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Recombination of Methyl Radicals and Atomic Cracking of Ethyl Radicals*

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The characteristics of this atomic cracking reaction and of the pressure and steric effects associated with the recombination of methyl radicals are all intimately related. The available data on these reactions are correlated by means of a previously developed theory. Some experimental results on the steric factor and the data on the remaining subjects appear to be consistent with the assumption that the methyl radicals must be highly oriented with respect to each other in order that recombination occur. However, experimental steric factors of unity have also been reported in the literature. The corresponding assumption of no orientation leads to disagreement with the remaining data unless some of the rotational degrees of freedom of the "active" molecule, in addition to the vibrations, are assumed to be "active." Even then, the difficulties are not completely removed. Further experimental work on these reactions is needed.

INTRODUCTION

SEVERAL studies on the pressure and steric effects associated with the recombination of methyl radicals have been reported recently.[1,2] While there seems to be general agreement as to the pressure dependence of the rate constant, different experimental techniques gave widely different values for the steric factor. The reaction appears to be independent of the pressure of inert gases[1b,2b] above 5 mm. No measurements have been reported at lower pressures. Steric factors of unity and 10^{-5} (references 1 and 2, respectively) have been estimated. Still another experimental approach[3] has suggested a steric factor less than 0.1.

The following discussion suggests that the characteristics of the recombination of methyl radicals are closely related, from a theoretical viewpoint, to the relative rates of the "atomic cracking" reaction (1) and the recombination reaction (2). It will be assumed that reactions (1) and (2) may be written in a more illuminating manner as (3), (4), and (5).

$$H+C_2H_5=2CH_3, \quad (1)$$

$$H+C_2H_5=C_2H_6, \quad (2)$$

$$H+C_2H_5=C_2H_6^*, \quad (3)$$

$$C_2H_6^*+M=C_2H_6+M, \quad (4)$$

$$C_2H_6^* \xrightarrow{k_a} 2CH_3. \quad (5)$$

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[1] By use of intermittent light: (a) V. E. Lucas and O. K. Rice, J. Chem. Phys. 18, 993 (1950). (b) R. Gomer and G. B. Kistiakowsky, J. Chem. Phys. 19, 85 (1951). (c) R. E. Dodd, Trans. Faraday Soc. 47, 56 (1951). However, it should be mentioned that there is some slight doubt about the nature of the recombination reaction studied by (a) and (c).

[2] By comparison with reaction of CH_3+NO: (a) R. A. Marcus and E. W. R. Steacie, Z. Naturforsch. 4a, 332 (1949), and subsequent unpublished work in which the NO was admitted into the reaction system continuously. The latter research, which eliminated some difficulties present in the former, gave a steric factor 10^{-5} to 10^{-6}, while the former gave a steric factor of at least 10^{-3}. (b) D. M. Miller and E. W. R. Steacie, J. Chem. Phys. 19, 73 (1951).

[3] A. O. Allen and C. E. H. Bawn, Trans. Faraday Soc. 34, 463 (1937).

$C_2H_6^*$ represents a high energy ("active") molecule containing about 98 kcal mole^{-1} of vibrational energy arising from the newly formed C—H bond. M denotes any molecule capable of deactivating a $C_2H_6^*$ molecule. The value of k_a associated with (5) was estimated to be[4] *ca* $1.1\times10^7\lambda$ sec^{-1}, where λ is the efficiency of the deactivating collision (4).

The recombination of methyl radicals is closely related to the atomic cracking reactions since it involves the reverse of (5) followed by (4) or alternatively by (5). One important difference is that in this case the average $C_2H_6^*$ molecule has an energy of *ca* 85 kcal mole^{-1} (the C—C bond strength in ethane) rather than 98 kcal mole^{-1}.

The problem of interpreting the "atomic cracking" and methyl radical recombination reactions reduces to a discussion of the nature of the degrees of freedom of $C_2H_6^*$ and of the activated complex, $C_2H_6^+$, involved in reaction (5). In the following treatment specific assumptions about $C_2H_6^*$ and $C_2H_6^+$ will be introduced into rather general theoretical expressions[5] for pressure and steric effects and for the magnitude of k_a.

