Reprinted from THE JOURNAL OF CHEMICAL PHYSICS, Vol. 20, No. 3, 355–359, March, 1952
Printed in U. S. A.

Lifetimes of Active Molecules. II*

R. A. MARCUS†
University of North Carolina, Chapel Hill, North Carolina
(Received August 14, 1951)

Experimental data on the atomic cracking of propyl radicals and on the deuterization of methyl radicals are compared with some theoretical calculations. With the aid of some assumptions concerning intramolecular energy transfer in the dissociating molecules involved in these and other reactions and concerning the corresponding activated complexes, data on a number of free radical reactions are correlated.

INTRODUCTION

IN an earlier communication[1] the specific dissociation constants of some vibrationally excited ("active") molecules were estimated from data on the deuterization of free radicals and on atomic cracking reactions. In the present paper, theoretical estimates of these dissociation constants will be made using some equations derived earlier.[2] These calculations will be given in some detail after a comparison of the experimental and theoretical results.

The atomic cracking of ethyl radicals has been considered earlier[3] and assumptions similar to those employed in that treatment will be made here. For brevity some familiarity with these assumptions and notation will be taken for granted.

DISCUSSION OF RESULTS

1. Deuterization of Methyl Radicals

The deuterization of methyl radicals and of deuteromethyl radicals can be interpreted in terms of the following reaction sequence,

$$CH_nD_{3-n}+D \rightleftharpoons CH_nD_{4-n}^*, \quad (1)$$

$$CH_nD_{4-n}^* \overset{k_a}{=} CH_{n-1}D_{4-n}+H, \quad (2)$$

$$M+CH_nD_{4-n}^*=M+CH_nD_{4-n}, \quad (3)$$

where $n=1$, 2, or 3 and M is any third body capable of deactivating the active molecule $CH_nD_{4-n}^*$. From the experimental data k_a was estimated to be[1] *ca* $5\times10^8\lambda$ and $8\times10^8\lambda$ sec^{-1} for $n=2$ and 3, respectively. λ is the efficiency of the deactivating collision (3).

In the following calculations the vibrational degrees of freedom of the active molecule are assumed to be "active" and the rotational degrees of freedom, "adiabatic," using the terminology of reference 2. This is essentially equivalent to assuming that all vibrations can contribute their energy to the breaking bond while the rotations cannot. If one further assumes the activated complex to be "rigid,"[4] then the theoretical value for k_a is found to be 4.4×10^7 and 1.3×10^8 sec^{-1} for $n=2$ and 3, respectively. If, on the other hand, a "loose"[5] activated complex is assumed, k_a is calculated to be 2.6×10^9 and 6.6×10^9 sec^{-1} for $n=2$ and 3, respectively.

A comparison of these theoretical estimates with the data indicates the activated complex to be rigid if one assumes $\lambda\cong0.1$, or loose if $\lambda\sim1$ (λ cannot be greater than unity). We shall return to this question later.

2. Atomic Cracking of Propyl Radicals

Regarding the mechanism of this reaction as given by (4), (5), and (6), k_a was estimated from the data to be *ca* $3.6\times10^5\lambda$ sec^{-1}.

$$H+C_3H_7=C_3H_8^*, \quad (4)$$

$$C_3H_8^* \overset{k_a}{=} CH_3+C_2H_5, \quad (5)$$

$$M+C_3H_8^*=M+C_3H_8. \quad (6)$$

Adopting the previous assumptions of active vibrations and adiabatic rotations k_a is found to be about 2×10^4 and 2×10^8 sec^{-1} for a rigid and loose activated complex, respectively. Clearly, the loose complex gives very poor agreement with the data while if the complex is rigid, $\lambda\cong0.1$.

3. Atomic Cracking of Ethyl Radicals

For comparison with the previous results we recall that using the same assumptions, the loose complex gave[3] very poor agreement with the data while if the complex is rigid, $\lambda\cong0.7$.

