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SESSION ON FREE RADICALS

THE KINETICS OF THE RECOMBINATION OF METHYL RADICALS AND IODINE ATOMS[1, 2]

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I. INTRODUCTION

The process of recombination of free radicals may be formally regarded as proceeding *via* an intermediate complex (the so-called activated complex) in which the radicals are more or less rigidly bound together to form an "active" molecule. The term "active" here denotes a molecule containing a large excess of vibrational energy arising from the formation of the new bond. This excess energy must be removed through a deactivating collision, else it will reaccumulate in the new bond, and the molecule will decompose shortly after it has been formed.

This study treats the two main problems presented by radical recombinations: the magnitude of the steric effects tending to reduce the rate below that calculated by the kinetic theory of collisions (this effect gives rise to the so-called "steric" factor) and the effect of pressure on the rate of recombination. For example, if the activated complex is a rigid structure, i.e., the radicals are rigidly bound together, some of the rotational degrees of freedom of the radicals in their free state must be "frozen out" into bending vibrations of the new bond so that the activated complex may be formed. The relatively small probability of such a process results in a reduced chance of the formation of the activated complex and thus not every collision of radical and atom is effective in producing an active molecule. If, on the other hand, the activated complex has a loose structure, i.e., one in which the radicals rotate freely, then there will be no such restrictions on the rate of formation of the activated complex and every collision will be effective in producing an active molecule.

It may be noted that in speaking of a loose or rigid activated complex we are using the convenient terminology introduced by Eyring (4), which may not always give an accurate picture of the actual course of events in a reaction (10). We shall return to a discussion of this matter later in the paper.

The effect of concentration of third bodies, i.e., of total pressure, on the reaction rate is determined by the relative values of the lifetime of the active molecule and the time between deactivating collisions. If the former is small compared to the latter, then most of the active molecules formed will redissociate, and thus the effect of pressure will be a marked one, and conversely.

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These two problems are not unrelated, for, if the activated complex is a highly probable state (i.e., a "loose structure") and so is readily formed from a collision of a radical and an atom, it will also be easily formed from an active molecule, which will thus have a small lifetime. Thus we expect a marked pressure effect and no steric effect to go hand in hand. Similar reasoning shows that a small pressure effect and a high steric effect will be concurrent, at least at the pressures generally used.

The two problems are thus reduced to a single one of determining the nature of the activated complex. The absence of a large well-defined energy hump along the reaction path makes it very difficult to determine the properties of the activated complex. We have therefore made two sets of calculations,—one based on an assumed rigid complex, the other on a loose one.

Specifically, we consider the recombination of methyl radicals and iodine atoms. While this reaction is believed by many experimental workers to proceed at every collision, the value of the average half-life of the resultant active molecule was calculated by Kimball (7) on a classical basis to be about 3.6×10^{-12} sec. He suggested, too, that a quantum calculation could lead to an even smaller value. Thus one would infer from this that under the common experimental conditions of a pressure of, say, 100 mm. only about 10^{-3} of the collisions would be effective. These latter calculations are discussed in the light of the present study.

However, instead of calculating directly the absolute rate of recombination, we have calculated the rate of the unimolecular decomposition of methyl iodide as a function of pressure, and the equilibrium constant for the reaction

$$CH_3I \rightleftarrows CH_3 + I$$

The ratio of these last two quantities gives the absolute rate of recombination as a function of pressure. In this manner a three-body problem is reduced to a two-body one. We may note that while the effect of pressure on unimolecular reactions was discussed by Rice and Ramsperger, and quantum theory was applied by Kassel, the results were rather rough and a considerably more detailed theory is needed in the case of a small molecule such as methyl iodide.

II. THEORETICAL

Consider the unimolecular decomposition of methyl iodide:

$$CH_3I + M \underset{k_2}{\overset{k_1}{\rightleftarrows}} CH_3I^* + M$$

$$CH_3I^* \xrightarrow{k_a} CH_3I^+$$

$$CH_3I^+ \xrightarrow{k_3} CH_3 + I$$

Here M denotes any molecule (or wall of reaction vessel) capable of transferring vibrational energy to methyl iodide, CH_3I^* denotes a molecule with sufficient vibrational energy to dissociate, i.e., an active molecule, and CH_3I^+ denotes an activated complex. The calculations can be made for a specific value of the total energy of CH_3I^* (actually we always take a small range of energies). To get the observed reaction rate it is then necessary to integrate over all energies.

It is assumed as usual that a steady state is attained in which the concentrations of the CH_3I^* and CH_3I^+ are constant. These considerations lead to the equation

$$k_e = (k_1 k_a / k_2)/(1 + k_a/k_2 p) \tag{1}$$

where p denotes the total pressure and k_e is the rate constant for the net rate of decomposition of methyl iodide, through complexes having a given energy. The total rate constant is found as stated, by integration.

We now proceed to evaluate the rate constants in equation 1 as a function of energy and of the type of assumed complex, at first neglecting throughout the contribution of rotation of the molecule as a whole to the reaction rate, but incorporating this contribution in an approximate manner later.