THEORETICAL

Before considering these assumptions, a classification[5] of the degrees of freedom of the active molecule will be reviewed briefly. These degrees of freedom were classified into two groups according to whether they do or do not remain in the same "quantum state" during the lifetime of the active molecule. The former group is said to be "adiabatic." Those of the latter group may be further specified with regard to their role in intramolecular energy transfer. They are termed "inactive" if they are not capable of transferring (or receiving) energy to the breaking (or newly formed) chemical bond. Those which are so capable are said to be "active." All vibrational degrees of freedom will be assumed to be active. The rotations corresponding to the two larger moments of inertia of ethane will, for purposes of approximate angular momentum conservation,[5] be assumed to be adiabatic.

Several alternative assumptions will be made about the two remaining degrees of freedom, rotation about the symmetry (C—C) axis and internal hindered rotation. If the active molecule retained its symmetric top configuration during the course of decomposition of the molecule, the angular momenta associated with these rotations would be constants of the motion. The rotations would, in turn, be classified as adiabatic. However, due to the appreciable increase of C—C distance the deviations from a symmetric top configuration may be so large that the rotations become active. Finally if these deviations are only appreciable when the molecule is essentially an activated complex, the rotations would behave as inactive degrees of freedom. As will be seen later, the adiabatic and inactive assumptions lead to rather similar results. In the absence of any suitable guide as to the correct assumptions, calculations will be made for all three cases.

TABLE I. Degrees of freedom of C_2H_6 and of $C_2H_6^+$.

Assumptions		Degrees of freedom of C_2H_6			Degrees of freedom of $C_2H_6^+$	
About $C_2H_6^+$	About two rotations	Adiabatic	Active	Inactive	Adiabatic rotations	Non-adiabatic rotations
loose	adiabatic	4	17	0	4	4
loose	inactive	2	17	2	2	6
loose	active	2	19	0	2	6
rigid	adiabatic	4	17	0	4	0

Two rather extreme assumptions may be made about the activated complex for reaction (5). (1) The complex consists of freely rotating radicals. (2) The degrees of freedom of the complex are very similar to those of ethane with the exception that a C—C stretching vibration in the latter has become, in the former, an internal translational motion along the reaction path.

These complexes are termed "loose" and "rigid," respectively. The rigid complex corresponds to a requirement of a highly oriented collision of methyl radicals, while the assumption of a loose complex is equivalent to a steric factor of the order of magnitude of unity.[5] The absence of an activation energy for these reactions makes a specification of the activated complex rather difficult *a priori*. A more detailed discussion of this problem will be reserved for a later date. For the present, calculations will be made for both complexes.

The various alternative assumptions employed in the following calculations, together with the corresponding specification of the degrees of freedom of ethane and of the activated complex for reaction (5), are summarized in Table I. It will be noted that some alternative assumptions in the case of the rigid complex were not investigated. However, the numerical results for these omitted cases can be roughly extrapolated from the results given in the following.

For purposes of brevity only the detailed calculation of the unimolecular rate constant k_{uni} will be discussed. However, the values of k_a, the dissociation constant of (5), and of k_{bi}, the bimolecular rate constant for the recombination of methyl radicals given in the following, may be estimated in a similar manner using Eqs. (17), (25), and (26) of reference 5 and the data given in Appendix I.

The following expression for k_{uni} as a function of the pressure p was derived earlier.[5]

$$k_{uni}=\frac{kT}{h}\frac{P^+}{P}\cdot\frac{\exp(-E_a/kT)}{\Gamma(1+r/2)}\int_{x=0}^{\infty}\frac{x^{r/2}e^{-x}dx}{1+ax^{r/2}}, \quad (6)$$

where

$$a^{-1}=P_1hk_2p\Gamma(1+r/2)N^*(E_a)\sum_{E_i\leq xkT}D(E_i)/P_3^+, \quad (7)$$

[4] R. A. Marcus, J. Chem. Phys. **20**, 352 (1951).
[5] R. A. Marcus, J. Chem. Phys. **20**, 359 (1951); see R. A. Marcus and O. K. Rice, J. Phys. Colloid Chem. **55**, 894 (1951).

TABLE II. Numerical values of integrals in Eqs. (11), (16), and (21).

