These extreme types of activated complexes were termed "loose" and "rigid," respectively. The latter is also associated with a high pressure frequency factor of $10^{12}$ sec$^{-1}$ for the corresponding unimolecular dissociation, since in Eq. (19) we have $P^2 \approx P$ (and $kT / \epsilon \approx 10^{10}$ sec$^{-1}$) for this case. The corresponding factor for the loose complex is $\approx f_{rot} \times 10^{10}$ 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, $\nu$, 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.

ACKNOWLEDGMENT

I should like to express my appreciation to Professor O. K. Rice for stimulating discussions and suggestions about the many problems associated with these reactions.

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$^{3,4}$ above 5 mm. No measurements have been reported at lower pressures. Steric factors of unity and $10^{-3}$ (references 1 and 2, respectively) have been estimated. Still another experimental approach$^5$ 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).

\begin{align*}
H + CH_3 &= 2CH_4, \quad (1) \\
H + C_2H_6 &= C_3H_7, \quad (2) \\
H + C_2H_6 &= C_2H_5^*, \quad (3) \\
C_2H_5^* + M &= C_2H_4 + M, \quad (4) \\
C_2H_4^* &= 2CH_4. \quad (5)
\end{align*}

METHYL RADICAL RECOMBINATION

C$_2$H$_4^*$ 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$_2$H$_6^*$ molecule. The value of $k_a$ associated with (5) was estimated to be $a_11.1 \times 10^{11}$ sec$^{-1}$, where $\lambda$ 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$_2$H$_6^*$ 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$_2$H$_6^*$ and of the activated complex, C$_2$H$_6^*$, involved in reaction (5). In the following treatment specific assumptions about C$_2$H$_6^*$ and C$_2$H$_6^*$ will be introduced into rather general theoretical expressions for pressure and steric effects and for the magnitude of $k_a$.

THEORETICAL

Before considering these assumptions, a classification 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, 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.

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.6 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 $k_{ad}$, 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.6

$$k_{uni} = \frac{kT}{h} \frac{P^+}{P} \frac{\exp(-E_a/kT)}{\Gamma(1+r/2)} \int_0^\infty \frac{x^{r/2}e^{-x}dx}{1+ax^{1/2}}$$  

(6)

where

$$a^{-1} = P \hbar \sqrt{p \Gamma(1+r/2) N^*(E_a)} \sum_{E \leq E_a} \frac{D(E_a)/P^*}{1 + a \sqrt{E}}$$  

(7)

---

and \( N^\alpha(E_a) \) 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 \( C_2H_4^+ \), 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 \( P_s^+ \) 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. \( \Gamma \) 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 \( \lambda \). The number of nonadiabatic rotations of the activated complex \( r \) is given in the last column of Table I. \( D(E_0) \) is the number of quantum states of the inactive degrees of freedom when they have an energy \( E_0 \). According to the present assumptions, these are nonvibrational in nature so that the sum in (7) may be replaced by an integral over \( E_0 \) from 0 to \( kT \) (the rotational energy levels are sufficiently closely spaced). The corresponding integral 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 \( E_0 \) should be replaced by unity. With the previous equations and the data in Appendix I, \( k_{unr} \) was evaluated.

The dissociation constant of \( C_2H_4^+ \), \( k_n \), 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 \( P(E_0) \), the number of vibrational states of an activated complex whose nonfixed \( i \) vibrational energy is \( E_i \). \( P(E_0) \) is estimated from the vibrational frequencies of the activated complex by a straightforward procedure.\(^6\)

\(^{6}\)For example, let \( \nu_i \) be the vibrational frequency of the \( i \)th oscillator, which is \( \nu_0 \)-fold degenerate, say. If the molecule has \( m \) different frequencies, then the number of vibrational modes is \( \sum \nu_i = \nu_1 + \cdots + \nu_m = \sum \nu_i \). Consider a particular vibrational energy level whose nonfixed energy is \( E_n = \sum \nu_i n_i \nu_0 \), the \( n_i \) being integers. The number of quantum states associated with the distribution of \( n_i \) quanta among \( \nu_i \) vibrational modes is equal to the number of ways, \( (n_1 + p_i - 1)!/n_1!(p_i - 1)! \), that \( n_i \) identical balls can be distributed among \( p_i \) boxes. The total number of vibrational

