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Unimolecular Dissociations and Free Radical Recombination Reactions*

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The steric and pressure effects associated with the recombination of free radicals both depend on the nature of the activated complex, and are therefore intimately related. From a consideration of the reverse process of unimolecular dissociation, some equations are derived for these properties using an extension of earlier transition state and quasi-unimolecular theories. The present formalism differs from previous formulations of the latter in a number of ways, particularly in the expression used for the density of quantum states of the high energy molecules. Subsequent applications of the theory tentatively suggest that essentially all vibrational degrees of freedom of these molecules can contribute their energy to the vibrationally excited molecules. Consequently, vibrational anharmonicity would appear to be an important factor in intramolecular energy transfer. The present paper is an extension of a previously developed theory for the recombination of methyl radicals and iodine atoms.

INTRODUCTION

RECENTLY,[1] a correlation of the steric effects and pressure dependence of reactions involving the recombination of free radicals was suggested. Such processes are naturally the reverse of those unimolecular dissociations which produce free radicals, and the general theoretical approach was an elaboration of earlier quasi-unimolecular and transition state theories.

The unimolecular reaction rate constant falls off with decreasing pressure when the lifetime of the decomposing (so-called "active") molecules becomes comparable to the time between successive deactivating collisions. The lifetime of these active molecules is a function of the extent of intramolecular energy transfer and also of the nature of the activated complex. Since the steric effects associated with the reverse process of radical recombination are solely dependent on the properties of the same activated complex, there is a close relation between these two effects.

Equations correlating these properties were developed specifically for the decomposition of methyl iodide. The approach was such that several specific assumptions were introduced in the early stages of the derivation, thus necessitating an individual treatment for each different type of molecule and for each specific assumption. A much more general derivation is given in the present paper. Application of the final equations to the available experimental data will be reserved for a later paper.

As before, the unimolecular dissociation is considered initially and then the bimolecular rate constant is estimated with the aid of a calculated equilibrium constant. However, the expressions for the unimolecular rate constant are quite general and could therefore be applied to other unimolecular processes.

UNIMOLECULAR RATE CONSTANT

We consider the following reaction sequence,

$$A+M \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A^*+M, \tag{1}$$

$$A^* \overset{k_a}{=} A^+, \tag{2}$$

$$A^+ \overset{k_3}{=} \text{products}. \tag{3}$$

A^* and A^+ denote the active molecule and activated complex respectively, while M is any third body capable of deactivating A^*. Steady-state treatment for A^* and A^+ leads to a relation between the unimolecular rate constant, k_{uni}, and the pressure, p.

$$k_{uni}=k_a(k_1/k_2)/(1+k_a/k_2p). \tag{4}$$

These k's, which are functions of the energy of the

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[1] R. A. Marcus and O. K. Rice, J. Phys. and Colloid Chem. 55, 894 (1951).

initial A^* molecule, are first evaluated for a small energy range. k_{uni} is then obtained by integration over all possible energies so that (4) is replaced by

$$k_{uni}=\int\frac{k_a d(k_1/k_2)}{1+k_a/k_2 p}. \tag{5}$$

In Eq. (5) $d(k_1/k_2)$ is the fraction of active molecules having energy in a given energy range. Evaluation of the integrand of (5) will involve a calculation of the number of ways of distributing energy among the various degrees of freedom of the active molecule and of the activated complex. However, the vibrational zero-point energy of A^* and A^+, and also the potential energy of the newly broken bond of the activated complex cannot be so distributed. The remaining energy, which we shall term "nonfixed energy," of the active molecule and of its corresponding activated complex will be denoted by E^* and E^+, respectively. We set $E^*-E^+=E_a$ where the constant E_a is approximately equal to the bond strength of the breaking bond.

The degrees of freedom of the active molecule may be classified with respect to their role in intramolecular energy transfer as "active," "adiabatic," or "inactive." The "active" degrees of freedom are defined as those which can contribute their energy to the breaking bond without restrictions. On the other hand the "adiabatic" ones are assumed to remain in the same quantum state during the course of decomposition of the molecule, and so contribute relatively little energy to the breaking bond. The transfer of energy between the "inactive" degrees of freedom and this bond is assumed to occur with sufficient rapidity only when the molecule has become essentially an activated complex. Since the energy of the latter degrees of freedom is therefore not available to the breaking bond, A^* in Eq. (1) has a nonfixed energy E^* such that $E^*\geq E_a+E_i$, where E_i is the nonfixed energy of the "inactive" degrees of freedom.