A. *Evaluation of k_a*

$2k_a/k_3$ is the equilibrium constant[3] for $CH_3I^* \rightleftarrows CH_3I^+$ and thus, for a given energy, equals the relative numbers of ways that this energy can be distributed among the degrees of freedom of the activated complex and active molecule. The energy fixed as zero-point energy, or, in the case of the complex, as potential energy of the newly broken carbon–iodine bond, must be subtracted, since it obviously does not contribute to the number of ways of distribution. Let E' and E denote the nonfixed internal energy of the active molecule and corresponding activated complex, i.e., the total energy of the molecule minus that energy "fixed" as zero-point energy and as potential energy of the newly broken carbon–iodine bond in the activated complex. Then the number, $N_{E'}\mathrm{d}E'$, of energy levels of the active molecule in the range E', E', + $\mathrm{d}E'$ is given by the semiclassical formula:[4]

$$N_{E'}\,\mathrm{d}E' = \left[(E' + E_0)^{s-1}/\Gamma(s)\prod_{i=1}^{s}(h\nu_i)\right]\mathrm{d}E' \tag{2}$$

where s, Γ, ν_i, and E_0 are the number of modes of vibration, the gamma function, the frequency of the normal mode i, and the sum of the zero-point energies, respectively.

We consider first the case of the rigid activated complex, with one internal

[3] The factor 2 arises from the relation between the reactions $CH_3I^+ \rightarrow CH_3I^*$ and $CH_3I^+ \rightarrow CH_3 + I$ at equilibrium. The rates of these are the same at equilibrium but in the unimolecular reaction, $CH_3I^+ \rightarrow CH_3I^*$ does not occur, the molecules which would go in this direction being absent, and k_3 refers to the molecules actually there.

[4] See R. C. Tolman (12, page 492, equation 111.12). If this latter equation, whose derivation neglected the presence of zero-point energies, is modified as indicated by equation 2 here, a better approximation is obtained. Equation 2 provides a good approximation if E' is sufficiently large, as in the case of the active molecule. For the activated complex, however, the nonfixed internal energy is small and quantum restrictions become important, so that a more exact formulation must be employed.

translation and eight modes of vibration. Let an amount of energy equal to E_v be distributed among the oscillators. Then the remaining translational energy lies in the range $E - E_v$ to $E + \mathrm{d}E - E_v$. The number of translational levels in this range is

$$\int_{E-E_v}^{E+\mathrm{d}E-E_v} (\mathrm{d}n/\mathrm{d}E_1)\,\mathrm{d}E_1$$

where $\mathrm{d}n/\mathrm{d}E_1$, the number of levels per unit energy, is calculated from the expression for the translational energy levels, $E_1 = n^2h^2/8b^2m$. Here m and b denote the reduced mass and the extension of the transition state along the bond; b may be chosen more or less arbitrarily, since it cancels out in the final expression. The total number, $N_E\mathrm{d}E$, of levels of the activated complex in the range E to $E + \mathrm{d}E$ is then obtained by multiplying the integral by the number of ways, P_{E_v}, that the energy E_v can be distributed among the oscillators, and summing for all possible values of E_v less than E. Thus:

$$N_E\,\mathrm{d}E = \sum_{E_v<E} P_{E_v} \int_{E-E_v}^{E+\mathrm{d}E-E_v} (2m/E_1)^{1/2}(b/h)\,\mathrm{d}E_1 \qquad (3)$$

$2k_a/k_3$ is then equal to $N_E/N_{E'}$. However, we obtain $k_aN_{E'}$ directly if we multiply the integrand of equation 3 by $(2E_1/m)^{1/2}/b$, the value of k_3 for a given translational level of energy E_1, and divide by 2. Integration of the resulting equation leads to

$$k_a = \sum_{E_v<E} P_{E_v}/hN_{E'} \qquad (4)$$

We next consider the loose activated complex possessing six modes of vibration and two rotational and one translational degrees of freedom.[5] With P_{E_v}, E_v, n, and E_1 having the same significance as before, the number of rotational and translational levels in the range $E - E_v$, $E + \mathrm{d}E - E_v$ is given by $\iint(\mathrm{d}J/\mathrm{d}E_2)(\mathrm{d}n/\mathrm{d}E_1)\,\mathrm{d}E_1\mathrm{d}E_2$, with limits of integration as follows: E_1 from $E - E_v - E_2$ to $E - E_v + \mathrm{d}E - E_2$, and E_2 from 0 to $E - E_v$. Here the number of rotational levels per unit energy $\mathrm{d}J/\mathrm{d}E_2$ is found from the energy expression for the energy levels of a rigid rotator, $E_2 = J(J + 1)\,h^2/8\pi^2I \cong J^2h^2/8\pi^2I$. The value of $\mathrm{d}J/\mathrm{d}E_2$ is then multiplied by the multiplicity, $(2J + 1)/\sigma \cong 2J/\sigma$. I and σ are the moment of inertia and symmetry number, respectively. As before we obtain $k_aN_{E'}$ directly by multiplying the integrand by $(2E_1/m)^{1/2}/b$ and dividing by 2, and we find for k_a:

$$k_a = 8\pi^2I\left[\sum_{E_v<E}(E - E_v)P_{E_v}\right]/\sigma h^3N_{E'} \qquad (5)$$

B. Evaluation of remaining constants

Instead of considering k_1/k_2 as such, we consider the differential quantity,

[5] The axis of rotation of the methyl radical perpendicular to the plane of the three hydrogens forms an axis of rotation of the molecule as a whole. We are only concerned with the rotation about the two axes perpendicular to this one (see figure 1).

