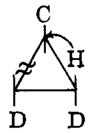
and only a fairly wide range of values for the recyclization rate constant can be given. In an absence of this knowledge, and in recognition of the mechanism of H "turn-over" of Smith[14] (which was later modified by him[6] to include some ring expansion, with consequent less real difference and increasing semantic difference between his and our viewpoints), we may simply characterize the mechanism by its activated complex, namely, as "expanded ring." On this basis, Simons[24] has calculated a complete fall-off curve for geometric isomerization of cyclopropane-d_2 in good agreement with experiment, both with respect to shape and absolute pressure.

The *cis–trans* isomerizations of cyclopropane-d_2 and dimethylcyclopropane involve, respectively, the rotations of $>C<^{H}_{D}$ or $>C<^{H}_{CH_3}$ groups. Geometric isomerization of methylcyclopropane-d_2 may involve both motions and the total rate will reflect the magnitude of each. The rate constant obtained in this work is a measure of k_{12} (or k_{13}) and k_{32} (or k_{23}), but it is impossible so far to evaluate the individual contributions. We had hoped to determine the relative magnitude of k_{21} (or k_{31}) and k_{32} (or k_{23}), and whether only one group at a time can rotate, as proposed by Smith, or whether both groups of the expanded-ring complex can rotate simultaneously, as proposed by us. The starting reactant should be either isomer II or III, or, less desirably, data for I could be combined with present measurements; these preparative efforts continue.

Some specific experimental evidence already can be cited, however, against the Smith mechanism. Consider the relative rates of formation of butene-1 by either



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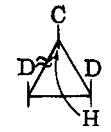
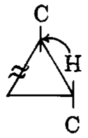
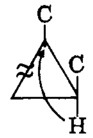


Since H (or D) turn-down into the plane is involved in Smith's reaction coordinate, then a difference in rate would be expected when the more mobile H was *cis* or *trans* to the CH_3 substituent; as described in the results, none was found. Similarly, none was found earlier by Flowers and Frey[12] between the rates of formation of 2-methylbutene-1 from *cis*- and *trans*-dimethylcyclopropane



and



Benson[15b] has given a qualitative argument that Smith's mechanism should involve an activation energy appreciably greater that 65 kcal.

Finally, it should be noted that calculation of the rate constant for cyclopropane structural isomerization in no way depends on formation of a trimethylene intermediate or its properties, since a separate activated complex for structural isomerization having higher free energy exists, as pointed out by Schlag and Rabinovitch[6,25]; RSW noted that reasonable models for these complexes, considered as formed from a trimethylene intermediate (see also ref. 15a), gave back the proper relative magnitudes of A factors, *i.e.*, entropies of activation and relative observed rates of geometric (*cf.* ref. 22) and structural (*cf.* ref. 7c, 8b) isomerization of cyclopropane-d_2.

[23] H. J. Dauben, Jr., private communication, gives the value as 9.7 kcal. Reference 6 cites explicit experimental evidence from work of Flowers and Frey for a recyclization barrier. Owing to the relative rate[15a] of internal rotation, absence of a barrier would support a Smith[14] type mechanism.

[24] J. W. Simons and B. S. Rabinovitch, submitted to *J. Phys. Chem.*

[25] The statement by Benson and Nangia[19] that SR described the geometric and structural complexes to have the same E_a value is explicitly contradicted in ref. 6 (see also footnote *b*, Table II); various other statements in this and earlier references by these authors also reflect some misunderstandings concerning our interpretations.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE PENNSYLVANIA STATE UNIVERSITY, UNIVERSITY PARK, PENNA.]

The Xenon-Radiosensitized Deuterium–Methane Exchange. Recombination Rate Constant for Deuterium Atoms and Methyl Radicals

BY A. MASCHKE AND F. W. LAMPE

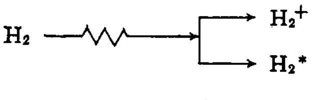
RECEIVED AUGUST 31, 1963

The radiation-induced deuterium–methane exchange, sensitized by xenon, is shown to proceed *via* deuterium atoms and methyl radicals. All deuteriomethanes (d_1–d_4) are formed simultaneously, and, at low partial pressures of deuterium, significant amounts of deuterioethanes, deuteriopropanes, and deuteriobutanes are formed. A kinetic treatment of the deuteriomethane formation results in an estimate of the recombination rate constant for deuterium atoms and methyl radicals that is in good agreement with the specific collision rate assuming a collision diameter of 2.6 Å.