Translation of the molecule as a whole makes no contribution to the reaction rate and will not be included in the following. Conservation of angular momentum, which presents some barrier to intramolecular molecular energy transfer, will be treated approximately as follows: The initial molecule may generally be regarded as roughly ellipsoidal in shape and the formation of the corresponding activated complex will frequently correspond to a stretching of the ellipsoid along its major axis (e.g., the rupture of a C—C bond in ethane). On the average, the largest contribution of the angular momentum will come from those two rotational degrees of freedom possessing the larger moments of inertia. This statement applies both to the active molecule and to its activated complex. Conservation of angular momentum thus insures that throughout the course of decomposition the molecule will remain in approximately the same quantum state with respect to these degrees of freedom. Thus these two rotations contribute only the centrifugal energy $J(J+1)h^2/8\pi^2\mu r^2$ to the breaking bond, with J approximately constant. When averaged[2] over all J's the net contribution of these rotations to the reaction rate is a factor P_1^+/P_1, the ratio of the partition functions of these rotations for the activated complex and active molecule, respectively. When, because of additional restrictions, other degrees of freedom (e.g., the remaining rotation) also remain in essentially the same quantum state during the course of reaction, then P_1^+/P_1 becomes the product ratio of the partition functions of all these "adiabatic" degrees of freedom.

In the following, E^*, E^+, and E_i will include neither the energy of translation of the molecule as a whole nor the energy of those degrees of freedom involved in P_1^+/P_1. The results will then be corrected by this factor.

$d(k_1/k_2)$ is equal to the fraction of molecules having energy in the range E^*, E^*+dE^*, where $E^*\geq E_a+E_i$. Let $N^*(E^*-E_i)$ denote the number of energy states per unit energy of the "active" degrees of freedom, and $D(E_i)$, the degeneracy of the inactive ones when they contain the energies (E^*-E_i) and E_i, respectively. We then have

$$d(k_1/k_2)=\frac{\sum_{E_i=0}^{E^*-E_a} N^*(E^*-E_i)D(E_i)\exp(-E^*/kT)dE^*}{\sum_{E_i=0}^{\infty}\int_{E^*=E_i}^{\infty} D(E_i)N^*(E^*-E_i)\exp(-E^*/kT)dE^*}. \tag{6}$$

More exactly $N^*(E^*-E_i)$ should be the number of possible energy states of an active molecule whose energy is (E^*-E_i) and correspondingly the integral in (6) should be a sum. The present treatment anticipates a subsequent semiclassical approximation for $N^*(E^*-E_i)$. Introduction of a new variable $x=(E^*-E_i)$ into the denominator factors the latter into a product which is readily seen to be the product of the partition functions of the active and inactive parts and which will be denoted by the symbol P_2.

k_a may be estimated in the following way: The expressions for $dA^*/dt=0=dA^+/dt$ at complete equilibrium show that the ratio of the equilibrium concentrations of A^+ and A^* is equal to $2k_a/k_3$ if the rate constant for (3) is assumed[3] equal to that for the reverse of (2). The ratio of the equilibrium concentrations of A^+ and A^* molecules of the same energy equals the relative number of quantum states per unit energy of

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[2] See O. K. Rice and H. Gershinowitz, J. Chem. Phys. 2, 853 (1934).

[3] This assumption is consistent with the usual assumption of Eyring that motion along the reaction coordinate is a simple translation, so that in our model the velocity is equal in magnitude for the above reactions. We note further that our A^+ refers to those activated complexes which form radicals, rather than the sum of these plus those proceeding in the opposite direction along the reaction coordinate (see reference 1).

A^+ and A^*, respectively. The total number of quantum states per unit energy available to active molecules whose nonfixed energy is E^*, is[4] $N_o^*(E^*)$, where

$$N_o^*(E^*)=\sum_{E_i=0}^{E^*-E_a} N^*(E^*-E_i)D(E_i). \tag{7}$$

One of the degrees of freedom of A^+ is assumed to be a simple translational motion along the reaction coordinate. Let $N_1(x)$ and $N_2(E^+-x)$ denote the number of quantum states per unit energy of this translational motion and of the remaining degrees of freedom of A^+, respectively, when their respective energies are x and (E^+-x). Then the number of quantum states per unit energy of an activated complex which contains a nonfixed energy E^+ is

$$N^+(E^+)=\int_{x=0}^{E^+} N_2(E^+-x)N_1(x)dx. \tag{8}$$

Finally, $2k_a/k_3=N^+(E^+)/N_o^*(E^*)$, where k_3 corresponds to the average value of x. However, the value of k_3 corresponding to a given value of x is equal to $(2x/m)^{\frac{1}{2}}/b$ where m is the reduced mass and b, the extension of the activated complex in coordinate space. Consequently, we may write for k_a,

$$2k_aN_o^*(E^*)=\int_{x=0}^{E^+} N_2(E^+-x)N_1(x)[(2x/m)^{\frac{1}{2}}/b]dx. \tag{9}$$

