The Absolute Rate of a Chemical Reaction: The Formal Thermodynamic Treatment

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The Absolute Rate of a Chemical Reaction: The Formal Thermodynamic Treatment

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(Received July 20, 1936)

In order to assign a definite value to the entropy of activation, it is necessary to make definite assumptions as to the topography of the energy surface traversed by the reacting system. When this is done, the entropy of activation becomes the difference between the entropy of the average molecule and the entropy of the activated complex at the steady state concentration required for unit rate of reaction. The racemization of diphenyl derivatives is considered as a special case of unimolecular reaction where $h\nu \ll kT$.

SOME years ago the author published a discussion of the relation between thermodynamics and the absolute rate of a gaseous chemical reaction.[1] Since then the subject has been discussed by Polanyi, Eyring, Rice, and collaborators in great detail.[2] Most of these treatments have used the methods of statistical mechanics. They have gone beyond the simple kinetic theory of collisions between molecules in that they have introduced assumptions as to the topography of energy barriers which have yielded more specific results. These treatments are certainly adequate, and may be criticized only as to style of presentation. The treatments are perhaps unavoidably rather difficult to follow. On the other hand, the final results may appear too simple, since complicated functions are concealed in simple symbols.

The author[1] has stated that he felt that the thermodynamic approach was at once more simple and more general, and wishes to point out some conclusions from this method by way of clarification and comment. In his original treatment, he discussed the Arrhenius equation

$$k = A e^{-Q/RT} \qquad (1)$$

and pointed out that the constant A could be identified formally with an entropy of activation ΔS, just as Q was the heat of activation. He discussed the case of a unimolecular dissociation. It followed from his treatment that the molecule which was on the point of dissociation (the "activated complex") could be assigned formally an entropy in the significant degree of freedom of kT/h. This entropy could not be given any real significance, however, without further assumptions as to the interatomic forces which lie entirely outside of thermodynamics.

In 1923 the author[3] had made the assumption that a unimolecular dissociation took place by the acquirement of a critical energy in a certain significant degree of freedom, and that when this energy was acquired, the molecule would dissociate at the end of the vibration. This assumption has been generalized by Polanyi and Eyring in the postulates that the crest of the energy barrier to be traversed is nearly flat and that the chance of reflection at the barrier is small.

The first of these postulates is probably a good approximation except in the case of predissociations. The second is not likely to lead to serious error, since the reflection coefficient will probably not be greater than one-half. A value of one-half may be anticipated in case the energy barrier has a basin, as has been calculated by Eyring. The existence of this basin is in accord with the picture that was in the author's mind when he wrote the former paper, since he supposed the activated complex to have a degree of stability, and equal probability of a transformation in either direction.

The procedure is then very simple. From the rate of disappearance of the activated molecules, one calculates the steady state concentration of these molecules. At unit rate of reaction, the entropy of activation is then the difference between the entropy of the activated molecules at their steady state concentration and the entropy of all other molecules at unit concentra-

[1] W. H. Rodebush, J. Chem. Phys. **1**, 440 (1933).
[2] H. Eyring, J. Chem. Phys. **3**, 107 (1935); Evans and M. Polanyi, Trans. Faraday Soc. **21**, 875 (1935); O. K. Rice and H. Gershinowitz, J. Chem. Phys. **2**, 857 (1934); see also V. K. La Mer, J. Chem. Phys. **1**, 289 (1933).
[3] W. H. Rodebush, J. Am. Chem. Soc. **45**, 606 (1923).

tion. This entropy difference involves one degree of freedom only. The heat of activation is known from other data, and the rate constant is thus completely determined.

Let us consider as an example the dissociation of the diatomic molecule which was discussed in the original article.

$$A_2 = 2A. \qquad (2)$$

In the familiar potential energy diagram for a diatomic molecule, a point moving on this curve represents the internuclear distance and the molecule may be said to be completely dissociated when this point lies on the flat part of the curve. The number of activated molecules is the number having energy in excess of the dissociation energy. The rate of dissociation R is given by the equation

$$R = k_1 n = c\bar{v}. \qquad (3)$$

k_1 is the rate constant, and n the total concentration of molecules. On the other hand, c is the concentration of activated molecules whose internuclear distances lie within a unit interval $r_0 - 1 < r < r_0$, where r_0 is the distance for complete dissociation and $\bar{v}$ is the rate at which the atoms of the molecule move apart. If we make use of the graphical representation referred to above, c is the *linear concentration* of points on the flat crest of the energy curve and $\bar{v}$ is the rate at which these points traverse this curve. A simple application of kinetic theory shows that

$$\bar{v} = (kT/2\pi\mu)^{\frac{1}{2}}, \qquad (4)$$

where μ is the reduced mass of the molecule.

We may write from Eqs. (3) and (4)

$$\ln k_1 = \ln (c/n) + \ln (kT/2\pi\mu)^{\frac{1}{2}}. \qquad (5)$$

Since c and n are assumed to be in statistical equilibrium

$$\ln (c/n) = -(Q/RT) + (Sc/R) - (Sn/R). \qquad (6)$$

Here Q is the heat of activation, as usually defined, and Sc and Sn are the entropies of the activated and unactivated molecules at unit concentration. These entropies differ only in the vibrational degree of freedom, and we may, therefore, write, except for some constants which may be absorbed in the Q/RT term,

$$\ln k_1 = -(Q/RT) + \ln (2\pi\mu kT/h^2)^{\frac{1}{2}}$$
$$+ \ln (kT/2\pi\mu)^{\frac{1}{2}} - Sv, \qquad (7)$$

where Sv is the vibrational energy of the unactivated molecules. We may now remember that the entropy of the activated molecules is for unit concentration in (7), so that the term $\ln (1/c)$ does not appear in the second term of (7). At unit rate of reaction (one molecule per second), however, $1/c$ is equal to $(kT/2\pi\mu)^{\frac{1}{2}}$. Hence, if we combine the second and third terms of (7), we obtain $\ln (kT/h)$.