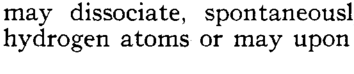
Introduction

The use of rare gases to sensitize hydrogen atom reactions in gaseous systems subjected to ionizing radiation was reported some time ago.[1,2] This technique potentially can provide rather high concentrations of hydrogen atoms and thus seems to afford a convenient way to study reactions of hydrogen atoms with molecules and free radicals. This paper reports the results of studies in which xenon was used to sensitize the deuterium atom-induced exchange between deuterium and methane.

Briefly, the technique is based upon the use of high concentrations of sensitizer and hydrogen (or deuterium) and relatively low concentrations of substrate. In this way more than 90% of the energy absorbed by the system, in the passage of the ionizing radiation, can be absorbed by sensitizer and hydrogen (or deuterium); the result of such energy absorption is ionization and excitation. Letting X represent sensitizer, we may thus write for the primary act



(A)



(B)

Electronically and/or vibrationally excited hydrogen may dissociate, spontaneously or upon collision, to hydrogen atoms or may upon collision be deactivated.

[1] F. W. Lampe, *J. Am. Chem. Soc.*, **82**, 1551 (1960).

[2] C. F. Smith, B. G. Corman, and F. W. Lampe, *ibid.*, **83**, 3559 (1961).

Electronically excited sensitizer may dissociate molecular hydrogen to hydrogen atoms similar to the manner of mercury photosensitization. The net result of this primary excitation is either the formation of hydrogen atoms or degradation of the energy used in producing excitation. The ionic species X^+ and H_2^+ are known, by direct observation[3] and indirect kinetic evidence,[4] to react very rapidly by the reactions

$$X^+ + H_2 \longrightarrow XH^+ + H \quad (C)$$

$$H_2^+ + H_2 \longrightarrow H_3^+ + H \quad (D)$$

$$H_2^+ + X \longrightarrow XH^+ + H \quad (E)$$

$$H_3^+ + X \longrightarrow XH^+ + H_2 \quad (F)$$

The protonated species XH^+ can most likely undergo only neutralization to xenon and hydrogen atoms. Thus the kinetically significant result of energy absorption in such a system is that of forming hydrogen atoms which may then react with either the relatively low-concentration substrate or with themselves.

Xenon was chosen as the sensitizer in this study of the deuterium-methane exchange for several reasons: (1) Its high atomic number enables one to get the largest sensitizing effect for a given pressure and hence permits the use of rather low pressures; (2) the occurrence of reaction (F), which takes place only for Kr and Xe,[4] leads to the common ion XH^+ whether energy is absorbed by sensitizer or by hydrogen; (3) the ground state xenon ion, $Xe^+(^2P_{3/2})$, cannot charge-exchange efficiently with methane since the reaction is endothermic by about 23 kcal./mole. Hence, interaction between ionized sensitizer and substrate is minimized; (4) CH_4^+ ions, which are formed upon direct absorption of energy by methane, can charge-exchange efficiently with xenon, which would then be followed by (C) to yield again XeH^+. Thus the choice of xenon as sensitizer would appear to result in nearly all ionization leading to XeH^+ and its neutralization products Xe + H. (Direct ionization of CH_4 to CH_3^+ + H would not; however, under our conditions less than 4% of the total energy absorbed would be so utilized.) This ion-scavenging action of xenon, in a methane-hydrogen system, which is most likely due to formation of XeH^+, has been reported by Pratt and Wolfgang.[5]

Experimental

Radiation Source.—The radiation employed in this work was the electron beam from the 3-Mev. Van de Graaff electrostatic accelerator at the Radiation Laboratory of the Mellon Institute. In all experiments the accelerating voltage was maintained at 2.5 Mev. and the electron beam current at approximately 10 μamp.