From the usual expression for the energy levels of a particle in a box, $x=n^2h^2/8b^2m$, we have $N_1(x)(=dn/dx)=2b/h(2x/m)^{\frac{1}{2}}$. On introducing a new variable $y=(E^+-x)$ into (9), the value of k_a, when corrected by the factor P_1^+/P_1, becomes

$$k_a=P_1^+\int_{y=0}^{E^+} N_2(y)dy/P_1h\sum_{E_i=0}^{E^+} N^*(E^*-E_i)D(E_i). \tag{10}$$

From (5), (6), and (10) we find after some cancellation,

$$k_{uni}=\frac{P_1^+\exp(-E_a/kT)}{P_1P_2h}\times\int_{E^+=0}^{\infty}\frac{\int_0^{E^+} N_2(y)dy\exp(-E^+/kT)dE^+}{1+k_a/k_2p}, \tag{11}$$

where k_a is given by (10).[5]

We next derive an expression for $N_2(y)$, the number of quantum states per unit energy of the degrees of freedom of A^+ (not involved in P_1^+ and excluding the translational motion along the reaction co-ordinate) when their energy is y. These degrees of freedom will be vibrational and rotational in nature. We shall assume that the rotations can be treated as independent of each other and of those rotations involved in P_1^+ so that their energy is approximately equal to $\sum_{i=1}^{p} J_i^2h^2/8\pi^2I_i$, where p is the number of rotations while J_i and I_i are the quantum number and moment of inertia of the i'th degree of freedom, respectively. The number of quantum states of the i'th rotation is 2 or $2J_i$ according as it is singly or doubly degenerate. In the former case the factor of two arises since rotation in a plane may occur in 2 (opposite) directions. We shall therefore write this number as $2(J_i)^{d_i-1}$, where d_i is the degeneracy of the i'th rotation ($d_i=1, 2$).[6]

Of the energy y consider first those quantum states of A^+ for which the vibrational energy is E_v and let the degeneracy of the vibrational states be $P(E_v)$. The number of rotational states per unit energy is equal to $(dy)^{-1}\int\cdots\int\prod_i 2(J_i)^{d_i-1}dJ_i$ where the integration is over that region of J_i space where $\sum_i J_i^2h^2/8\pi^2I_i$ lies between $(y-E_v)$ and $(y+dy-E_v)$. The number of rotational-vibrational quantum states per unit energy is simply this multiplied by $P(E_v)$. To obtain $N_2(y)$ we must sum over all vibrational energy levels, E_v, such that $E_v\leq y$. That is,

$$N_2(y)=\sum_{E_v\leq y} P(E_v)(dy)^{-1}\int\cdots\int\prod_i 2(J_i)^{d_i-1}dJ_i. \tag{12}$$

Integration of (12) with respect to all J_i leads to

$$N_2(y)=\sum P(E_v)[\Gamma(r/2)]^{-1}\times(8\pi^2/h^2)^{r/2}(y-E_v)^{r/2-1}\prod_i I_i^{d_i/2}\Gamma(d_i/2), \tag{13}$$

where

$$r=\sum_{i=1}^{p} d_i$$

and Γ is the gamma-function. That is, r is the total number of these rotational degrees of freedom, regarding a d_i-fold degenerate rotation as d_i rotational degrees of freedom.

The product of the partition functions of these de-

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[4] The upper limit of the summation arises from the condition that an active molecule has $E^*-E_a\geq E_i$.

