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Lifetimes of Active Molecules. I*

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The specific dissociation constants for various vibrationally excited molecules (methane, ethane, and propane) are inferred from an interpretation of experimental data on atomic cracking reactions and on the deuterization of free radicals. As was to be expected, these dissociation constants decrease with increasing number of degrees of freedom of the decomposing molecule.

INTRODUCTION

IN the past, the well-known Rice-Ramsperger, Kassel, and Hinshelwood quasi-unimolecular reaction rate theories have been applied to many unimolecular reactions. However, it is now known that many of these reactions are not simple unimolecular reactions, but rather are complex chain reactions. Thus, for purposes of testing the various unimolecular rate theories and thereby gaining information about intra- and intermolecular energy exchange, it would be well to examine other possible sources of data.

Effectively, the quasi-unimolecular theories were largely concerned with evaluation of the lifetime of the average decomposing molecule. When the pressure in such a reaction system was such that the time between successive collisions was comparable to or greater than this lifetime, the over-all unimolecular rate constant was smaller than the high pressure rate constant.

In the present paper, we shall attempt to deduce the lifetimes of various decomposing molecules from experimental data on the deuterization of methyl radicals and on the atomic-cracking of ethyl and propyl radicals. In a later paper, comparison with theoretical considerations and correlation with data on recombination of free radicals will be given.

To anticipate somewhat, the half-lives deduced below, while probably of the correct order of magnitude, can only be regarded as tentative pending further detailed study of these systems.

A. Deuterization of Methyl Radicals

The mercury photosensitized decomposition of methane results in the production of methyl radicals and hydrogen atoms, and in the presence of deuterium the following reactions can occur:

$$CH_4+Hg(^3P_1)=CH_3+H+Hg(^1S_0) \tag{1}$$

$$D_2+Hg(^3P_1)=2D+Hg(^1S_0) \tag{2}$$

$$CH_3+D=CH_2D+H \tag{3}$$

$$CH_2D+D=CHD_2+H, \text{ etc.} \tag{4}$$

Deuterated methanes then result from the recombination of these radicals with deuterium atoms. At sufficiently high deuterium atom concentrations, the corresponding reactions of hydrogen atoms may be neglected. Furthermore, at sufficiently low temperatures the high activation energy reactions

$$CH_3+D_2=CH_3D+D \tag{5}$$

$$CH_4+D=CH_3+HD \tag{6}$$

may also be disregarded.

It seems reasonable to assume that reactions (3) and (4) together with those of the recombination of radicals and atoms may be written, respectively, in a more fundamental manner as follows:

$$CH_3+D=CH_3D^* \tag{7}$$

$$CH_3D^*+M=CH_3D+M \tag{7'}$$

$$CH_3D^* \overset{k_7}{=} CH_2D+H \tag{7''}$$

$$CH_2D+D=CH_2D_2^* \tag{8}$$

$$CH_2D_2^*+M=CH_2D_2+M \tag{8'}$$

$$CH_2D_2^* \overset{k_8}{=} CHD_2+H \tag{8''}$$

and a similar sequence for CHD_2 radicals (which shall be designated as reaction sequence (9)). The starred molecules ("active molecules") contain about 100 kcal mole^{-1} of vibrational energy arising from the newly formed C$-$D bond. M denotes any third body capable of deactivating an active molecule. We wish to evaluate the specific dissociation constants k_7, k_8, and k_9. The corresponding half-life periods are then given by $\tau_i=(\ln_e 2)/k_i$, $i=7, 8, 9$.

In a preliminary investigation of such a system[1] Taylor and co-workers analyzed for the deuteromethanes by infrared methods. Their data are summarized in Table I, where the units may be regarded as arbitrary. The total pressure in the reaction system was 230 mm in each run. The rate constants k_i can be evaluated from this data. Consider the reaction sequence (7). If a CH_3D^* molecule reacts via (7′), CH_3D will be produced, and at small percent conversions this CH_3D will not undergo further reaction. If on the other hand CH_3D^* disappears via (7″), the resulting CH_2D radicals will finally end up as a mixture of CH_2D_2, CHD_3, and CD_4.