$d(k_1/k_2)$, which is the chance that the active molecules have a nonfixed energy in the range E' to $E' + dE'$, and is given by:

$$d(k_1/k_2) = N_{E'} \exp(-E'/kT)\, dE'/f \tag{6}$$

where $N_{E'}$ is given by equation 2, and f, the partition function for vibration, equals

$$\prod_{i=1}^{s} [1 - \exp(-h\nu_i/kT)]^{-1}$$

k_2 is calculated from kinetic theory and we assume that every collision is effective in deactivating an active molecule.

C. Contribution of rotation to reaction

The three rotational degrees of freedom of methyl iodide consist of one about the symmetry axis and a doubly degenerate one about axes perpendicular to this. We consider the latter rotation first. On the average, the angular momentum about these axes is much greater than about the symmetry axis, owing to the much (some 35-fold) greater related moment of inertia. Thus, any interaction of these rotations, caused by the bending vibrations disturbing the symmetry of the molecule, alters the angular momentum of this rotation very little, and we may consider this degree of freedom to be approximately separable. The correction to k_a/k_3 and therefore to k_a is now immediately evident. The previous value is to be multiplied by the ratio of the partition functions, $(8\pi^2 I_1^* kT/h^2)/(8\pi^2 I_1 kT/h^2)$, where I_1^* and I_1 are the corresponding moments of inertia of the activated complex and active molecule, respectively (10).

The methyl group is probably planar in the activated complex, though nonplanar in the active molecule, and thus the moment of inertia of the rotation about the symmetry axis is slightly less for the latter case, so k_a is to be multiplied by a second factor which we shall call $(I_2^*/I_2)^{1/2}$. The total correction factor will be designated as κ in the following.

The rotation about the symmetry axis interacts with the doubly degenerate bending vibration and this interaction is reflected in certain anomalies in the spectrum of methyl iodide (14, p. 140). We have not yet estimated the importance of this for the present case and shall neglect this additional complication for the present.

D. Evaluation of k_{uni}

With $E_a(=E' - E)$ depending slightly on the nature of the assumed complex, the expression for the unimolecular rate constant for the rigid complex becomes, from equations 1, 2, 4, and 6:

$$k_{\mathrm{uni}} = \int_0^\infty k_e dE = (\kappa/hf)e^{-E_a/kT} \int_0^\infty \frac{\sum P_{E_v}\, e^{-E/kT}\, dE}{1 + \alpha \sum P_{E_v}(E + E_0 + E_a)^{-(s-1)}\, p^{-1}} \tag{7}$$

where

$$\alpha = \Gamma(s) \prod_{i=1}^{s} (h\nu_i)\kappa/hk_2$$

The sums are taken as indicated in equation 4 or 5. For the loose complex we derive from equations 1, 2, 5, and 6:

$$k_{\text{uni}} = (8\pi^2 I\kappa/\sigma h^3 f)e^{-E_a/kT} \cdot \int_0^\infty \frac{\sum (E - E_v)P_{E_v}\, e^{-E/kT}\, dE}{1 + \alpha' \sum (E - E_v)P_{E_v}(E + E_0 + E_a)^{-(s-1)}\, p^{-1}} \tag{8}$$

where

$$\alpha' = \Gamma\ (s) \prod_{i=1}^{s} (h\nu_i) 8\pi^2 I\kappa/k_2\sigma h^3$$

E. Determination of E_a

E_a is the difference between the nonfixed internal energies of the active molecule and its corresponding activated complex, and is also seen from equations 7 and 8 to be the activation energy at high pressures ($p = \infty$) at 0°K.

The manner in which E_a varies with the nature of the complex is readily seen from a consideration of the reverse reaction, the recombination of methyl radicals and iodine atoms. If these recombine *via* a rigid complex, they must have sufficient energy to supply the zero-point energy of the doubly degenerate methyl–iodine bending vibrations. If, however, the complex is loose, no such energy has to be supplied for recombination (before the release of the large potential energy of the incipient carbon–iodine bond). Since the heat of reaction is independent of the nature of the complex, the activation energy for the unimolecular decomposition will be greater for the rigid than for the loose complex.