[5] We note that at high pressures, the second term in the denominator of (11) is negligible and (11) may be readily integrated by reversing the order of integration so that the limits for E^+ and y become y to ∞ and 0 to ∞, respectively. Integration with respect to E^+ then yields $kT\int_0^\infty N_2(y)\exp(-y/kT)dy=kTP_2^+$ say, which is simply kT multiplied by the partition function of those degrees of freedom of A^+ not involved in P_1^+ and also excluding the internal translation along the reaction co-ordinate. Thus at high pressures, $k_{uni}=(kT/h)\exp(-E_a/kT)P_1^+P_2^+/P_1P_2$, an expression derived by Eyring (J. Chem. Phys. 3, 107 (1935)) and Rice and Gershinowitz. (See reference 2.) However, their approach cannot be used as such for the derivation of the pressure effect.

[6] We observe that it is possible to have several doubly degenerate rotations in an activated complex, although just one in a stable molecule. If, for example, the methyl radicals rotate freely in the activated complex corresponding to the dissociation of ethane, there are three doubly degenerate rotations, one per methyl radical and one for the rotation of the complex as a whole.

grees of freedom is given by[7]

$$P_R^{+}=\prod_i\int_0^{\infty}2(J_i)^{d_i-1}\exp(-J_i^2h^2/8\pi^2I_ikT)dJ_i$$
$$=(8\pi^2kT/h^2)^{r/2}\prod_i\Gamma(d_i/2)I_i^{d_i/2}. \tag{14}$$

Therefore (13) becomes,

$$N_2(y)=\sum_{E_v\leq y}P(E_v)\left(\frac{y-E_v}{kT}\right)^{r/2-1}P_R^{+}/kT\Gamma(r/2). \tag{15}$$

To calculate $\int_0^{E^+}N_2(y)dy$ from (15), the order of summation and integration is interchanged so that the limits for E_v and for y become $\leq E^+$ and E_v to E^+, respectively. Integration over y then leads to

$$\int_0^{E^+}N_2(y)=\sum_{E_v\leq E^+}P(E_v)\left(\frac{E^+-E_v}{kT}\right)^{r/2}\times P_R^{+}/\Gamma(1+r/2). \tag{16}$$

From (10) and (16) we then obtain:

$$k_a=\frac{P_1^{+}P_R^{+}\sum_{E_v\leq E^+}\left(\frac{E^+-E_v}{kT}\right)^{r/2}P(E_v)}{P_1\Gamma(1+r/2)\sum_{E_i\leq E^+}hN^*(E_a+E^+-E_i)D(E_i)}. \tag{17}$$

From (11) and (16) we also find:

$$k_{uni}=\frac{P_1^{+}P_R^{+}\exp(-E_a/kT)}{P_1P_2h\Gamma(1+r/2)}\times\int_0^{\infty}\frac{\sum_{E_v\leq E^+}P(E_v)\left(\frac{E^+-E_v}{kT}\right)^{r/2}\exp(-E^+/kT)dE^+}{1+k_a/k_2p}, \tag{18}$$

where k_a is given by (17)

Equation (18) may be further simplified by two approximations. In most of our applications of (18), the vibrational frequencies of A^+ will be assumed to be rather high so that the majority of such activated complexes are produced in their ground vibrational states. Since E_v is the nonfixed vibrational energy, $E_v=0$ and $P(E_v)=1$ for such states. Thus the sum $\sum_{E_v\leq E^+}(E^+-E_v)^{r/2}P(E_v)$ is approximately equal to its first term, $(E^+)^{r/2}$. At very low pressures this approximation results in no error, for unity may be neglected in the denominator of (18) so that this sum cancels out. The error would seem to be largest at $p=\infty$. On integration at $p=\infty$, it is found that k_{uni} is in error by a factor equal to the vibrational partition function of A^+, P_v^{+} say. Although P_v^{+} generally will be closely equal to unity, the foregoing sum will be replaced by $(E^+)^{r/2}P_v^{+}$ as a better approximation.

In the summation over E_i in Eq. (17) $N^*(E_a+E^+-E_i)=N^*(E_a)$ to a good approximation; for E_a, which is essentially the bond strength, is of the order of 50 to 100 kcal mole^{-1}, while (E^+-E_i) is less than several kcal mole^{-1} on the average.