Reaction Vessels.—The gaseous irradiations were carried out in spherical 1-l. Pyrex vessels having freeze-out fingers and which had been painted externally with conductive silver paint to provide a path to ground for any electrons stopped in the glass. Each vessel was fitted with a break-seal so that during an irradiation, and any subsequent storage time, the gases were not in contact with stopcock grease. Before filling the vessels for an irradiation they were evacuated to about 10^{-6} mm. and pumped for 1 to several hours.

Materials.—Phillips research grade methane, stated to have a purity of 99.6 mole %, was allowed to distil slowly from a trap immersed in liquid nitrogen in such a way that the middle third was retained and stored in a 5-l. storage bulb on the vacuum line. Research grade xenon, obtained from the Matheson Co., was treated in a manner similar to that for methane. Matheson "best" grade hydrogen and deuterium (99.5%) obtained from the Isomet Corporation were used as received. Phillips research grade propylene, which was used for dosimetry purposes, was used as received.

Analyses.—Analyses of all radiolysis products of the methane-xenon-deuterium (or hydrogen) mixtures were carried out on a Bendix Model 14-101 time-of-flight mass spectrometer. Analyses for molecular hydrogen in the dosimetry irradiations of propylene were carried out by gas chromatography using a silica gel column and nitrogen as carrier gas. As we were unable to find a column that would separate satisfactorily xenon and the relatively small amounts of ethane formed in the irradiations, it was not feasible to separate the irradiated samples by gas chromatography before analyzing them mass spectrometrically.

Dosimetry.—Propylene was used as a gas phase dosimeter. It has been reported[6] that hydrogen is formed in the radiolysis of propylene with $G(H_2) = 1.1$ and that the yield of hydrogen produced is directly proportional to dose over a conversion range much wider than that used in our dosimetry runs. In our four dosimetry irradiations, the percentage of hydrogen in the final products was never greater than 0.333%. Using $G(H_2) = 1.1$ and standard electron energy-loss data,[7] the dose rate to 150 mm. of xenon for 2.5-Mev. electrons at a current of 10 μamp. was determined to be 9.65×10^{14} e.v.-cm.$^{-3}$-sec.$^{-1}$, with a precision of about 0.5%. However, the accuracy, which was limited by uncertainty in $G(H_2)$, is considered to be of the order of 5%. Standard energy-loss data[7] were used to compute energy absorption by deuterium (or hydrogen) and methane.

Nature of the Irradiations.—All irradiations were carried out at room temperature or slightly above, owing to some heating of vessel walls at the entrance and exit areas of the electron beam. All irradiations were carried out with 150 mm. of xenon and 50 mm. of methane, but with varying deuterium (or hydrogen) pressure. Three series of irradiations were carried out: (1) In the first series, mixtures with 100, 150, 200, and 300 mm. of deuterium were irradiated at varying doses, with the maximum methane conversion being somewhat less than 8%. (2) When it was established by these experiments that product formation in this range of conversion was reasonably linear with dose, a number of single-dose experiments with deuterium pressures ranging from 25 to 175 mm. and with methane conversions of the order of 3-5% were carried out. (3) Finally, a series of single-dose irradiations at the same methane conversion levels but for various pressures of hydrogen ranging from 0 to 250 mm. were conducted.

Results and Discussion

HD and Deuteriomethane Formation.—The 100-e.v. yields of HD and the deuteriomethanes as a function of deuterium pressure are shown in Fig. 1. What is not conveyed by this figure is the important fact that all deuteriomethanes are formed simultaneously. This is shown in Fig. 2, in which are plotted the observed deuteriomethane partial pressures as a function of total dose to the system. This finding of simultaneous deuteriomethane formation is in apparent disagreement with the results of Firestone, Lemr, and Trudel.[8] These authors studied the deuterium-methane exchange initiated by tritium β-rays and found that the only initial exchange product was CH_3D. This apparent disagreement between two studies is attributable, we think, to quite large differences in experimental conditions and will be discussed in a later section.