More exactly, let ν_6 denote the frequency of the doubly degenerate methyl–iodine bending vibration, and ΔH_0 denote the heat of the forward reaction at 0°K. Let E'' denote the nonfixed internal energy, including relative translational energy, of the separated radical and atom corresponding to an active molecule of nonfixed internal energy E'. Then it is readily seen that $E' - E'' = \Delta H_0$. Also from the preceding discussion, it is evident that $E'' - E = h\nu_6$ or 0, for the rigid or loose complex, respectively. Thus $E_a(=E' - E)$ equals $\Delta H_0 + h\nu_6$ for the rigid complex and ΔH_0 for the loose complex.

F. Numerical data

We employ the following data[6,7]: $E_a = 54$ kcal. mole^{-1} (2), $I = 3.07 \times 10^{-40}$ g. cm.^{2} molecule^{-1}, $T = 300$°K., $k_2 = 2.42 \times 10^6$ mm.$^{-1}$ sec.$^{-1}$, and $\sigma = 2$. The nine vibrational frequencies (14, page 238) of methyl iodide are 8.17, 3.58, 1.52, 8.79, 4.13, 2.53 kcal. mole^{-1}, the last three being doubly degenerate. The third mode is a parallel vibration of the methyl radical against the iodine atom

[6] Though Butler and Polanyi's (2) data indicate this value of E_a to be a maximum value, owing to possible complications resulting from the occurrence of back-reaction, we adopt it freely. The only place where this value occurs in the equation for k_{uni} is in the expression for $N_{E'}$. It is readily verified that in the neighborhood of $E' = 54$ kcal., $N_{E'}$ varies only by a factor of 3 for a change in E' of as much as 10 kcal.

[7] I is the moment of inertia for the mode of rotation of a planar methyl radical indicated in figure 1. A carbon–hydrogen distance of 1.11 Å. was assumed.

and is roughly the one which goes over into a relative translation of the parts. The last mode (2.53) is the methyl–iodine bending vibration. κ has been taken as 3.45, assuming a carbon–iodine distance of 4.0 Å. in the activated complex and taking values for I_1, I_2, and I_2^* given below.

With these numerical data the constants in equations 7 and 8 become:

Rigid complex:

$$\begin{aligned} \kappa/hf &= 3.24 \times 10^{13} \\ \alpha &= 2.26 \times 10^{17} \\ E_0 + E_a &= 76 \end{aligned} \tag{9}$$

Loose complex:

$$\begin{aligned} (8\pi^2 I/\sigma h^3)\kappa f^{-1} &= 6.21 \times 10^{14} \\ \alpha' &= 4.34 \times 10^{18} \\ E_0 + E_a &= 76 \end{aligned} \tag{10}$$

Pressures are in millimeters, and the energies are in kilocalories per mole. ΣP_{E_v} and $\Sigma P_{E_v}(E - E_v)$ are given in table 1 as functions of energy. The values of the latter two quantities are readily inferred from the theory of combinations.[8]

G. Evaluation of integrals

The integrals may be reduced to simple forms by two approximations.[9] Calculation of the integrands of equations 7 and 8 as functions of energy shows that most of the area under the curve k_e *vs.* E lies in the region where $\Sigma P_{E_v} = 1$ and $\Sigma P_{E_v}(E - E_v) = E$, for the rigid and the loose complex, respectively (i.e., the area lies between the abscissas $E = 0$ to 2.53 and $E = 0$ to 3.58, respectively). It is evident from equations 7 and 8 that the error in adopting these values for the entire range of E is zero at $p = 0$ but rises steadily to a maximum at $p = \infty$. At the latter pressure the unmodified and modified integrals assume a very simple form, and it is easily verified that the error at $p = \infty$ inherent in this approximation is 3 per cent and 0.5 per cent for the rigid and the loose complex, respectively.

These modified integrals are then further simplified by retaining only the first term of the expansion of $(E + E_0 + E_a)^{s-1}$:

$$(76 + E)^8 = (76)^8 + 8(76)^7E + \cdots$$

[8] For example, for a rigid complex with energy E such that $4.13 \leqslant E < 5.06$, the number of ways of distributing the energy among the oscillators is $\Sigma P_{E_v} = 6$. These are: one way corresponding to the excitation of no vibrational modes, one way for the second mode (3.58 kcal. mole^{-1}) raised to the first excited state, and two ways each for the degenerate fifth (4.13) and sixth (2.53) raised to their first states.

[9] Physically, these approximations are most valid if most of the recombining radicals are in their ground vibrational states. Thus they will be less valid at higher temperatures and for radicals which have many ways of distributing the first vibrational quanta, i.e., for large radicals. Nevertheless, a rough calculation of the latter indicates that, for the alkyl iodides at least, the error will still be small.

The resultant error is small, since k_e is appreciable only for small E's, i.e., where this approximation is valid. From equations 7 and 8 it is apparent that this error is a maximum at low pressures and falls to zero at $p = \infty$. Here again, the integrals assume a simple form at low pressure and it is readily verified that for $p = 0$, the error due to this approximation is -6.7 per cent for both complexes.