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[1] Morikawa, Benedict, and Taylor, J. Chem. Phys. 5, 212 (1937).

Thus the relative rate of (7′) and (7″) is given by the ratio, $(CH_3D)/(CH_2D_2+CHD_3+CD_4)$. The rate constant for (7′) is equal to $z_7\lambda_7$, where z_7 is the kinetic theory collision number and λ_7 is some factor equal to or less than unity, representing the efficiency of a deactivating collision.

Thus, if p denotes the total pressure, we have

$$\frac{k_7}{z_7\lambda_7 p}=\frac{k_7(CH_3D^*)}{z_7\lambda_7(CH_3D^*)p}=\frac{(CH_2D_2+CHD_3+CD_4)}{(CH_3D)}, \quad (9)$$

and similarly,

$$k_8=z_8\lambda_8 p \quad (CHD_3+CD_4)/(CH_2D_2)$$
$$k_9=z_9\lambda_9 p \quad (CD_4)/(CHD_3).$$

While the amount of CD_4 produced was not determined, it may be neglected for the present purpose, according to the trends in Table I. For simplicity of notation, set $z_n\lambda_n=z\lambda$ and take $z=5\times10^6$ mm^{-1} sec^{-1} leaving λ arbitrary for the present. Averaging the data of Table I, we find for k_7 and k_8 the values $8\times10^8\lambda$ and $5\times10^8\lambda$ sec^{-1}, respectively. In quasi-unimolecular theories, it is customary to set $\lambda=1$, though there is neither sufficient theoretical nor sufficient experimental justification for this as yet.

B. Atomic Cracking of Ethyl Radicals

The atomic cracking of ethyl radicals, described by Eq. (10), competes with the recombination reaction (11). These reactions

$$H+C_2H_5=2CH_3 \quad (10)$$

$$H+C_2H_5=C_2H_6 \quad (11)$$

may be assumed to occur in the following manner:

$$H+C_2H_5=C_2H_6^* \quad (12)$$

$$C_2H_6^*\overset{k_{12}}{=}2CH_3 \quad (12')$$

$$M+C_2H_6^*=C_2H_6+M. \quad (12'')$$

With suitable experimental conditions, the methyl radicals will end up largely as methane, which can then be measured. If the rate of (12″) can also be estimated, then from the relative rates of (12′) and (12″), k_{12} can be determined.

In the mercury photosensitized reaction of ethane the occurrence of (12″) (or really, of (11)) has been suggested as a principal cause for the low quantum yields at low ethane pressures and also to account for the variation of this yield with pressure. A detailed study of this photosensitized reaction at room temperature has recently been made,[2] and the following mechanism together with Eqs. (10) and (11) (or essentially, (12), (12′), and (12″)), seems to account for most features of the experimental data fairly well.

TABLE I. Deuteromethanes produced by mercury photosensitization of CH_4+D_2.

Run	CH_3D	CH_2D_2	CHD_3
47	12	7	2
91	25	12	7
97	16	6	3

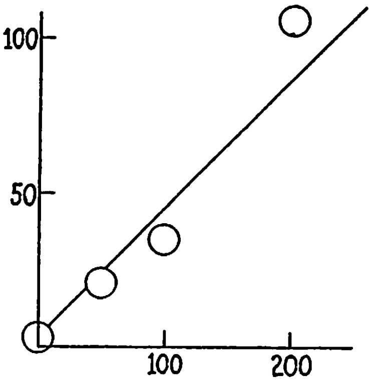

FIG. 1. Experimental data for estimation of k_{12}. Ordinate: $2(1-\phi_{H_2})/\phi_{CH_4}$. Abscissa: pressure in mm.