4. Effect of Pressure on Recombination of Methyl Radicals

In this case, too, the previous assumptions coupled with a postulated rigid complex were consistent with the data while the loose complex was not.[3]

* This work was financially assisted by the ONR, Contract No. N8onr-77900.
† Present address: Department of Chemistry, Polytechnic Institute of Brooklyn.
[1] R. A. Marcus, J. Chem. Phys. **20**, 352 (1951).
[2] R. A. Marcus, J. Chem. Phys. **20**, 359 (1951).
[3] R. A. Marcus, J. Chem. Phys. **20**, 364 (1952).
[4] The degrees of freedom of this activated complex are similar to those of the active molecule with the exception that a stretching vibration has become a translational motion in the activated complex.
[5] In this complex, the radicals resulting from the decomposition rotate freely.

5. Conclusions

While the experimental data are not very accurate—in some cases an error of a factor of five or ten is possible—it does appear that data on a variety of topics can be correlated in an approximate way by assuming a rigid activated complex, active vibrations, adiabatic rotations and $\lambda \sim 0.1$. If the rotations are treated as adiabatic the data are not consistent with the assumption of a loose complex. Conservation of angular momentum requires that the rotations associated with the two largest moments of inertia of the decomposing molecule will be adiabatic.[2] However, if the remaining rotations acted as energy sinks for the large energy of the active molecule, that is, if they were "active," the calculated lifetime would be increased, k_a decreased, and agreement with the data possibly obtained. Calculations for this assumption were made[3] for data (3) and (4). As pointed out in that discussion, a measurement of the steric factors of the appropriate free-radical-recombination reactions (in the present case, of CH_3+H, $2CH_3$ and $CH_3+C_2H_5$) will throw considerable light on this question. The loose complex is associated with a steric factor of the order of magnitude of unity while the rigid complex, with appreciably smaller steric factors. However, the available data on this question are, at present, conflicting.

CALCULATIONS

1. General

Since no degrees of freedom are assumed to be "inactive," Eq. (17) of reference 2 may be simplified by setting

$$\sum_{E_i \le E^+} N^*(E_a - E_i + E^+) D(E_i) = N^*(E_a + E^+).$$

This expression for k_a then becomes

$$k_a = \frac{P_1^+ P_R^+ \sum_{E_v \le E^+} \left(\frac{E^+ - E_v}{kT}\right)^{r/2} P(E_v)}{P_1 \Gamma(1+r/2) h N^*(E_a + E^+)}, \qquad (7)$$

where P_1 is the rotational partition function of the active molecule and P_1^+ that of the corresponding rotational degrees of freedom of the activated complex. P_R^+ is the partition function of those r, say, rotational degrees of freedom of the activated complex which originally were vibrations in the active molecule. From the definitions of rigid and loose complexes it follows that $r=0$ for a rigid complex but equals 2 for a nonlinear loose complex consisting of a radical and an atom, and equals 4 for one consisting of two radicals.

$P(E_v)$ is the number of vibrational states of an activated complex whose nonfixed vibrational energy is E_v, while E^+ is the total nonfixed energy of the complex. E_a is the bond strength of the breaking bond and $N^*(E_a+E^+)$ the number of quantum states per unit energy of an active molecule whose energy is (E_a+E^+). In the present calculations the rotational degrees of freedom of the active molecule are assumed to be adiabatic so that N^* is given by the following expression,[2]

$$N^*(E_a+E^+) = \frac{(E_a+E^++E_o)^{s-1}}{\Gamma(s)\prod_i h\nu_i}, \qquad (8)$$

where the ν_i are the s vibrational frequencies of the active molecule,

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

and Γ is the gamma-function.

The dissociation constants k_a associated with reactions (2) and (5) will now be evaluated with the aid of Eqs. (7) and (8).

2. Deuterization of Methyl Radicals

The rigid and loose activated complexes corresponding to reaction (2) will have[6] a nonfixed energy, E^+, approximately equal to $3kT$ and $5kT$, respectively. Since this energy is smaller than the vibrational quanta[7] of these complexes, $E_v=0$, and the sum in (7) reduces to its first term. Setting $E^+=3kT$ in this equation and noting that $r=0$ and $P_R^+=1$ for the rigid complex, we have

$$k_a = \frac{(P_1^+/P_1)}{hN^*(E_a+3kT)}. \qquad (9a)$$

For a loose complex E^+ equals $5kT$ and $r=2$ so that in this case

$$k_a = \frac{5(P_1^+/P_1)P_R^+}{hN^*(E_a+5kT)}. \qquad (9b)$$

The moments of inertia of the deuteromethanes needed for the determination of P_1 were, with the exception of CH_2D_2, taken from data given by Herzberg.[8]