Introducing these approximations into (17) and (18), and multiplying (18) by P_T^{+}/P_T, the ratio of the partition functions for the three external translational degrees of freedom $(P_T^{+}=P_T)$, the following expression for k_{uni} is obtained,

$$k_{uni}=\frac{kT}{h}\frac{P^+}{P}\frac{\exp(-E_a/kT)}{\Gamma(1+r/2)}\int_{w=0}^{\infty}\frac{w^{r/2}e^{-w}dw}{1+aw^{r/2}}, \tag{19}$$

where we have set $E^+/kT=w$. $P^+(=P_1^{+}P_R^{+}P_v^{+}P_T^{+})$ is the partition function for all degrees of freedom of A^+ (excluding the internal translational motion along the reaction coordinate) and $P(=P_1P_2P_T)$, the partition function for A. These are calculated by conventional methods. a is given by (20).

$$a^{-1}=P_1hk_2p\Gamma(1+r/2)N^*(E_a)\sum_{E_i=0}^{wkT}D(E_i)/P_3^{+}, \tag{20}$$

where $P_3^{+}=P_1^{+}P_R^{+}P_v^{+}$. The sum in (20) is naturally replaced by integration for those inactive degrees of freedom which can be treated classically. k_2 is simply the kinetic theory collision frequency which, if deactivation does not occur at every collision, should be multiplied by some inefficiency factor.

To complete the derivation, an expression for $N^*(E_a)$ in (20) is needed. $N^*(u)$ is the number of quantum states per unit energy of the "active" part of the active molecule when the energy of that part is u. The majority of these degrees of freedom are vibrational in nature and should therefore, in general, be treated as quantized. A classical treatment of such degrees of freedom is much simpler than the exceedingly laborious quantum treatments but generally gives a gross overestimate of $N^*(u)$. For such quantized vibrations we have found that a good approximation to the average number of vibrational quantum states per unit energy, $N_v^*(u)$ say, is given by the following semiclassical expression[1] when u is large (which it is, for active molecules).

$$N_v^*(u)=(u+E_o)^{s-1}/\Gamma(s)\prod_{i=1}^{s}h\nu_i, \tag{21}$$

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[7] We note here that the present treatment of the rotational degrees of freedom of a molecule leads to the usual classical expression for the partition function of a symmetric top molecule having (or not having) free internal rotation. This provides some justification for our using a very simple expression for the rotational energy levels of a molecule. In the case of an asymmetric top, Eq. (14) leads to the correct classical expression for the partition function if the rotations associated with two moments of inertia, I_1 and I_2, are treated as one doubly degenerate rotation possessing a moment of inertia equal to $(I_1I_2)^{\frac{1}{2}}$.

where

$$E_s=\sum_{i=1}^{s} h\nu_i/2,$$

ν_i is the i'th vibrational frequency of A and s is the number of "active" vibrational modes.

If some rotational degrees of freedom (other than those involved in P_1) are active and if their number of quantum states per unit energy is $N_R^*(x)$ when their energy is x, then $N^*(u)$ is given by (22). Otherwise $N^*(u)$ is equal to $N_v^*(u)$.

$$N^*(u)=\int_{x=0}^{u} N_v^*(u-x)N_R^*(x)dx. \qquad (22)$$

The derivation of an expression for $N_R^*(x)$ is similar to that employed in the treatment of the rotational degrees of freedom involved in (15). Examination of this equation shows that

$$N_R^*(x)=P_a(x/kT)^{(t/2)-1}/kT\Gamma(t/2), \qquad (23)$$

where P_a is the partition function for the t active rotations of the active molecule.

The rotational degrees of freedom associated with $N_2(y)$ and $N_R^*(x)$ have been assumed to be unhindered. If some of these are in fact hindered, then the above treatment will be assumed to provide a reasonable approximation. However, for such degrees of freedom, the correct hindered rotational partition functions will be introduced into P_R^+ and P_a. We have found this procedure to provide a good approximation to some more complicated calculations for the dissociation of ethane to methyl radicals.

BIMOLECULAR RATE CONSTANT

The equilibrium constant for $A\rightleftharpoons$radicals is given by (24).

$$k_{uni}/k_{bi}=\exp(-\Delta H/kT)(P_{rad}/P)g, \qquad (24)$$

where ΔH is the heat of reaction, P_{rad}, the partition function for radicals, P, that for the molecule, A, and g is the electron spin-orbital degeneracy of the radicals. We have omitted the corresponding factor for A (and A^+) since these are generally in a singlet $\sum$ electronic state. From (19) and (24) we find for k_{bi}

$$k_{bi}=\frac{kT}{h}\,\frac{P^+\exp[(\Delta H-E_a)/kT]J(a)}{P_{rad}g}, \qquad (25)$$

where

$$J(a)=\frac{1}{\Gamma(1+r/2)}\int_{w=0}^{\infty}\frac{w^{r/2}e^{-w}dw}{1+aw^{r/2}}.$$