The summations in (8), (13), (18), and (23) are over all vibrational energy levels of the complex \( E_0 \) such that \( E_0 \leq E^+ \). 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) \textit{Adiabatic}

\[
k_a = \frac{7.4 \times 10^{10} \sum P(E_0)(E_0 - E_a)^2}{(130 + E^+)^{16}} \sec^{-1},
\]

\[
k_{un} = 5.0 \times 10^{14} J(A) \exp(-E_a/RT) \sec^{-1},
\]

\[
k_{is} = 0.25 ZJ(A),
\]

where

\[
J(A) = 0.5 \int_{x=0}^{\infty} x^2 e^{-x} dx
\]

and

\[
A = 0.69/\lambda \nu.
\]

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) \textit{Inactive}

\[
k_a = \frac{4.2 \times 10^{14} \sum P(E_0)(E_0 - E_a)^3}{(130 + E^+)^{17} - (130)^{17}} \sec^{-1},
\]

\[
k_{un} = 5.0 \times 10^{16} K(B) \exp(-E_a/RT) \sec^{-1},
\]

\[
k_{is} = 0.25 ZK(B),
\]

where

\[
K(B) = \frac{1}{6} \int_{x=0}^{\infty} x^3 e^{-x} dx
\]

and

\[
B = 0.23/\lambda \nu.
\]

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

(c) \textit{Active}

\[
k_a = \frac{4.2 \times 10^{14} \sum P(E_0)(E_0 - E_a)^3}{(130 + E^+)^{17}},
\]

\[
k_{un} = 5.0 \times 10^{14} L(C) \exp(-E_a/RT) \sec^{-1},
\]

\[
k_{is} = 0.25 ZL(C),
\]

quantum states \( P(E_0) \) corresponding to the energy level \( E_n \), is

\[
\prod_{i=1}^{\nu} \nu_i ! / (\nu_0 - 1)! \]

if the vibrational frequencies are not commensurable.


where

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

(21)

and

$$C = 0.018/\lambda \rho.$$  

(22)

In Eqs. (18) and (22) a term, $\lambda \rho$ has been neglected in comparison with $(130+E^+)$ 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

$$k_a = \frac{4.4 \times 10^{-18} \sum P(E_x)}{(130+E^+)^{16}} \text{ sec}^{-1},$$

(23)

$$k_{uni} = \frac{4.3 \times 10^{-9}}{1 + 0.011/\lambda \rho} \exp(-E_a/RT) \text{ sec}^{-1},$$

(24)

$$k_{li} = \frac{2.2 \times 10^{-9}}{1 + 0.011/\lambda \rho} \exp(-\epsilon/RT) \text{ sec}^{-1},$$

(25)

The quantum-mechanical origin of the activation energy $\epsilon$ has been discussed elsewhere. According to the present formalism, $\epsilon$ 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$^{-1}$. $\epsilon$ 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 $P(E_x)$ as indicated in reference 6, $k_a$ is given in Table III.

DISCUSSION

1. $k_a$

The experimental value associated with reactions (3), (4), and (5) was found to be $1.1 \times 10^{13}$ 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 $\lambda \sim 1$, 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 $\lambda \leq 1$.

<table>
<thead>
<tr>
<th>$E^+$ (kcal mole$^{-1}$)</th>
<th>Rigid complex (adiabatic)</th>
<th>Rigid complex (adiabatic)</th>
<th>Loose complex (inactive)</th>
<th>Loose complex (active)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>6.6 $10^{14}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>4.0 $10^{14}$</td>
<td>2.0 $10^{14}$</td>
<td>7.2 $10^{14}$</td>
<td>3.4 $10^{14}$</td>
</tr>
<tr>
<td>8</td>
<td>1.5 $10^{14}$</td>
<td>7.2 $10^{14}$</td>
<td>2.6 $10^{14}$</td>
<td>1.6 $10^{14}$</td>
</tr>
<tr>
<td>10</td>
<td>2.7 $10^{15}$</td>
<td>1.4 $10^{15}$</td>
<td>4.9 $10^{14}$</td>
<td>3.6 $10^{14}$</td>
</tr>
<tr>
<td>13</td>
<td>7.5 $10^{14}$</td>
<td>3.5 $10^{14}$</td>
<td>1.2 $10^{14}$</td>
<td>1.0 $10^{14}$</td>
</tr>
</tbody>
</table>

* Units are sec$^{-1}$.