[6] Defining the dissociation energy of a bond as the energy required to produce an activated complex from the parent molecule, the difference in the C—H and C—D dissociation energies is, for the rigid complex, equal to the difference in the zero-point energies of the corresponding stretching vibrations. Thus, the C—D dissociation energy exceeds that of a C—H bond by an amount approximately equal to 450 cm^{-1} or 1.3 kcal $mole^{-1}$. Clearly the activated complexes of reaction (2) have a nonfixed energy of 1.3 kcal $mole^{-1}$ in addition to the average initial relative kinetic energy (*ca* $kT=0.6$ kcal $mole^{-1}$ at 300°K) of the initial deuteromethyl radical and deuterium atom. The net energy of these complexes is therefore *ca* $3kT$.

In the case of a loose activated complex the difference in the C—H and C—D dissociation energies is equal to the difference in zero-point energies of the one stretching and two bending frequencies of the corresponding bonds. This amounts to *ca* 2.3 kcal $mole^{-1}$, so that the net nonfixed energy, E^+, of the loose activated complexes of reaction (2) is about (2.3+0.6) kcal $mole^{-1}$ $\cong 5kT$ at 300°K.

[7] The corresponding vibration frequencies are inferred from those of the active molecule if the complex is rigid or from the isolated free radicals if the complex is loose.

[8] G. Herzberg, *Molecular Spectra and Molecular Structure* (D. Van Nostrand Company, Inc., New York, 1949), Vol. 2.

The product of the three principal moments of inertia of CH_2D_2 which occurs in the classical expression for P_1, was estimated to be 4.8×10^{-118} (g cm^2 molecule^{-1})^3. Using an equation of Wilson and Hirschfelder[9] the corresponding products for the rigid activated complexes CHD_3^+, $CH_2D_2^+$, CH_3D^+ and CH_4^+ were found to be 4.1, 3.0, 2.1, and 1.4×10^{-117} (g cm^2 molecule^{-1})^3. In these calculations, the hydrogen atom of the activated complex was assumed to be at the apex of a pyramid whose height is 2.8A and whose base is the planar methyl radical. The C—H (and C—D) distance in the radical was taken to be 1.1A.

The rotational partition function of the loose activated complex, $P_1^+P_R^+$, was evaluated as follows: The nonvibrational motion of the radical can be resolved into a rotation about, and a translation of, its center of gravity. The relative motion of the centers of the radical and of the atom may in turn be resolved into radial and transverse motions. The former corresponds to a translation along the reaction coordinate, while the latter may be regarded as the rotation of a diatomic molecule of reduced mass, $\mu=m_am_b/(m_a+m_b)$, where m_a and m_b are the masses of the radical and of the atom, respectively. Thus, the rotational partition function of the loose complex is equal to the rotational partition function of the radical multiplied by that of a diatomic molecule whose moment of inertia is $(2.8)^2\mu$. The products of the three moments of inertia of the radicals which appear in this partition function were estimated from the previously assumed geometry to be 0.55, 1.2, 2.3, and 4.4×10^{-118} (g cm^2 molecule^{-1})^3 for CH_3, CH_2D, CHD_2, and CD_3, respectively.

The vibration frequencies, ν_i, which appear in Eq. (8) were taken from reference 8.[10] Finally, there is a statistical factor equal to the number of alternative C—H bonds of CH_nD_{4-n}* which can be broken (namely n). However, this factor appears automatically via the symmetry numbers in the rotational partition functions of the activated complex and of the active molecule. The C—H bond dissociation energy,[11] E_a is 102 kcal mole^{-1}. With $T=300$°K and the previous data, the k_a values given in Table I were estimated.

Reactions (2) and (3) can occur if $n=4$ though reaction (1) cannot. Nevertheless, the value of k_a for this case is included in Table I for completeness.

TABLE I. k_a for deuteromethanes (sec^{-1}).

n	Loose complex	Rigid complex
1	8.2×10^8	1.2×10^7
2	2.6×10^9	4.4×10^7
3	6.6×10^9	1.3×10^8
4	1.3×10^{10}	3.2×10^8

3. Atomic Cracking of Propyl Radicals

(A) *Rotational Degrees of Freedom*

Because of the geometric complexity of the propane molecule and of the corresponding activated complex, the various rotational partition functions in the expression for k_a will be estimated in a rather approximate manner. However, this estimate should be sufficiently adequate for the present purposes.