A^{-1}	$J(A)$	B^{-1}	$K(B)$	C^{-1}	$L(C)$
0	0.00	0	0.00	0	0.00
0.25	0.071	0.25	0.035	8.58	0.26
1	0.19	1	0.11	32.0	0.45
4	0.40	4	0.28	91.1	0.62
16	0.67	16	0.54	250	0.77
36	0.80	36	0.71	1141	0.92
∞	1.00	∞	1.00	∞	1.00

and $N^*(E_a)$ is given by Eqs. (21) or (22) of reference 5 depending on the number of assumed active rotations. E_a is the activation energy for the dissociation of ethane. P and P^+ are the partition functions for all degrees of freedom of C_2H_6 and $C_2H_6^+$, respectively, with the exception that P^+ does not include one degree of freedom of the activated complex, namely, the internal translational motion along the reaction coordinate. P_1 is the partition function for the adiabatic degrees of freedom of ethane, and P_3^+ is the partition function for all rotations and vibrations of the activated complex. These partition functions are estimated by conventional methods from the data given in Appendix I. Γ is the gamma-function and k_2 the collision frequency for the deactivation of active molecules. In the following, the inefficiency of this process is represented by a factor λ. The number of nonadiabatic rotations of the activated complex r is given in the last column of Table I. $D(E_i)$ is the number of quantum states of the inactive degrees of freedom when they have an energy E_i. According to the present assumptions, these are nonvibrational in nature so that the sum in (7) may be replaced by an integral over E_i from 0 to xkT (the rotational energy levels are sufficiently closely spaced). The corresponding integrand is simply the number of rotational quantum states per unit energy for the inactive rotations and is given by an expression similar to Eq. (23) of reference 5. When no degrees of freedom of ethane are assumed to be inactive, the sum over E_i should be replaced by unity. With the previous equations and the data in Appendix I, k_{uni} was evaluated.

The dissociation constant of $C_2H_6^*$, k_a, is given below as a function of the energy of the corresponding activated complex E^+. In the following equations, Z is the frequency of collisions of methyl radicals and $P(E_v)$, the number of vibrational states of an activated complex whose "nonfixed" vibrational energy is E_v. $P(E_v)$ is estimated from the vibrational frequencies of the activated complex by a straight-forward procedure.[6]

The summations in (8), (13), (18), and (23) are over all vibrational energy levels of the complex E_v such that $E_v \leqslant E^+$. The nature of the assumption about the two rotational degrees of freedom discussed earlier is indicated in *italics*. The present calculations correspond to a temperature of 300°K. However, the temperature dependence of the numerical results is rather minor. Pressures are in mm and energies, in kcal mole^{-1}.

1. Loose Activated Complex

(a) *Adiabatic*

$$k_a=\frac{7.4\times10^{40}\sum P(E_v)(E^+-E_v)^2}{(130+E^+)^{16}}\ \text{sec}^{-1}, \tag{8}$$

$$k_{uni}=5.0\times10^{15}J(A)\exp(-E_a/RT)\ \text{sec}^{-1}, \tag{9}$$

$$k_{bi}=0.25ZJ(A), \tag{10}$$

where

$$J(A)=0.5\int_{x=0}^{\infty}\frac{x^2e^{-x}dx}{1+Ax^2} \tag{11}$$

and

$$A=0.69/\lambda p. \tag{12}$$

The integral $J(A)$ may be expressed[7] in terms of exponential sine and cosine integrals. Evaluated from tables[8] of the latter, $J(A)$ is given as a function of A in Table II.

(b) *Inactive*

$$k_a=\frac{4.2\times10^{41}\sum P(E_v)(E^+-E_v)^3}{(130+E^+)^{17}-(130)^{17}}\ \text{sec}^{-1}, \tag{13}$$

$$k_{uni}=5.0\times10^{15}K(B)\exp(-E_a/RT)\ \text{sec}^{-1}, \tag{14}$$

$$k_{bi}=0.25ZK(B), \tag{15}$$

where

$$K(B)=\frac{1}{6}\int_{x=0}^{\infty}\frac{x^3e^{-x}dx}{1+Bx^2} \tag{16}$$

and

$$B=0.23/\lambda p. \tag{17}$$

$K(B)$, estimated in the same manner as $J(A)$, is given in Table II as a function of B.