TABLE 1

ΣP_{E_v} and $\Sigma P_{E_v}(E-E_v)$ as a function of internal energy of activated complex

LIMITS OF E	ΣP_{E_v}	LIMITS OF E	$\Sigma P_{E_v}(E-E_v)$
0 to 2.53	1	0 to 3.58	$1(E-0) = E$
2.53 to 3.58	3	3.58 to 4.13	$E + 1(E - 3.58) = 2E - 3.58$
3.58 to 4.13	4	4.13 to 7.71	$2E - 3.58 + 2(E - 4.13) = 4E - 11.84$
4.13 to 5.06	6	7.71 to 8.17	$4E - 11.84 + 2(E - 4.13 - 3.58) = 6E - 27.26$

With these two approximations expressions 7 and 8 become:

Rigid complex:

$$k_{\text{uni}} = 1.93 \times 10^{13}\,(1 + 207/p)^{-1}e^{-E_a/RT} \tag{11}$$

Loose complex:

$$k_{\text{uni}} = 9.47 \times 10^{10}\,p[1 + xe^{x}Ei(-x)]e^{-E_a/RT} \tag{12}$$

where $x = 0.000429p$, with p the pressure in millimeters, and $Ei(-x)$ is the exponential integral, $-\int_x^{\infty} e^{-t}/t\,dt$. The values of $Ei(-x)$ were taken from the Federal Works Agency *Table of Sine, Cosine, and Exponential Integrals.*[10]

H. Equilibrium constant

The equilibrium constant for the reaction $CH_3I \rightleftarrows CH_3 + I$ was calculated as usual from the partition functions. For the vibration frequencies of the methyl radical, the values 8.17, 3.58, 8.79, and 4.13 kcal. mole^{-1} were adopted, the last two being doubly degenerate. The moments of inertia (14, page 239) were taken to be 110×10^{-40} (I_1) and 5.46×10^{-40} g. cm.^{2} molecule^{-1} for methyl iodide, and 3.07×10^{-40} and 6.14×10^{-40} for a planar methyl radical. (The latter value corresponds to a rotation at right angles to that indicated in figure 1, in the plane of the paper, and is readily seen to be one of the factors, I_2^*, occurring in κ. I_2 is 5.46×10^{-40}.) For $K = k_{\text{bi}}/k_{\text{uni}}$, we thus estimate 1.57×10^{-24} exp (ΔH_0RT) cc. molecule^{-1} sec.$^{-1}$ at 300°K. However, this neglects spin–orbit degeneracy (see following paragraph).

[10] If the first two terms of the expansion for $(76 + E)$ had been retained, the error in k_{uni} would have been -0.38 per cent at $p = 0$ and of course 0 at $p = \infty$ for both complexes. The resultant expressions could again have been reduced to exponential integrals.

k_{uni} is given as a function of the pressure p and of the assumed complex in figure 2.

I. Steric factor

k_{bi} is obtained from $k_{uni}K$, and the collision efficiency was calculated assuming a collision diameter of 4 Å. (the carbon–iodine distance where the Morse curve for C—I becomes practically flat, that is, the distance of separation in the activated complex). This corresponds then to a collision number of 3.46×10^{-10} cc. molecule^{-1} sec.$^{-1}$ The collision efficiency at any pressure thus becomes $1.57 \times 10^{-24} \exp(\Delta H_0/RT)(3.46 \times 10^{-10})^{-1} k_{uni}$ or $4.53 \times 10^{-15} k_{uni} \exp(\Delta H_0/RT)$, where k_{uni} is given in figure 2. These values have been tabulated in table 2 as a function of pressure and of the assumed complex. However, the values in the table have been corrected for spin–orbit degeneracy by dividing the above expressions by 8. This factor arises because there are two spin states for the methyl

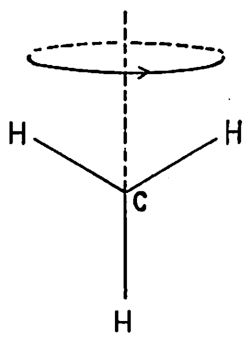

FIG. 1

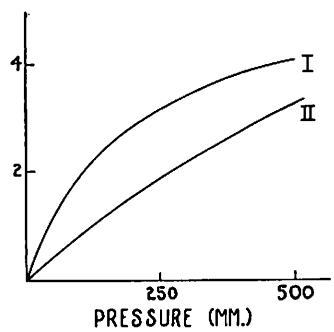

FIG. 2

FIG. 1. Doubly degenerate rotation about the axis in the plane of the paper

FIG. 2. Rate of decomposition of methyl iodide at 300°K. Ordinate for curve I, rigid activated complex, $k_{uni} \times 3 \times 10^{-13}e^{E_a/RT}$ sec.$^{-1}$ ($k_{uni} = 1.9 \times 10^{13}e^{-E_a/RT}$ sec.$^{-1}$ at $p = \infty$.) Ordinate for curve II, loose activated complex, $k_{uni} \times 10^{-13}e^{E_a/RT}$ sec.$^{-1}$ ($k_{uni} = 2.2 \times 10^{14}e^{-E_a/RT}$ sec.$^{-1}$ at $p = \infty$.)

radical and four possible orientations of the iodine in the ground state ($^2P_{3/2}$). Only one combination can give the ground state of methyl iodide; however, it is possible that there might be an excited singlet attractive state, arising from these configurations, which could interact with the ground state. Depending on the half-life of such an excited state and its rate of transition to the ground state, it might affect the unimolecular decomposition rate by as much as a factor of 2, and therefore also have some influence on the pressure effect. This we have not taken into account.