The four degrees of freedom of the loose complex which contribute to P_R^+ are two rotations of the methyl group about axes perpendicular to the latter's symmetry axis and two of the ethyl group about axes perpendicular to its own C—C axis. Assuming that the C—H distance in the radical is equal to 1.1A, the appropriate moment of inertia of the methyl group was estimated to be 3.02×10^{-40} g cm^2 molecule^{-1}. The corresponding moment of the ethyl group was inferred from that of ethane to be *ca* 42.3×10^{-40} g cm^2 molecule^{-1}. With this data P_R^+ for the loose complex was found to be 3.6×10^3 at 300°K. As noted earlier P_R^+ equals unity for a rigid complex.

A rough measure of the ratio, P_1^+/P_1, may be inferred in the following way: The three principal moments of inertia of the activated complex will be somewhat larger than those of the active molecule. Furthermore, the rotation of the molecule as a whole has a symmetry number of 2 while the complex is unsymmetrical. These rotations therefore contribute to P_1^+/P_1 a factor somewhat greater than 2. The two internal rotations of the active molecule are hindered while only one is probably hindered in the complex. The partition function of one of these degrees of freedom will be the same in the complex, approximately, as in the active molecule. The remaining internal rotation, which is restricted in the molecule but free in the complex, will contribute to P_1^+/P_1 a factor roughly equal to that obtained for an analogous degree of freedom in ethane[3], namely, 2.0 (at 300°K). Thus the ratio P_1^+/P_1 will be somewhat greater than (2×2). A reasonable value appears to be about 6.

(B) *Vibrational Degrees of Freedom*

The active molecule, C_3H_8*, has an energy[11] of 95 kcal mole^{-1} arising from the formation of the C—H bond in reaction (4). Since only 83 kcal mole^{-1} is required to break the C—C bond in propane[11] the nonfixed energy, E^+, of the activated complex of (5) is[12] approximately 12 kcal mole^{-1}.

Since the number of different vibration frequencies of propane is considerable and E^+ is quite large, the sum in Eq. (7) will have numerous terms corresponding to

[9] E. B. Wilson, Jr., Chem. Revs. 27, 17 (1940). J. O. Hirschfelder, J. Chem. Phys. 8, 431 (1940).
[10] See reference 8, p. 306 ff.
[11] See E. W. R. Steacie, *Atomic and Free Radical Reactions* (Reinhold Publishing Corporation, New York, 1946), p. 79.
[12] A more correct value might be 12 plus the difference of the zero-point energies of the activated complexes of (4) and (5). This zero-point energy difference appears to be less than the experimental error in the difference of the C—H and C—C bond strengths and will be disregarded.

all the vibrational energy levels of the activated complex for which $E_v \leq E^+$. In order to make a simpler though less accurate estimate of this sum, the smaller vibration frequencies will be treated in a semiclassical fashion, so that the sum becomes, in part, an integral. The remaining frequencies will, as before, be considered in a quantum manner. While the final results of this calculation still involve a sum, the number of terms involved is significantly less.

With this assumption, E_v becomes a continuous variable and Eq. (7) can be modified by setting

$$\sum_{E_v \leq E^+} (E^+ - E_v)^{r/2} P(E_v) = \int_{E_v=0}^{E^+} (E^+ - E_v)^{r/2} P'(E_v) dE_v, \quad (10)$$

where $P'(E_v)$ is the number of vibrational states per unit energy of an activated complex whose energy is E_v. We next consider a particular set of quantum states for which the energy of the "quantized vibrations" is x_v while that of the "semiclassical vibrations" is $E_v - x_v$. The number of quantum states per unit energy of the semiclassical vibrations is[2]

$$\frac{(E_o' + E_v - x_v)^{q-1}}{\Gamma(q) \prod_i h w_i}, \quad (11)$$

where the w_i are the frequencies of the q semiclassical vibrations and

$$E_o' = \sum_{i=1}^{q} h w_i / 2.$$

When the energy of the quantized vibrations is x_v, let there be $Q(x_v)$ vibrational states of these degrees of freedom and therefore we have

$$P'(E_v) = \sum_{x_v \leq E_v} \frac{(E_o' + E_v - x_v)^{q-1} Q(x_v)}{\Gamma(q) \prod_i h w_i}. \quad (12)$$

after introducing (12) into (10) and interchanging the order of summation and integration so that the new limits are $x_v \leq E^+$ and E_v from x_v to E^+, the right-hand side of Eq. (10) becomes

$$[\Gamma(q) \prod_i h w_i]^{-1} \sum_{x_v \leq E^+} Q(x_v) \times \int_{E_v=x_v}^{E^+} (E_o' + E_v - x_v)^{q-1} (E^+ - E_v)^{r/2} dE_v. \quad (13)$$

