, to be the average energy of a stream of particles flowing out over a potential energy hill, above the minimum energy necessary to get over the hill.⁵ For high temperatures, and for all practical purposes for all temperatures this may be set equal to kT . This is, in fact, the value obtained by direct integration, setting e' constant, which would naturally be assumed to give the correct value, as the variation in e' must take place at a very low temperature. Thus the average energy of all the molecules which decompose minus the minimum energy $\epsilon_{a,0}$ necessary for decomposition at $^\circ\text{K}$, which is $\epsilon_a - \epsilon_{a,0} + \bar{\epsilon}$, is equal to the average energy of all the degrees of freedom of the molecule which decomposes except that degree of freedom connected with the bond which breaks, plus kT . Now this is exactly the case in Kassel's quantum theory of unimolecular reactions.⁶ But the calculation of the rate constant as a function of pressure in Kassel's quantum theory, as well as in the original Rice-Ramsperger-Kassel theory of unimolecular reactions, depends not alone on the average energy of the molecules which react but on the energy *distribution*. However, by a theorem due to Ehrenfest,⁷ if an average energy is known as a function of temperatures for all temperatures the corresponding energy distribution is exactly determined. Hence we may say that Kassel's quantum theory is entirely equivalent to the assumption that exact orientation is required for the reverse reaction at all temperatures. This is, indeed, a fairly obvious result.

Since the distribution of energy of the reacting molecules must be the same for any reaction and its reverse, it is seen that on recombination those degrees of freedom of the fragments which have to be frozen out on association will correspond, as far as their energy

distribution (of energy above the zero point energy) is concerned, with the vibrational degrees of freedom which they form. It is natural to suppose that some energy of activation will be required in order to supply the zero point energy, but this cannot be proved definitely, for some of this zero point energy may be furnished by redistribution of energy from the bond which is formed.⁸ If this happens the energy of activation of the unimolecular reaction will be correspondingly lowered and at absolute zero the energy of activation will be less than it would be were there no zero point energy. (This energy of activation without zero point energy at 0°K we shall call \mathfrak{E}_a for the unimolecular reaction and the corresponding quantity for the association reaction we shall call \mathfrak{E}_a' . The energy of breaking of the bond, \mathfrak{E} , is then equal to $\mathfrak{E}_a - \mathfrak{E}_a'$.) On the other hand, if the association does require an energy of activation to provide the excess zero point energy, then the energy of activation at absolute zero would be practically unchanged (changed only by the amount of the zero point energy of the one bond which breaks) if the zero point energy could be wiped out, and we could write, approximately,

$$\mathfrak{E}_a = \epsilon_{a,0}. \quad (6)$$

More generally, if we let $\epsilon'_{a,0}$ be the energy of activation of the association reaction at absolute zero and ΔE_0 the energy of dissociation at absolute zero, we have, as in our former paper,

$$\epsilon_{a,0} = \epsilon'_{a,0} + \Delta E_0 \quad (7)$$

and the relation between ΔE_0 , \mathfrak{E} , and the change in zero point energy on dissociation, $\Delta \epsilon^0$, namely,

$$\Delta E_0 = \mathfrak{E} + \Delta \epsilon^0, \quad (8)$$

gives us finally

$$\mathfrak{E} = \epsilon_{a,0} - \epsilon'_{a,0} - \Delta \epsilon^0. \quad (9)$$

The case in which $\epsilon'_{a,0} = \mathfrak{E}_a'$, and accordingly

$$\mathfrak{E}_a = \epsilon_{a,0} - \Delta \epsilon^0 \quad (10)$$

represents either the case of no orientation, or the case discussed above, in which the extra

⁵ See O. K. Rice and Gershinowitz, J. Chem. Phys. 2, 857 (1934).

⁶ Kassel, J. Phys. Chem. 32, 1065 (1928).

⁷ Ehrenfest, Ann. d. Physik 36, 111 (1911).

⁸ Essentially this assumes the rate is not determined by the entropy of a "normal" (see preceding article, §1) activation complex, for at the top of the saddle point no energy is available from the bond to be formed.

zero point is supplied from the energy of the bond formed. The case of no orientation we have discussed in detail in our former paper.² In general, unless the process of activation involves some special mechanism such as we assumed in the preceding paper in the case of the decomposition of azomethane, we may assume that \mathfrak{E}_a lies between the values given by (6) and (10), and all present indications are that these will be rather close together, since $\Delta\epsilon_0$ will be of the order of the zero point energy of only a few vibrations (those changed to translations or rotations in the decomposition) most of which are of the bending type. In the case of exact orientation $\epsilon_{a,0}$ may be evaluated from the observed ϵ_a by Eq. (5). The first integral on the right of (5) is less than kT , the other is equal to kT . In this case, therefore, $\epsilon_{a,0}$ may be taken for all practical purposes to be equal to ϵ_a , and $\epsilon_{a,0}$ is a fair measure of \mathfrak{E}_a which is really the fundamental quantity.

If the process of activation does involve a special mechanism such as assumed in the preceding paper for the decomposition of azomethane, then no direct relation exists between the energy of activation and the energy necessary to break the bond.

If we consider the reaction from the point of view of an activation complex, we may say that Kassel's quantum theory of unimolecular reaction is equivalent to the assumption that the frequencies of the activation complex are the same as those of the molecule which is decomposing; the quantum theory of Rice,⁹ on the other hand, corresponds to a general lowering of frequencies in the activation complex. The evidence now at hand favors Kassel's hypothesis as the basis of an approximate method for calculating the rate of a unimolecular reaction as a function of pressure.

⁹ O. K. Rice, Proc. Nat. Acad. Sci. **14**, 114 (1928).

The Absolute Rate of Reactions in Condensed Phases

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The theory of absolute reaction rates is developed for condensed phases. The equation for the rate of a reaction of any order in any phase where the slow process is the passage over an energy barrier consists of the product of a transmission coefficient κ , a frequency kT/h , an equilibrium constant between an activated complex and the reactants and an activity coefficient factor. Previous theories of reaction rates such as Brönsted's, the collision theory of Mc C. Lewis, etc., are seen to be special cases of the general theory. A variety of examples are considered.

IN a previous paper one of us¹ outlined the theory of the absolute rate of reactions in terms of the activated complex and the probability of its formation from the reacting substances. Here we propose to consider in greater detail the properties of the activated complex and, by application of the equation already derived, to show how the rates of reaction in solution and at interfaces may be calculated. The relation of this treatment to certain empirical generalizations will be considered and the existence of numerous

anomalous reaction rates will be explained.

Reaction rates in solution have usually been considered as too complex to yield to any simple treatment and the work of Christiansen² and of Norrish and Smith³ seemed to show that rates in solution were abnormally slow. Moelwyn-Hughes⁴ from an examination of a large mass of data showed that for many reactions the rate was not far from that calculated on the simple kinetic

² Christiansen, Zeits. f. physik. Chemie **113**, 35 (1924).

³ Norrish and Smith, J. Chem. Soc., 129 (1928).

⁴ Moelwyn-Hughes, *Kinetics of Reactions in Solution*, Oxford Univ. Press.

¹ Eyring, J. Chem. Phys. **3**, 107 (1935).