Ethane and Higher Product Formation.—It is apparent, from close inspection of Fig. 1, that the HD formed is in excess of the deuterium accounted for in the deuteriomethanes, and that the amount of this excess decreases with increasing deuterium pressure. The dependence of this material balance on pressure can be seen more clearly in Fig. 3 in which is plotted the ratio of the number of deuterium atoms appearing in the deuteriomethanes to the HD formed. Thus at 300 mm. of deuterium the deuteriomethanes account for nearly 80% of the HD formed, but only for about 20% at 25 mm. of deuterium. This means, of course, that other products containing deuterium must be formed, and in increasing amounts as the deuterium pressure is lowered. Mass spectrometric analyses of the runs at a deuterium pressure of 150 mm. indeed showed significant amounts of ethanes with deuteration up to ethane-d_5. Although an approximate mass spectral analysis of the deuterated ethanes, for the irradiations at 150 mm. of deuterium, was carried out

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(3) D. P. Stevenson and D. O. Schissler, *J. Chem. Phys.*, **23**, 1353 (1955).

(4) O. A. Schaefer and S. O. Thompson, *Radiation Research*, **10**, 671 (1959).

(5) T. H. Pratt and R. Wolfgang, *J. Am. Chem. Soc.*, **83**, 10 (1961).

(6) K. Yang and P. L. Gant, *J. Phys. Chem.*, **65**, 1861 (1961).

(7) NBS Circular 577 and Supplement, U. S. Dept. of Commerce, 1958.

(8) R. F. Firestone, C. F. Lemr, and G. J. Trudel, *J. Am. Chem. Soc.*, **84**, 2279 (1962).

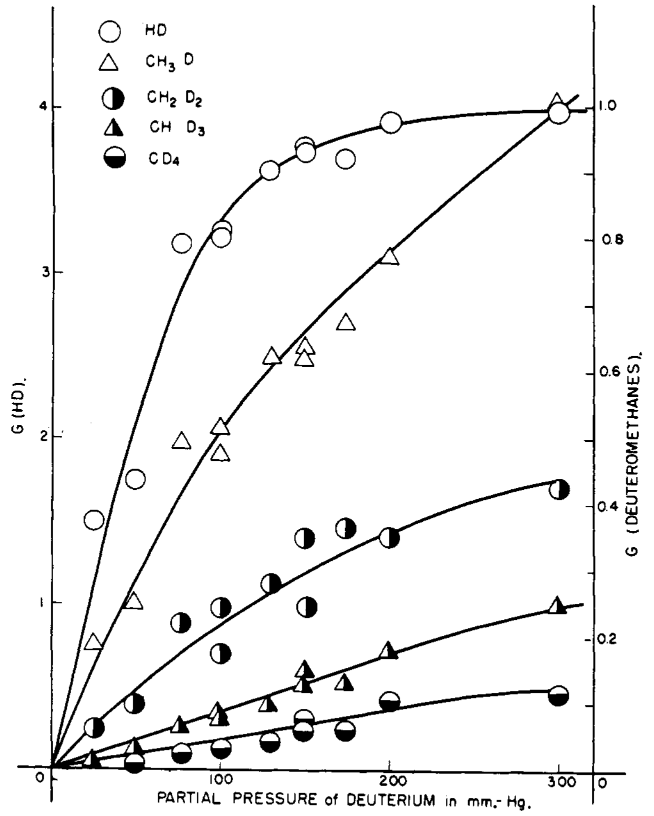

Fig. 1.—HD and deuteriomethane yields as a function of deuterium pressure.

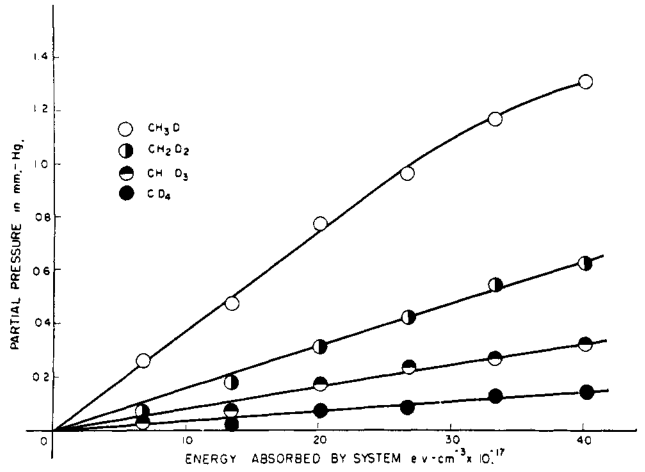

Fig. 2.—Deuteriomethane formation as a function of dose for $P(D_2)$ of 150 mm.