In the present calculations r equals 0 and 4 for the rigid and loose complex, respectively, and in the latter case the integral of (13) was evaluated by introducing a new integration variable, $y = (E_o' + E_v - x_v)$.

The discrepancy between (13) and the left-hand side of (10) was estimated for the relatively simple rigid activated complex involved in $C_2H_6 = 2CH_3$. The results of these calculations are given in Table II. The relatively close agreement between the two calculations for large E^+ suggests that (13) will also provide a reasonable approximation to the left-hand side of (10) for the present calculations on propane.

The vibration frequencies of propane used in the calculation of $N^*(E_a + E^+)$ were taken[13] to be 375, 748, 868, 922, 940, 1053, 1155, 1179, 1278, 1355 (3), 1460 (5), and 2950 (8) cm^{-1}. The latter three frequencies were rounded slightly to facilitate some subsequent calculations. By definition these are the vibration frequencies of the rigid complex with the exception that the latter has one C—C stretching frequency while propane has two, namely 868 and 1053 cm^{-1}. The lone C—C frequency of the ethyl group was assumed to be 993 cm^{-1} which is the corresponding frequency in ethane.

The vibration frequencies of the loose activated complex are simply those of the isolated methyl and ethyl radicals. Those of the methyl group were inferred from the frequencies of methyl iodide[14] to be 1252, 1450 (2), and 2960 (3) cm^{-1} while those of the ethyl group were inferred from the characteristic group and bond frequencies[8,13] to be 1000 (5), 1375 (1), 1450 (3), and 2960 (5) cm^{-1}. The remaining vibration of the ethyl radical is a restricted rotation, whose contribution to k_a was considered earlier.

In the calculation for the rigid complex, the frequencies 375, 748, 922, 940, 993, 1155, 1179, and 1278 cm^{-1} were taken to be semiclassical and for the loose complex, 1252 and 1000 (5) cm^{-1} were so adopted.

TABLE II.

E^+ (kcal mole^{-1})	L.H.S. of Eq. No. (10)[a]	Eq. (13)[b]
0	1	7.85
5	11	18.8
8	58	69.8
10	139	188
13	532	670

[a] This sum had been previously estimated in reference 3.
[b] For the vibration frequencies of (see reference 3 for references and discussion) we have chosen: semiclassical vibrations, 827 (2) and 1120 (2) cm^{-1}, i.e., $q=4$: quantized vibrations, 1380 (2), 1470 (4), 2927 (2), and 2975 (4) cm^{-1}.

TABLE III.

E^+ (kcal mole^{-1})	k_a (Eq. (5)) (sec^{-1})	
	Rigid complex	Loose complex
9.85	1.2×10^4	—
12.85	3.2×10^4	—
14.0	4.6×10^4	3.8×10^8

[13] K. S. Pitzer, J. Chem. Phys. 12, 310 (1944).
[14] T. Y. Wu, *Vibrational Spectra and Structure of Polyatomic Molecules* (J. W. Edwards, Ann Arbor, Michigan, 1946). The second and third frequencies were rounded to facilitate the calculation of k_a.

k_a is given as a function of the energy of the complex, E^+, in Table III. Clearly the assumption of a loose complex is inconsistent with the data ($E^+=12$ kcal mole^{-1}, $k_a=3.6\times10^5\lambda$ sec^{-1}) so that the corresponding calculations were made for only one value of E^+. Because of a possible error in the present estimates of the C—H and C—C bond strengths E^+ may be slightly different from 12 kcal mole^{-1}. The effect on the calculated value of k_a of assuming a somewhat different value for E^+ may be inferred from Table III.

ACKNOWLEDGMENT

I should like to acknowledge a number of very helpful discussions with Professor O. K. Rice.