(c) *Active*

$$k_a=\frac{4.2\times10^{41}\sum P(E_v)(E^+-E_v)^3}{(130+E^+)^{17}}, \tag{18}$$

$$k_{uni}=5.0\times10^{15}L(C)\exp(-E_a/RT)\ \text{sec}^{-1}, \tag{19}$$

$$k_{bi}=0.25ZL(C), \tag{20}$$

[6] For example, let ν_i be the vibrational frequency of the ith oscillator, which is p_i-fold degenerate, say. If the molecule has m different frequencies, then the number of vibrational modes is $(p_1+\cdots+p_m)=\sum_i p_i$. Consider a particular vibrational energy level whose nonfixed energy is $E_v=\sum_i n_i h\nu_i$, the n_i being integers. The number of quantum states associated with the distribution of n_i quanta among p_i vibrational modes is equal to the number of ways, $(n_i+p_i-1)!/n_i!(p_i-1)!$, that n_i identical balls can be distributed among p_i boxes. The total number of vibrational quantum states $P(E_v)$ corresponding to the energy level E_v, is

$$\prod_{i=1}^{m}\frac{(n_i+p_i-1)!}{n_i!(p_i-1)!},$$

if the vibrational frequencies are not commensurable.

[7] D. Bierens de Haan, *Nouvelles Tables D'Integrales Definies* (G. E. Stechert and Company, New York, 1939), p. 133.

[8] "Tables of Sine, Cosine and Exponential Integrals" (Federal Works Agency, W. P. A., New York, 1940), Vol. 1.

where

$$L(C)=\frac{1}{6}\int_{x=0}^{\infty}\frac{x^3e^{-x}dx}{1+Cx^3} \tag{21}$$

and

$$C=0.018/\lambda p. \tag{22}$$

In Eqs. (18) and (22) a term, $(45)^{17}$, has been neglected in comparison with $(130+E^+)^{17}$ and $(130)^{17}$, respectively. The error thus incurred is negligible.

$L(C)$, calculated in Appendix II as a function of C, is given in Table II.

2. Rigid Activated Complex, *Adiabatic*

$$k_a=\frac{4.4\times10^{38}\sum P(E_v)}{(130+E^+)^{16}}\ \text{sec}^{-1}, \tag{23}$$

$$k_{uni}=\frac{4.3\times10^{13}\exp(-E_a/RT)}{1+0.011/\lambda p}\ \text{sec}^{-1}, \tag{24}$$

$$k_{bi}=\frac{2.2\times10^{-3}Z\exp(-\epsilon/RT)}{1+0.011/\lambda p}. \tag{25}$$

The quantum-mechanical origin of the activation energy ϵ has been discussed elsewhere.[5] According to the present formalism, ϵ is simply equal to the zero-point energy of the four new vibrational modes produced when a rigid activated complex is formed from methyl radicals. The corresponding vibrations in ethane are doubly degenerate (as they are in the complex) rocking vibrations and have a zero-point energy of 5.6 kcal mole^{-1}. ϵ will be somewhat less than 5.6 since the corresponding vibration frequencies of the complex should be smaller than in the molecule, and secondly, the levels may be appreciably broadened as a result of the possibly short lifetime of the activated complex.

Evaluating $P(E_v)$ as indicated in reference 6, k_a is given in Table III.

TABLE III. Dissociation constant[a] k_a of ethane as a function of E^+.

E^+ (kcal mole^{-1})	Rigid complex (adiabatic)	Loose complex (adiabatic)	Loose complex (inactive)	Loose complex (active)
0	$6.6\ 10^4$	0	0	0
5	$4.0\ 10^5$	$2.0\ 10^8$	$7.2\ 10^7$	$3.4\ 10^7$
8	$1.5\ 10^6$	$7.2\ 10^8$	$2.6\ 10^8$	$1.6\ 10^8$
10	$2.7\ 10^6$	$1.4\ 10^9$	$4.9\ 10^8$	$3.6\ 10^8$
13	$7.5\ 10^6$	$3.5\ 10^9$	$1.2\ 10^9$	$1.0\ 10^9$

[a] Units are sec^{-1}.