(using the mass spectral patterns recently reported[9]) such measurements were not capable of yielding the total ethane formed. This is because the relatively small amounts of deuterated propanes and butanes formed contribute such large amounts of deuterated ethyl ions to the spectrum that reliable values for the concentrations of the lower deuterated ethanes, particularly C_2H_6, could not be obtained. Thus the experiments using hydrogen instead of deuterium were carried out. The *G*-values for ethane, propane, and butane are shown in Fig. 4, in which 100-e.v. yields for the three species are plotted as a function of hydrogen pressure. The decrease of yields to a plateau with increasing hydrogen pressure is typical of the effect of hydrogen on rare gas sensitized radiolyses[2,10] and has been shown[2,10] to be a result of the competition between hydrogen and substrate for ionized and excited rare gas.

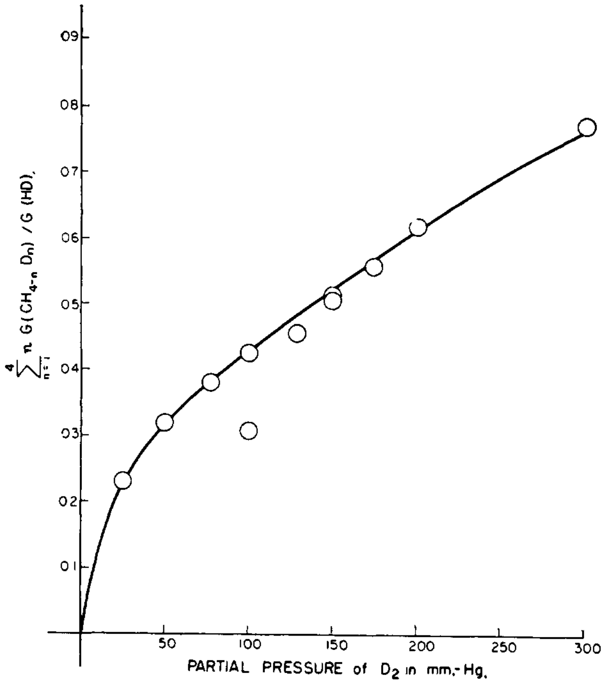

Fig. 3.—Dependence of material balance on deuterium pressure.

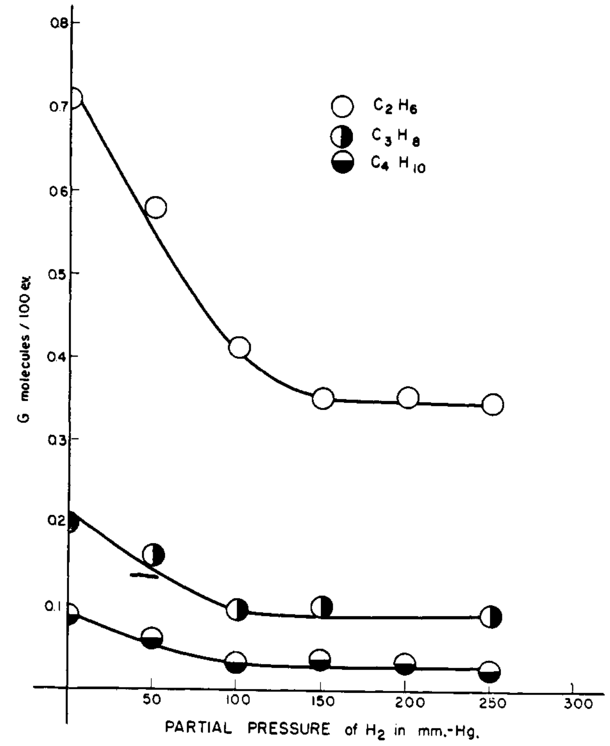

Fig. 4.—Ethane, propane, and butane formation as a function of hydrogen pressure.

Mechanistic Considerations.—Pratt and Wolfgang[5] have shown that xenon effectively scavenges ionic exchange intermediates in the tritium–methane system. Similarly, Schaefer and Thompson[4] have shown that xenon effectively scavenges ionic exchange intermediates in the hydrogen–deuterium system, presumably by formation of XeH^+ or XeD^+. Our experiments bear this out also, for no reasonable exchange scheme *via* D_3^+, CH_5^+, and their isotopically substituted analogs can account for simultaneous formation of the

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[9] J. A. Bell and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **84**, 3417 (1962).