$$C_2H_6+Hg(^3P_1)=C_2H_5+H+Hg(^1S_0) \quad (13)$$

$$H+C_2H_6=C_2H_5+H_2 \quad (14)$$

$$CH_3+H=CH_4 \quad (15)$$

$$2C_2H_5=C_4H_{10}. \quad (16)$$

These free radicals may also undergo other reactions and several of these are considered in the Appendix. Steady-state equations for CH_3, H, and $C_2H_6^*$ can be shown to lead to the relation,

$$2(1-\phi_{H_2})/\phi_{CH_4}=z\lambda p/k_{12}+3, \quad (17)$$

where ϕ denotes quantum yield. From the data of reference 2 we have plotted in Fig. 1, $2(1-\phi_{H_2})/\phi_{CH_4}$ *vs* the pressure, p. $z\lambda/k_{12}$ is estimated from the slope to be 0.45 mm^{-1}. Setting $z=5\times10^6$ mm^{-1} sec^{-1}, k_{12} is estimated to be $1.1\times10^7\lambda$ sec^{-1}.

C. Atomic Cracking of Propyl Radicals

Hydrogen atoms and propyl radicals may react via (18) and (19).

$$H+C_3H_7=CH_3+C_2H_5 \quad (18)$$

$$H+C_3H_7=C_3H_8. \quad (19)$$

As before, these reactions may also be written as:

$$H+C_3H_7=C_3H_8^* \quad (20)$$

$$C_3H_8^*\overset{k_{20}}{=}CH_3+C_2H_5 \quad (20')$$

$$C_3H_8^*+M=C_3H_8+M. \quad (20'')$$

Data on the mercury photosensitized reaction of propane[3] at room temperature may be interpreted by a

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[2] B. de B. Darwent and E. W. R. Steacie, J. Chem. Phys. **16**, 381 (1948).

[3] B. de B. Darwent and E. W. R. Steacie, J. Chem. Phys. **13**, 563 (1945).

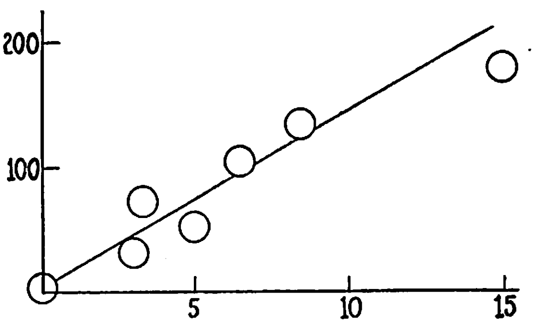

FIG. 2. Experimental data for estimation of k_{20}. Ordinate: $(1-\phi_{H_2})/\phi_{CH_4}$. Abscissa: pressure in mm.

set of reactions analogous to those for ethane:

$$C_3H_8+Hg(^3P_1)=C_3H_7+H+Hg(^1S_0) \quad (21)$$

$$H+C_3H_8=H_2+C_3H_7 \quad (22)$$

$$2C_3H_7=C_6H_{14} \quad (23)$$

together with the sequence (20), (20′), (20″) and some reactions involving the methyl and ethyl radicals produced by (20′).

As before, the methyl radicals are assumed to end up largely as methane. (See Appendix for a discussion of this question.) Experimental data in references 2 and 3 suggest that ethyl radicals react largely via (11) and (16) in the pressure range given in Fig. 2. Steady-state considerations of reactions (15), (20) to (23), and (11) or (16) lead to the relation,

$$(1-\phi_{H_2})/\phi_{CH_4}=z\lambda p/k_{20}+n, \quad (24)$$

where $n=3$ or 2, according as reaction (11) or (16) be included. While only relative quantum yields are given in reference 3, absolute yields were obtained by comparison with the data of another study of this system.[4] We have plotted $(1-\phi_{H_2})/\phi_{CH_4}$ *vs* p in Fig. 2. Evidently from this graph, it makes little difference whether the intercept n equals 2 or 3. Setting $z=5\times10^6$ mm^{-1} sec^{-1}, k_{20} is estimated from the slope to be $3.6\times10^5\lambda$ sec^{-1}.

The half-lives, τ, corresponding to the specific dissociation constants estimated above, are summarized in Table II.