DISCUSSION

1. k_a

The experimental value associated with reactions (3), (4), and (5) was found to be $1.1\times10^7\lambda$ sec^{-1}. Since the active molecule has, in this case, an energy of 98 kcal mole^{-1} while the C—C bond strength is only 85 kcal mole^{-1}, the activated complex in reaction (5) will have an energy E^+ of (98—85) = 13 kcal mole^{-1}. From Table III the calculated value of k_a is, if $\lambda\sim1$, seen to be in good agreement with the experimental if the activated complex is assumed to be rigid. It is seen from Table III that an uncertainty in the difference of the C—H and C—C bond strengths of 3 kcal mole^{-1} introduces an uncertainty of a factor of 3 in the calculated value of k_a. On the other hand, k_a calculated on the basis of a loose complex appears to be larger than the observed value by a factor of about $100/\lambda$, and $\lambda\leqslant1$.

2. Recombination of Methyl Radicals

The loose and rigid complexes correspond to markedly different steric factors but, as noted earlier, the present experimental data are in an unsatisfactory state. It will be noted that the steric factor for the recombination of radicals via a loose complex is 0.25 since three-fourths of the collisions lead to a repulsive triplet state and there are no orientative restrictions.

The absence of any pressure dependence of the bimolecular rate constant in the pressure range 5 to 200 mm is quite interesting. This behavior is in complete agreement with that expected from the assumption of a rigid complex (Eq. 25). The predicted behavior of the loose complex is found by plotting the data of Table II *vs* λp using Eqs. (12), (17), and (22). From such graphs one finds that k_{bi} has fallen to one-half its high pressure value when $\lambda p=4.7$, 3.0, and 0.74 mm for the adiabatic, inactive, and active cases, respectively. With the usual assumption of $\lambda\sim1$, it is seen that the assumption of a loose complex corresponds to a large predicted pressure effect in the range 5–200 mm in the first two cases. In the third case the predicted effect would probably be smaller than the probable experimental error (which may be about 20 percent). Thus the observed pressure dependence may be explained on the basis of a loose activated complex only if the two rotational degrees of freedom are assumed to be active. On the other hand, as mentioned earlier, such assumptions do not appear to be consistent with the experimental value of k_a. Nevertheless, further experimental work along these lines, that is, on atomic cracking reactions, is necessary. An inconsistency with the present data can hardly be considered serious.

SUMMARY

The present calculations and discussion appear to favor the assumption of a rigid activated complex. Nevertheless, the dearth of reliable data makes this conclusion highly tentative. A knowledge of the pressure dependence of the rate of recombination of methyl radicals at pressures below 5 mm should prove very illuminating. A reliable estimation of the steric factor would be equally helpful. One might expect the activated complex to be intermediate in nature between the rigid and loose types. If this proves to be true, an interpolation

procedure could be developed for the correlation of the various characteristics discussed in the present paper.

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APPENDIX I. NUMERICAL DATA

The vibration frequencies of a methyl radical were inferred from those of methyl iodide[9] to be 2855, 1252, 1445 (2), and 3074 (2) cm^{-1}. Those of ethane were taken[10] to be 827 (2), 993, 1120 (2), 1380 (2), 1470 (4), 2927 (2), and 2975 (4) cm^{-1} (slightly rounded to facilitate computation of the $P(E_v)$ associated with a rigid complex). With the exception of the 993 cm^{-1} frequency (C—C stretching), these were assumed to be the vibration frequencies of the rigid activated complex. The loose complex was assumed to have vibration frequencies equal to those of the isolated radicals.

The moments of inertia of ethane were taken to be[11] 42.3, 42.3, and 11.0×10^{-40} g cm^2 $molecule^{-1}$. Assuming a planar configuration of a methyl radical and a C—H distance of 1.1A, its moments of inertia were estimated to be 6.03, 3.02, 3.02×10^{-40} g cm^2 $molecule^{-1}$. The rigid complex was assumed to be an elongated ethane molecule having planar methyl groups and a C—C distance of 3.3A. Its moments of inertia were estimated to be 142, 142, and 12.06 g cm^2 $molecule^{-1}$. The rotational partition function of the loose complex is equal to the product of the individual partition functions for each methyl radical multiplied by the partition function of a diatomic molecule (formed by the centers of gravity of the radicals) whose moment of inertia is $7.5(3.3)^2$.