[10] J. H. Futrell and T. O. Tiernan, *J. Chem. Phys.*, **38**, 150 (1963).

deuteriomethanes. Thus we assume that ionization of xenon or deuterium (which accounts for a minimum of 94% of the energy absorbed in our irradiations) leads only to deuterium atoms *via* formation and neutralization of XeD^+, *viz.*

$$Xe^+ + D_2 \longrightarrow XeD^+ + D \tag{C^1}$$

$$D_2^+ + D_2 \longrightarrow D_3^+ + D \tag{D^1}$$

$$D_2^+ + Xe \longrightarrow XeD^+ + D \tag{E^1}$$

$$D_3^+ + Xe \longrightarrow XeD^+ + D_2 \tag{F^1}$$

$$XeD^+ + e \longrightarrow Xe + D \tag{G}$$

Actually, this will be strictly true only at sufficiently high deuterium pressures, because deuterium and methane will compete for interaction with Xe^+ and Xe^*. However, the results shown in Fig. 4 suggest that such competition is only important at deuterium pressures less than about 100 mm. Even at lower pressures of deuterium our assumption that deuterium atoms are the only important intermediates (from the standpoint of chemical conversion of methane) formed in the primary act of energy absorption is at least partially valid. Certainly the direct absorption of energy of methane will produce CH_4^+ ions. With the excess of xenon with respect to methane, one expects a major reaction of CH_4^+ to be that of charge exchange with xenon which in turn is followed by reaction (C^1). As a result of these considerations, we make the assumption that all chemical change in methane is due to deuterium atoms formed in the primary acts of energy absorption and in the rapid ion–molecule reactions and neutralization of XeD^+. We take the rate of formation of deuterium atoms to be

$$\frac{d[D]}{dt} = \frac{2Q_{Xe}}{W_{Xe}} + \frac{2Q_{D_2}}{W_{D_2}} \tag{E1}$$

where Q is the rate of absorption of energy per unit volume and W is the average energy expended per ion-pair formation.[11] This really gives only a lower limit to the rate of formation of deuterium atoms since it neglects deuterium atom formation arising from nonionizing excitation processes.

In view of the very probable suppression of exchange *via* ionic intermediates,[4,5] and our observation of simultaneous deuteriomethane formation, the most reasonable exchange mechanism to form the major products, following D atom formation is[12,13]

$$D + CH_4 \longrightarrow HD + CH_3 \tag{1}$$

$$CH_3 + D \longrightarrow CH_3D^* \tag{2a}$$

$$CH_3D^* + M \longrightarrow CH_3D + M \tag{3a}$$

$$CH_3D^* \longrightarrow CH_2D + H \tag{4a}$$

$$CH_3D^* \longrightarrow CH_3 + D \tag{5a}$$

$$CH_2D + D \longrightarrow CH_2D_2^* \tag{2b}$$

$$CH_2D_2^* + M \longrightarrow CH_2D_2 + M \tag{3b}$$

$$CH_2D_2^* \longrightarrow CHD_2 + H \tag{4b}$$

$$CH_2D_2^* \longrightarrow CH_2D + D \tag{5b}$$

$$CHD_2^* + D \longrightarrow CHD_3^* \tag{2c}$$

$$CHD_3^* + M \longrightarrow CHD_3 + M \tag{3c}$$

$$CHD_3^* \longrightarrow CD_3 + H \tag{4c}$$

$$CHD_3^* \longrightarrow CHD_2 + D \tag{5c}$$

$$CD_3 + D \longrightarrow CD_4^* \tag{2d}$$

$$CD_4^* + M \longrightarrow CD_4 + M \tag{3d}$$

$$CD_4^* \longrightarrow CD_3 + D \tag{4d}$$

$$H + D_2 \longrightarrow HD + D \tag{6}$$

$$D + D + M \longrightarrow D_2 + M \tag{7}$$

$$CH_mD_n + CH_iD_k \longrightarrow C_2H_{i+m}D_{k+n} \tag{8}$$

Recombination of H and D atoms and abstraction of hydrogen from methane by H atoms has been omitted because we have never observed significant amounts of H_2 in the radiolysis products and because of the high probability of (6) with the large concentrations of deuterium present. As will be shown below, this mechanism leads to conclusions consistent with our data and to an estimated value for the rate constant for recombination of methyl radicals and deuterium atoms.