III. PREVIOUS TREATMENTS

The methyl iodide decomposition has been previously treated theoretically by Bawn (1) and Kimball (7). Using Ogg's (8) high-pressure value for the unimolecular rate constant, $3.93 \times 10^{12} e^{-43/RT}$, and a calculated value of the equilibrium constant for the reaction $CH_3I \rightleftarrows CH_3 + I$, Bawn estimated the steric factor to be unity (actually he calculated a value of 10). Now a preëxponential factor as low as Ogg's certainly corresponds to a rigid complex or some equivalent, and one would certainly expect therefore some steric effect. With the present estimated equilibrium constant,[11] it gives a steric factor of *ca.* 0.003 (not including the additional reduction due to the factor $e^{-h\nu_6/RT}$), and we feel justified in suggesting that Bawn's equilibrium constant is greatly in error.[12]

Kimball (7) roughly estimated a methyl iodide molecule to have two classical degrees of freedom and on that basis determined the half-life of an active molecule with an energy kT in excess of the activation energy to be 3.6×10^{-12} sec. at 300°C. Our corresponding values for the rigid and the loose activated complex are calculated from equations 4 and 5 for k_a, corrected as in Section II, C, to be 1.3×10^{-10} and 1.5×10^{-9} sec., respectively. Kimball's treatment suffers from the neglect of the quantized nature of the vibrations of the active molecule, as he and Kassel (6) have previously stated, and also from the neglect of the effect of anharmonicity on the coupling of the various vibrational modes. The effect of the former should reduce, and the latter increase, the half-life. The large discrepancy between our value and Kimball's is to be attributed to our assumption that all vibrational modes can contribute energy to the carbon–iodine bond.

TABLE 2

Collision efficiency for recombination of CH_3 *and* I

PRESSURE	ACTIVATED COMPLEX	
	Rigid	Loose
mm.		
20	0.0010	0.0010
60	0.0025	0.0030
150	0.0046	0.0068
300	0.0065	0.012
500	0.0078	0.019
∞	0.0109	0.125

The values for the efficiency should perhaps be further reduced if the activated complex is rigid, by a factor of $\exp(-h\nu_6/RT) = 0.014$ (see below).

IV. COMPARISON WITH EXPERIMENTAL DATA

A reliable knowledge of any one of the following effects would aid the decision as to the nature of activated complex: effect of pressure on the unimolecular rate constant, or on the rate of recombination, the magnitude of the high-pressure unimolecular rate constant, the activation energy, if any, for the recombination reaction, or, possibly, the variation of the recombination constant with the nature of the alkyl radical. Ogg (8) thermally decomposed methyl iodide in the presence of hydrogen iodide and interpreted the kinetics on the basis of two competing reactions, a bimolecular reaction of CH_3I and HI and a unimolecular de-

[11] Here we should use 43 kcal. mole^{-1} for ΔH_0 in our expression for the equilibrium constant. However, only preëxponential factors are involved in this calculation.

[12] The self-consistency, at least of the present estimated value for K, is reflected in the calculated high-pressure collision efficiency for the loose complex of unity (neglecting spin–orbit interaction), a result which of course is to be expected.

composition of CH_3I. However, it is quite possible that the equilibrium $CH_3I \rightleftharpoons CH_3 + I$ was partially established, followed by reactions of the methyl radical. Since the system is so complex, it would be fruitless to compare the pressure effect given in figure 2 with that roughly inferred from Ogg's data. While one could relate these experimental results to the effect of HI on the photolysis of methyl iodide, the correlations and conclusions would probably be pitted with assumptions.

The complex nature of Ogg's (8) system led Butler and Polanyi (2) to use a flow method to determine the unimolecular rate constant for methyl iodide. Their activation energy disagreed markedly with Ogg's. Unfortunately, there were still complications, due to possible occurrence of the back-reaction, and since the constant was estimated only at one temperature,[13] these data do not help us in arriving at a reliable decision.

While the reaction $CH_3 + I \rightarrow CH_3I$ is believed by many experimental workers to proceed at every collision, this controversy has not been settled and the bimolecular constant has not been determined quantitatively. Even less, of course, has the activation energy been determined.

We turn to the effect of the nature of the alkyl radical on the rate of recombination with iodine atoms. The rate of recombination decreases in the order CH_3, C_2H_5, C_3H_7. . . . This is inferred from the relative quantum yields for the liquid-phase photolysis.[14] Then, too, the same conclusion was reached by Jungers and Yeddanapalli (5) in their studies on the sensitization of ethylene polymerization by a series of alkyl iodides.