The collision frequency Z equals $(2\pi kT/\mu)^{\frac{1}{2}}\sigma_1^2$ where μ and σ_1 are the reduced mass ($\mu=7.5$) and collision diameter, respectively σ_1 equals 3.3A.

The partition function for restricted rotation was assumed to equal

$$\sum_{i=1}^{W_{\max}} \exp(-W_i/kT)+\frac{(8\pi^3IkT)^{\frac{1}{2}}}{\sigma h}\exp(-W_{\max}/kT),$$

where I is the effective moment of inertia for internal rotation ($I=(11.0/4)\times10^{-40}$ g cm^2 $molecule^{-1}$) and σ the symmetry number. The energy levels W_i were taken to be[12] 0, 275, 520, 726, and 965 cm^{-1} with the latter equal to $W_{\max}$. Internal rotation in the rigid activated complex was assumed to be free and to have a moment of inertia equal to 3.02×10^{-40} g cm^2 $molecule^{-1}$.

The collision frequency for deactivating collisions was taken to be 5.86×10^6 mm^{-1} sec^{-1}. The values adopted for the C—H and C—C bond strengths of ethane were weighted averages of three independent determinations,[13] (98, 97.5, 96.8) and (85.6, 87.0, 83.4) kcal $mole^{-1}$, respectively.

APPENDIX II. APPROXIMATE EVALUATION OF $\int_{x=0}^{\infty}\frac{ux^3e^{-x}dx}{u+x^3}=R(u)$

We have

$$R(u=\infty)-R(u)=\int_{x=0}^{\infty}\frac{x^6e^{-x}dx}{u+x^3}=\int_{x=0}^{\infty}e^{f(x)}dx, \tag{1A}$$

where

$$f(x)=6\ln x-x-\ln(u+x^3). \tag{2A}$$

This integral approaches $6!/u$ and $3!$ for large and small u, respectively. The Stirling approximation to $n!$ being quite good in this range of n, (1A) will be evaluated by a method which can also be used to derive the Stirling formula. Since $R(u=\infty)=3!$, $R(u)$ is then readily obtained.

Let the maximum value of the Gaussian-like function $\exp(f(x))$ and therefore of $f(x)$ occur at $x=\xi$ and expand $f(x)$ about $x=\xi$ in a Taylor series. Since $f'(\xi)=0$, we have

$$f(x)=f(\xi)+\frac{(x-\xi)^2}{2}f''(\xi) \tag{3A}$$

neglecting the higher order terms. Solving $f'(\xi)=0$ where $f'(x)$ is obtained from (2A), we find

$$6-\xi=3\xi^3/(u+\xi^3) \tag{4A}$$

while from (2A) $-f''(\xi)=N$ is given by

$$N=6/\xi^2+3(2u\xi-\xi^4)/(u+\xi^3)^2. \tag{5A}$$

By introducing (3A) into (1A), changing the lower limit from 0 to $-\infty$ (with but little error) and integrating, we find for $R(u)$

$$R(u)\leqq 3!-\left(\frac{2\pi}{N}\right)^{\frac{1}{2}}\frac{(6-\xi)}{3}\xi^3\exp(-\xi), \tag{6A}$$

$$\leqq 3!-\frac{2(6-\xi)}{27(3N)^{\frac{1}{2}}}\xi^3\exp(3-\xi). \tag{7A}$$

Equation (7A) is obtained by introducing Stirling's equivalent of $(2\pi)^{\frac{1}{2}}$, namely, $(3!/\sqrt{3})(e/3)^3$ into (6A). This procedure reduces the error in the expression for $R(u)$ to a smaller value, particularly for small values of u.

The error in $3!-R(u)$ as given by (6A) may be roughly estimated by comparing with the known error in Stirling's approximation of $n!$ Evaluation of $R(u)$ directly, instead of via (1A), would have been subject to greater error on the average.

Instead of solving the quartic Eq. (4A) for ξ, various values of ξ were chosen and the equation solved for u. Table II was built up in this manner.

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