Except for the constant term mentioned above, this is $1/R$ times the entropy of the activated molecules at such a concentration as to bring about unit rate of reaction. Hence, we may write

$$\ln k_1 = -Q/RT + \Delta S^*/R, \qquad (8)$$

where ΔS^* is the entropy of activation as defined earlier in this paper.

If the vibrational quantum of the dissociating molecule is small so that $h\nu \ll kT$, then Sv/R of Eq. (7) becomes $\ln (kT/h\nu)$ and $\Delta S^*/R$ becomes equal to $\ln \nu$. Thus, Eq. (1) becomes

$$k_1 = \nu e^{-Q/RT}, \qquad (9)$$

as was pointed out by the author in his earlier publication. For this condition to obtain, however, at 298°, ν must not be greater than 10^{11}, which is, of course, an extremely low vibrational frequency, and which is likely to be associated only with a very small heat of dissociation.

If ν is larger, so that $h\nu$ is comparable or greater than kT, then the term Sv becomes so small as to be negligible, and Eq. (1) becomes

$$k_1 = (kT/h)e^{-Q/RT} \qquad (10)$$

as obtained by Eyring.

For the temperature interval in which unimolecular dissociations have been studied kT/h is of the order of magnitude 10^{13}, and one reaches the surprising conclusion that the constant of a unimolecular dissociation reaction cannot be greater than this figure. One might suppose, of course, that a fundamental error had been made in estimating the entropy of a fugitive complex where the quantization cannot be sharp because of the short life period. So far as experiment shows, however, there is no certain contradiction of the above figure. All cases in which the con-

stant A of Eq. (1) is larger than 10^{13} may be explained as due either to the possibility of dissociation in several different degrees of freedom, as is the case with nitrogen pentoxide, or simply to experimental error. When the results of an experimental determination of k_1 are plotted on a $\log k - 1/T$ diagram one sees what a small interval the results cover. The heat of activation may be determined as a satisfactory approximation from the slope of the curve, but the constant A is the intercept on the $\log k_1$ axis and requires a long extrapolation. A slight error in the slope produces a very large error in k_1.

The one example which has come to the author's attention where the frequency is small so that Eq. (9) holds is the racemization of diphenyl derivatives. This case also illustrates the point made by the author[4] that the heat of activation may be calculated from measurements at a single temperature.

The racemization of diphenyl derivatives has been studied by Adams and collaborators[5] in various solvents. It has been demonstrated in the case of nitrogen pentoxide that the reaction rate in inert solvents is not greatly different from that in the vapor phase, and we may assume that the same will be true for the racemization of diphenyl.

The racemization of an optically active compound is an example of a reversible first-order reaction for which the constant is given by the expression

$$k_1 = (1/2t) \ln (\alpha_0/\alpha).$$

This constant, in turn, is given by the Arrhenius relation (1).

The best data of Li and Adams appear to be upon 2-nitro-6-carboxy-2'-ethoxydiphenyl. From these data, we calculate

$$Qi = 21{,}150 \text{ cal.}, \quad A = 3.0 \times 10^{11}.$$

This calculation involves the usual difficulty of a calculation of heat of activation in that with the accuracy of the experimental results obtainable, there is an uncertainty of several hundred calories in the heat of activation. Thus, the rates of

racemization of the methoxy and propoxy derivatives show about the same temperature coefficients as the ethoxy derivatives, and all that the authors could state was that the heats of activation were the same for the three compounds within the limits of experimental error. This in spite of the fact that the absolute rates of racemization differed by several fold.

Now we are not so much interested in the absolute value of the heats of activation as the differences in different compounds. The heat of activation is presumably the work of turning the diphenyl rings relative to each other when in the plane position. The constant A is the frequency of vibration multiplied by an *a priori* factor which is probably not greatly different from unity. This vibration is a partial rotation of the rings relative to each other about the common axis of symmetry. The value obtained for A, 3×10^{11}, appears to be the order of magnitude to be expected for this sort of vibration. This frequency will vary inversely as the square root of the frequency of the moment of inertia and directly as the square root of the constraint. The constraint is due to the interference of the substituted group, and may be expected to increase with an increase in the heat of activation. The replacement of methoxy by an ethoxy group would increase both the moment of inertia and the constraint, and leave the frequency almost unchanged. We shall, therefore, assume as a first approximation that the constant A is the same for all compounds and calculate the "relative" heats of activation. We obtain

Derivative	Heat of Activation
OCH_3	20,150
OC_2H_5	21,150
OC_3H_7	21,350

From the paper of Hanford and Adams, we obtain for the 4' substituted diphenyls the following values for the relative heats of activation.

Derivative	Heat of Activation
CH_3	19,350
Cl	19,900
Br	20,350

There can be little doubt that these figures give us the significant variations in the heats of activation in the different derivatives.

[4] W. H. Rodebush, J. Chem. Phys. **3**, 242 (1935).
[5] C. C. Li and Roger Adams, J. Am. Chem. Soc. **57**, 1565 (1935); W. E. Hanford and Roger Adams, J. Am. Chem. Soc. **57**, 1592 (1935).