If all alkyl radicals reacted with iodine atoms *via* a loose complex no such effect would be observed, reaction proceeding at every collision. On the other hand, if the complex were rigid, the observed effect would occur. In this case, the free rotation of the radical would have to be frozen out and thus radicals with larger moments of inertia would be less apt to react.

Further, examination of Polanyi's data (2, 3) on the unimolecular decompositions of the organic iodides indicates that the activation energies estimated from the temperature coefficient and from the equation $k = 10^{13}e^{-E/RT}$ agree rather closely for organic iodides with large radicals. With smaller radicals in several cases a discrepancy of as much as 20 kcal. occurs. Polanyi attributed this discrepancy to the recombination of radicals and iodine atoms.

Another possible interpretation, however, is that the complex is rather loose for methyl but becomes increasingly rigid with increasing size of the radical.

However, the use of the term "rigid complex" may not give a true picture of the reaction. The concept of a rigid complex with two fairly stiff methyl–iodine bending vibrations when the distance between the methyl radical and the iodine

[13] Dr. Szwarc has called our attention to the agreement of the C—H bond strength in methane, inferred from Polanyi's activation energy for the decomposition of methyl iodide, with the corresponding value derived by Kistiakowsky and Stevenson from other data (see 11, page 77, for detailed references).

[14] It is true, however, that the nature of the recombination process in the photolysis of the alkyl iodides is still controversial. The recombination may proceed by reaction of the alkyl radicals with iodine molecules. Detailed references are given by Steacie (11).

atom is as great as 4 Å. is a puzzling one. While the iodine atom at this distance will offer a steric hindrance which will prevent complete rotation of the methyl radical, we would certainly expect the vibrational frequency to be greatly lowered because the lateral stiffness of the bond would be lacking. Nevertheless one can readily show that the concept of a rigid complex leads to the "normal" frequency factor of 10^{13} sec.$^{-1}$ for unimolecular decompositions. On the other hand, a loose complex leads to a significantly higher value, whose magnitude depends on the nature of the decomposing molecule (e.g., for methyl iodide, 10^{14}; for ethane, 10^{15}; etc.) There are three possibilities for explaining this "normal" frequency factor. The first is that the bending vibrational frequencies, though lowered, are still not lowered sufficiently to allow excitation of more than one or two quantum states of the activated complex. A second possibility is that there are classical mechanical difficulties in the transfer of energy from one degree of freedom to another. The third possibility is that there are quantum restrictions which make it difficult to go over from a rotational (or loose vibration) state to a firmly bound bending vibration in the time required for the mutual vibration of the carbon and iodine atoms along their line of binding. It may be that the necessary energy exchanges and shifts in quantum states can be effected only if the methyl radical is oriented with respect to the carbon–iodine bond in such a restricted fashion as to be equivalent to freezing the rotation out into a vibration. If such an orienting effect is present in any form, the activation energy of the recombination will be increased by the sum of the zero-point energies of those vibrations which arise from the freezing out of rotations. However, the rotations, as indicated above, may not need to be frozen out as much as would be indicated by the bending frequencies of the completely re-formed molecule, and the activation energy indicated in this way may be much too high. For this reason, we have not included this factor in the calculated collision efficiency for the rigid complex given in table 2.

One additional assumption requires further amplification. The assumption that every collision is effective in deactivating an active molecule is the usual one made in treatments of unimolecular reactions. Deactivation can occur either by the transfer of one or more vibrational quanta to another molecule, or by the conversion of that energy to the translational and/or rotational energy of the colliding molecule. The latter problem of conversion has been treated quantum-mechanically by O. K. Rice (9), who found that deactivation was probable at such collisions, but an efficiency of unity—of even say, one-tenth—can hardly be said to have been established, owing to the complications of the problem and the difficulty of solving the equations. We have made some quantum-mechanical calculations for the other question of transfer of vibrational energy, and these will be given in a future report.

Application of the present formalism to some five other cases where quantitative data are available indicates that the rigid activated complex model may prove a useful tool. Tentatively therefore, we shall assume a rigid complex for the recombination of methyl and iodine.

To sum up, on this assumption the collision efficiency for recombination at 25°C. varies from *ca.* 0.001 at 20 mm. to *ca* 0.01 at 700 mm., and the effect of pressure is as indicated in figure 2 (curve I) or in equation 11. Evidently, from figure 2, the reaction is proportional to the total pressure, below 100 mm., regardless of which complex is assumed, and if a deactivation collision efficiency of 0.1 instead of unity had been assumed, the same remark would apply to pressures below 1000 mm. Naturally, however, as emphasized above, these remarks are highly tentative, pending further work.

Finally, it would be highly desirable to determine *a priori* which type of activated complex supplies the more logical picture of the reaction. By tracing those free rotations of the radicals which become frozen into vibrations as the interradical distance decreases, and considering the appropriate potential surfaces for these degrees of freedom in the activated complex, we have made one preliminary attack on this problem. We hope to present some results on this approach at a later date.