From the mechanism we can immediately write for the rates of formation of HD and the deuteriomethanes

$$d[HD]/dt = k_1[CH_4][D] + k_6[D_2][H] \tag{E2}$$

$$\frac{d[CH_3D]}{dt} = k_{2a}[CH_3][D]\,\frac{k_{3a}[M]}{k_{4a} + k_{5a} + k_{3a}[M]} \tag{E3}$$

$$\frac{d[CH_2D_2]}{dt} = k_{2b}[CH_2D][D]\,\frac{k_{3b}[M]}{k_{4b} + k_{5b} + k_{3b}[M]} \tag{E4}$$

$$\frac{d[CHD_3]}{dt} = k_{2c}[CHD_2][D]\,\frac{k_{3c}[M]}{k_{4c} + k_{5c} + k_{3c}[M]} \tag{E5}$$

$$\frac{d[CD_4]}{dt} = k_{2d}[CD_3][D]\,\frac{k_{3d}[M]}{k_{4d} + k_{3d}[M]} \tag{E6}$$

In order to treat such a complex system we must make several simplifying assumptions. First, the excited deuteriomethane molecules contain the vibrational energy of the C–D bond; since they then contain sufficient energy to break any bond in the molecule we assume that the total dissociation rate constants, ($k_4 + k_5$), are equal for all excited species. Second, we assume that the ratios of rate constants, k_4/k_5, are determined solely by statistics[14]; thus, for example, $k_{4a}/k_{5a} = 3$, etc. Third, we assume that the deactivation rate constants, k_3, and the association rate constants, k_2, are the same for all species. These assumptions, coupled with taking the ratios of rates to be equal to the ratio of G-values, when applied to eq. E3–E6 lead us to the expressions

$$\sum_{n=1}^{4} \frac{d[CH_{4-n}D_n]}{dt} = \frac{k_2k_3[M][D]}{k_d + k_3[M]}\{[CH_3] + [CH_2D] + [CHD_2] + [CD_3]\} \tag{E7}$$

where $k_d = k_{4a} + k_{5a} = k_{4b} + k_{5b}$, etc., and

$$\frac{(d[CH_3D]/dt)}{(d[CH_2D_2]/dt)} = \frac{[CH_3]}{[CH_2D]} = \frac{G(CH_3D)}{G(CH_2D_2)} \tag{E8}$$

$$\frac{(d[CH_3D]/dt)}{(d[CHD_3]/dt)} = \frac{[CH_3]}{[CHD_2]} = \frac{G(CH_3D)}{G(CHD_3)} \tag{E9}$$

$$\frac{(d[CH_3D]/dt)}{(d[CD_4]/dt)} = \frac{[CH_3]}{[CD_3]} = \frac{G(CH_3D)}{G(CD_4)} \tag{E10}$$

If we now further assume that the sum of the concentrations of methyl radicals in a deuterium irradiation is equal to the methyl radical concentration in a hydrogen irradiation at the same pressure, we can write

$$\{[CH_3] + [CH_2D] + [CHD_2] + [CD_3]\} = [CH_3]_0 = R^\circ{}_{C_2H_6}{}^{1/2}/k_8{}^{1/2} \tag{E11}$$

where k_8 is the rate constant for recombination of methyl radicals and $R^\circ{}_{C_2H_6}$ is the observed rate of formation of ethane in the hydrogen irradiation. It is easily shown that a steady-state treatment for H atom concentration, using the assumptions described, leads to the expression

$$k_6[D_2][H] = \frac{{}^3/{}_4k_2k_d[D]}{k_d + k_2[M]}\{[CH_3] + {}^2/{}_3[CH_2D] + {}^1/{}_3[CHD_2]\} \tag{E12}$$

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[11] J. Weiss and W. Bernstein, *Phys. Rev.*, **103**, 1253 (1956).