At sufficiently high pressures, $a=0$ and $J(a)=1$. Since there is presumably no potential energy barrier along the reaction co-ordinate, one might argue that the activation energy for the recombination process, $\Delta H-E_a$, should be zero. If there are no orientative restrictions on recombination so that the radicals rotate freely in the activated complex then (assuming no potential energy barrier) $\Delta H=E_a$. If, however, some orientation is necessary so that the activated complex has, in addition to the vibrational frequencies of the isolated radicals, several "bending frequencies," then the activation energy becomes equal to the sum of the zero point energies of these new vibrational modes, when they can be regarded as quantized. When the lifetime, t, of the activated complex is small, the energy levels become appreciably broadened by an amount $\sim h/t$, so that the activation energy is correspondingly less.

The relation between (25) and the simple collision theory expression for k_{bi} may readily be seen from the following approximate considerations. It is assumed that P^+ may be factored into $(8\pi^2Ikt/\sigma h^2)P_{rot}^+P_{vib}^+P_{trans}^+$, where the first factor is the rotational partition function associated with the two larger moments of inertia, I, of the approximately ellipsoidal activated complex and P_{rot}^+ is the partition function for the remaining rotations of the complex. The symmetry number, σ, equals 2 or 1 according as the radicals are, or are not, identical. We shall also factor P_{rad} into $P_{rot}P_{vib}P_{trans}$. If the masses of the radicals are m_a and m_b then the translational partition functions per unit volume are:

$$P_{trans}^+=[2\pi(m_a+m_b)kT]^{3/2}/h^3,$$

and

$$P_{trans}=[2\pi(m_am_b)^{1/2}kT]^3/h^6.$$

In addition, $I=\mu\sigma_{ab}^2$, where μ is $m_am_b/(m_a+m_b)$ and σ_{ab} is the distance between the centers of gravity of the radicals in the activated complex. With these expressions Eq. (25) becomes,

$$k_{bi}=(Z/g)(P_{rot}^+/P_{rot})(P_{vib}^+/P_{vib})J(a)\times\exp[(\Delta H-E_a)/kT], \qquad (26)$$

where Z is the kinetic theory collision number.

$$Z=\left[\left(\frac{8\pi^2kT}{\mu}\right)^{\frac{1}{2}}\frac{\sigma_{ab}^2}{\sigma}\right].$$

If the complex consists of freely rotating radicals then $P_{rot}^+=P_{rot}$, $P_{vib}^+=P_{vib}$ and consequently the steric factor is equal to $(1/g)$. If, however, a high degree of mutual orientation of the free radicals is necessary for the formation of an activated complex, then one might assume that the vibrational frequencies of the complex are the same as those of the molecule, A (except that a stretching vibration of A becomes an internal translation of A^+). With this assumption it still follows that $(P_{vib}^+/P_{vib})\cong 1$ for most reactions. Also, some of the partition functions in (P_{rot}^+/P_{rot}) will approximately cancel and the ratio reduces to a product of the partition functions, f_{rot} say, of those rotational degrees of freedom which are present in the isolated radicals but are "frozen out" when the activated complex is formed. The steric factor then becomes $(gf_{rot})^{-1}$ (see reference 2).

These extreme types of activated complexes were termed[1] "loose" and "rigid," respectively. The latter is also associated with a high pressure frequency factor of 10^{13} sec^{-1} for the corresponding unimolecular dissociation, since in Eq. (19) we have $P^{+}\cong P$ (and $kT/h\cong 10^{13}$ sec^{-1}) for this case. The corresponding factor for the loose complex is $\cong f_{\text{rot}}\times 10^{13}$ sec^{-1}.

While the true state of the complex would be expected to be intermediate between "loose" and "rigid," it should prove very interesting to see which of the above approximations gives a better explanation of the data. Although one could make some *a priori* calculations, based on potential energy curves, concerning the nature of the activated complex, such calculations should be regarded as highly tentative.

Another important problem is the role of the vibrational degrees of freedom in intramolecular energy transfer. From some applications of the present formalism to the experimental data, it seems quite possible that essentially all the vibrational modes of the molecule, A, are "active" degrees of freedom. Thus the variable, s, in Eq. (21) becomes equal to the number of such modes. It would appear from this that vibrational anharmonicity plays an important role in intramolecular energy transfer, and would have to be taken into account in more fundamental approaches to this problem.

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