V. SUMMARY

The steric factor of the recombination of free radicals and the effect of pressure on this recombination are not independent but mutually depend on the nature of the activated complex. For variously assumed complexes, both effects have been calculated for the recombination of methyl radicals and iodine atoms. The results are compared with the available data and with previous theoretical studies. It is tentatively inferred that the collision efficiency for the recombination increases from *ca.* 0.001 to *ca.* 0.01 as the total pressure is increased from 20 mm. to infinity. An expression is given for this pressure effect.

REFERENCES

(1) Bawn, C. E. H.: Trans. Faraday Soc. **31**, 1536 (1935).
(2) Butler, E. T., and Polanyi, M.: Trans. Faraday Soc. **39**, 19 (1943).
(3) Butler, E. T., Mandel, E., and Polanyi, M.: Trans. Faraday Soc. **41**, 298 (1945).
(4) Eyring, H.: J. Chem. Phys. **3**, 107 (1935).
(5) Jungers, J. C., and Yeddanapalli, L. M.: Trans. Faraday Soc. **36**, 483 (1940).
(6) Kassel, L. S.: J. Chem. Phys. **5**, 922 (1937).
(7) Kimball, G. E.: J. Chem. Phys. **5**, 310 (1937).
(8) Ogg, R. A.: J. Am. Chem. Soc. **56**, 526 (1934).
(9) Rice, O. K.: J. Am. Chem. Soc. **54**, 4558 (1932).
(10) Rice, O. K., and Gershinowitz, H.: J. Chem. Phys. **2**, 853 (1934); **3**, 479 (1935).
(11) Steacie, E. W. R.: *Atomic and Free Radical Reactions*, p. 242. Reinhold Publishing Corporation, New York (1946).
(12) Tolman, R. C.: *The Principles of Statistical Mechanics*. Oxford University Press, London (1938).
(13) West, W., and Paul, B.: Trans. Faraday Soc. **28**, 688 (1932).
(14) Wu, T. Y.: *Vibrational Spectra and Structure of Polyatomic Molecules*. J. W. Edwards, Ann Arbor, Michigan (1946).

APPENDIX

Approximations in integrals and per cent error incurred

(*i*) The assumption that $\Sigma P_{B_v} = 1$ for the rigid complex, and that $\Sigma P_{B_v}(E - E_v) = E$ for the loose complex for the entire range of E from 0 to ∞ leads to the following error:

(*a*) *Rigid complex:* No error for $p = 0$, since ΣP_{B_v} cancels in both numerator and denominator. The error is at a maximum for $p = \infty$. At $p = \infty$ the exact expression for k_{uni} except for a multiplicative constant is:

$$\int_0^{2.53} e^{-E/RT}\,dE + 3\int_{2.53}^{3.58} e^{-E/RT}\,dE + 4\int_{3.58}^{4.13} e^{-E/RT}\,dE + \cdots$$
$$= RT(0.986 + 0.036 + 0.006 + \cdots) = 1.03RT$$

The corresponding approximate expression for k_{uni} is proportional to:

$$\int_0^{\infty} e^{-E/RT}\,dE = 1.00RT$$

or more exactly, for comparison:

$$\int_0^{4.13} e^{-E/RT}\,dE = 0.999RT$$

The error is -3 per cent.

(*b*) *Loose complex:* The error is again at a maximum for $p = \infty$. At $p = \infty$ the exact value of k_{uni}, except for a multiplicative constant, is given by:

$$\int_0^{3.58} Ee^{-E/RT}\,dE + \int_{3.58}^{4.13} (2E - 3.58)e^{-E/RT}\,dE$$
$$+ \int_{4.13}^{7.71} (4E - 11.84)e^{-E/RT}\,dE + \cdots = RT^2\,(0.983 + 0.010 + 0.012 + \cdots)$$
$$= 1.005RT^2$$

(The higher terms are negligible.) The corresponding value for approximate k_{uni} is:

$$\int_0^{\infty} Ee^{-E/RT}\,dE = 1.000(RT)^2$$

or more exactly, for comparison:

$$\int_0^{7.71} Ee^{-E/RT}\,dE = 0.99997(RT)^2$$

The error is -0.5 per cent.

(*ii*) The error in retaining the first terms of expansion of $(76 + E)^8$: For both complexes there is no error at $p = \infty$, since here the expression disappears. The error is at a maximum for low pressures. For $p = 0$ the error is the same for the loose and the rigid complex and is calculated below.

The expression for k_{uni} as modified by (*i*) becomes, except for a multiplicative constant:

$$\int_0^{\infty} (76 + E)^8\, e^{-E/RT}\,dE = (76)^8RT(1 + 8RT/76) + 56(RT)^2/(76)^2 + \cdots$$
$$= (76)^8RT(1 + 0.0628 + 0.0035 + \cdots)$$

Thus retention of the first term only yields an error of -6.7 per cent, while retention of the first two terms yields an error of -0.38 per cent.