Assuming λ to have roughly the same value in each case, the half-life, τ, is seen to increase with the size of the active molecule, as expected. In each case the active molecule contains about 100 kcal mole^{-1} vibrational energy arising from the newly formed C—H or C—D bond. The larger molecules have more vibrational modes in which this energy can be distributed, so that there is less chance of this energy accumulating in one bond (which could result in decomposition of the molecule). Furthermore, since a C—C bond is about 10–15 kcal mole^{-1} weaker than a C—H bond, the excess of energy over and above that required for reaction is greater for the third and fourth reactions in Table II. If this energy excess were the same for all reactions in this Table, the spread of τ-values would be even greater than that indicated.

TABLE II. Half-lives of various active molecules.

Active molecule	Products	$\tau\times10^9\lambda$sec
CH_3D^*	CH_2D+H	1.4
$CH_2D_2^*$	CHD_2+H	0.9
$C_2H_6^*$	$2CH_3$	60
$C_3H_8^*$	$CH_3+C_2H_5$	2×10^3

APPENDIX

We would like to consider briefly some of the assumptions made in the above treatment.

(a) The low quantum yield in the ethane and propane reactions was attributed to the back reactions (11) and (19), respectively, but not to any possible inefficiency in the primary act. That is, reactions (13) and (21) were assumed to be 100 percent efficient. From the mechanisms given, it can be seen that theoretically, $\phi_{H_2}=1$ at sufficiently high pressures. Extrapolation of the experimental data indicates this to be quite possible, though further study of this question is necessary.

If an efficiency of the primary act, α, $(\alpha\leq1)$ is assumed, it can be shown that Eqs. (17) and (24) need be amended only in that the ϕ's should be replaced by ϕ/α. In the pressure range considered, $1-\phi_{H_2}/\alpha\cong1$ for both photosensitized reactions, so that the k values will be in error by a factor, α. The data[2] suggest that α lies within the range, 0.5 to 1.

(b) In the ethane photosensitized reaction, the following fates for methyl radicals may also be suggested:

$$CH_3+C_2H_6=CH_4+C_2H_5, \quad (25)$$

$$CH_3+C_2H_5=C_3H_8, \quad (26)$$

$$2CH_3=C_2H_6. \quad (27)$$

The experiments discussed above were carried out at room temperature, so that the relatively high activation energy reaction (25) is improbable. Nevertheless, inclusion of (25) in the steady-state equations yields an equation negligibly different from (17).

While the amount of propane produced, if any, was not measured, earlier work[5] on the same system indicated that reaction (26) could be neglected, at least if the ethane pressure exceeded 15 mm. Logically, one would expect the extent of (26) to be intermediate between that of (27) and that of butane production, (16). Since (26) may be neglected, while the butane production exceeds that of propane, (27) may likewise be disregarded.

(c) In these mercury photosensitized reactions, a so-called reaction volume effect enters. Most of the radiation is absorbed close to the incident face, so that the reaction is more or less confined to a small volume, whose dimensions are dependent on the pressure of the hydrocarbon. This effect is generally neglected as a first approximation in quantitative treatments of photosensitized reactions. Nevertheless, repetition of this work at lower mercury concentrations, i.e., under conditions corresponding to a large effective reaction volume, would be helpful in clarifying this question.

Finally, the values of the dissociation constants for ethane and propane may be checked by rather independent methods, e.g., by investigating the reaction of deuterium atoms with these hydrocarbons and analyzing for the amount of methane and deuterated ethanes and propanes produced. While some such data do exist in the literature, the conditions chosen do not appear to be the most desirable ones for evaluation of these constants.

ACKNOWLEDGMENT

I should like to thank Professor O. K. Rice for reading the manuscript and for making several helpful suggestions.

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[4] E. W. R. Steacie and D. J. Dewar, J. Chem. Phys. 8, 571 (1940).

[5] E. W. R. Steacie and N. W. F. Phillips, J. Chem. Phys. 6, 179 (1938).