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 reaction 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 in $\lambda \rho$ using Eqs. (12), (17), and (22). From such graphs one finds that $k_{li1}$ has fallen to one-half its high pressure value when $\lambda \rho = 4.7, 3.0$, and 0.74 mm for the adiabatic, inactive, and active cases, respectively. With the usual assumption of $\lambda \sim 1$, 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.

ACKNOWLEDGMENT

I should like to thank Professor O. K. Rice for his constructive criticisms and Professor Wayne A. Bowers for a helpful discussion on approximate integration methods.

APPENDIX I. NUMERICAL DATA

The vibration frequencies of a methyl radical were inferred from those of methyl iodide to be 2855, 1252, 1445 (2), and 3074 (2) cm$^{-1}$. Those of ethane were taken 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 $P(E)$ 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 42.3, 42.3, and 11.0 $\times 10^{-46}$ g cm$^2$ molecule$^{-1}$. Assuming a planar configuration of a methyl radical and a C$-$H distance of 1.1 A, its moments of inertia were estimated to be 6.03, 3.02, 3.02 $\times 10^{-46}$ 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 3.3 A. 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)$^{a}$. The collision frequency $Z$ equals $\left(2\pi kT/\mu\right)^{3/2}$ where $\mu$ and $s_1$ are the reduced mass ($\mu = 7.5$) and collision diameter, respectively $s_1$ equals 3.3 A.

The partition function for restricted rotation was assumed to equal

$$W_{\text{max}} \sum \exp(-W_i/kT) + \frac{(8\pi^2kT)^{1/2}}{\hbar} \exp(-W_{\text{max}}/kT),$$

where $I$ is the effective moment of inertia for internal rotation ($I = (11.0/4) \times 10^{-46}$ g cm$^2$ molecule$^{-1}$) and $\sigma$ is the symmetry number. The energy levels $W_i$ were taken to be $0$, 275, 520, 726, and 965 cm$^{-1}$ with the latter equal to $W_{\text{max}}$. Internal rotation in the rigid activated complex was assumed to be free and to have a moment of inertia equal to 3.02 $\times 10^{-46}$ g cm$^2$ molecule$^{-1}$.


The collision frequency for deactivating collisions was taken to be $5.86 \times 10^9$ mm$^2$ sec$^{-1}$. The values adopted for the C$-$H and C$-$C bond strengths of ethane were weighted averages of three independent determinations, $^c$ (98, 97.5, 96.8) and (85.6, 87.0, 85.4) kcal mole$^{-1}$, respectively.

APPENDIX II. APPROXIMATE EVALUATION OF

$$\int_{-\infty}^{\infty} \frac{ue^{u^2}}{u^2 + x^2} du = R(u)$$

We have

$$R(u = \infty) - R(u) = \int_{-\infty}^{\infty} \frac{e^{u^2}}{u^2 + x^2} du = \int_{-\infty}^{\infty} e^{\xi^2} d\xi,$$

where

$$f(x) = 6 \ln x - x - \ln(u + x^2).$$

This integral approaches 61/u and 31 for large and small u, respectively. The Stirling approximation to $\ln u$ being quite good in this range $u$, (1A) will be evaluated by a method which can be used to derive the Stirling formula. Since $R(u = \infty) = 31$, $R(u)$ is then readily obtained.

Let the maximum value of the Gaussian-like function $f'(x)$ 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

$$f(x) = f(\xi) + \frac{(x - \xi)^2}{2}$$

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

$$N = 6/\xi + 3(2\xi - \xi^2)/(u + \xi^2)^2, \quad (5A)$$

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

$$R(u) \cong 31 - \frac{(2\xi - \xi^2)}{3} exp(-\xi), \quad (6A)$$

$$\cong 31 - \frac{(2\xi - \xi^2)}{27(3\xi)} exp(3 - \xi). \quad (7A)$$

Equation (7A) is obtained by introducing Stirling's equivalent of $(2\xi)^1$, namely, $(3/\sqrt{3})(\xi/\tau)^3$ 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 $31 - R(u)$ as given by (6A) may be roughly estimated by comparing with the known error in Stirling's approximation of $\ln u$. 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 $\xi$, various values of $\xi$ were chosen and the equation solved for $u$. Table II was built up in this manner.