[12] K. Morikawa, W. S. Benedict, and H. S. Taylor, *J. Chem. Phys.*, **5**, 212 (1937).

[13] (a) R. Berisford and D. J. Leroy, *Can. J. Chem.*, **36**, 985 (1958); (b) A. Maschke and F. W. Lampe, *J. Am. Chem. Soc.*, **84**, 4601 (1962).

[14] Taking the vibrational energy of the excited deuteriomethane molecules as 103 kcal./mole and assuming equipartition of energy among vibrational degrees of freedom leads to a vibrational temperature of 5760 kcal./mole. For a difference in zero point energy of 1.2 kcal./mole we might thus expect an isotopic correction to the statistical factor ratio of 10%. Consideration of the manner in which these ratios enter the development leads to the conclusion that the error involved in neglecting the isotopic correction is of the order of 5%.

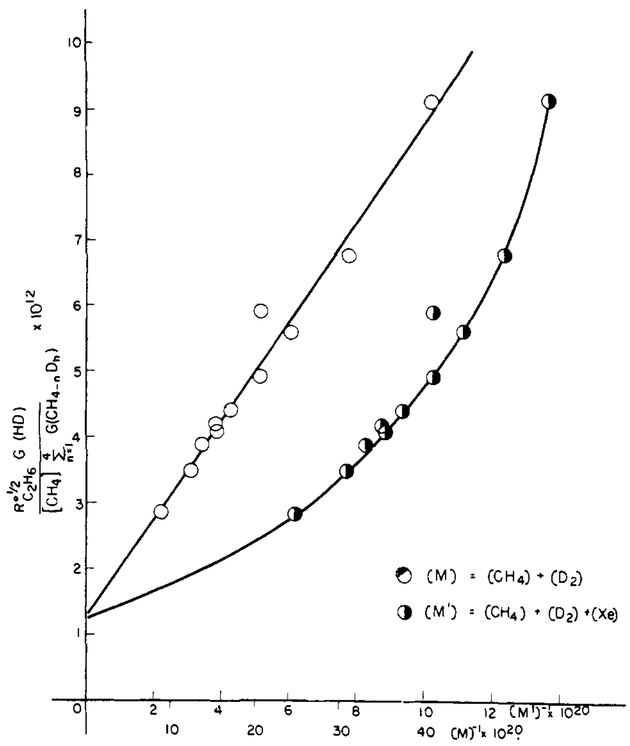

Fig. 5.—Dependence of exchange on third body concentration.

Substitution of E8–E10 into E11 permits calculation of the various methyl (d_0–d_3) concentrations from the experimental data, and thus provides a way to evaluate the methyl (d_0–d_3) concentration term in E12. When this is done, it is found that, over the entire range of deuterium concentration studied, the methyl (d_0–d_3) concentration term in E12 may be replaced with only ~3% error by the term

$$0.800(R^{\circ 1/2}{}_{C_2H_6}/k_8{}^{1/2})$$

Using E11, E12, and this last approximation it is easily shown that E2 and E7 lead to the expression

$$\frac{R^{\circ}{}_{C_2H_6}{}^{1/2}G(\mathrm{HD})}{[\mathrm{CH_4}]\sum\limits_{n=1}^{4} G(\mathrm{CH}_{4-n}\mathrm{D}_n)} = \frac{k_1k_8{}^{1/2}}{k_2} + \left(\frac{k_1k_dk_8{}^{1/2}}{k_2k_3} + \frac{0.6k_dR^{\circ}{}_{C_2H_6}{}^{1/2}}{k_3[\mathrm{CH_4}]}\right)\frac{1}{[\mathrm{M}]} \quad \text{(E13)}$$

in which the ratio of rates of HD and deuteriomethane formation have been replaced by the ratio of G-values. Thus a plot of the left-hand side of E13 *vs.* 1/[M] should yield an intercept containing k_1, k_2, and k_8 and, moreover, since $R^{\circ}{}_{C_2H_6}{}^{1/2}$ is approximately constant over our range of deuterium pressures, should yield a linear plot whose slope and intercept allow evaluation of the ratio k_d/k_3.

Two such plots are shown in Fig. 5 in which the third body concentration 1/[M] has been taken in two ways. On the abscissa designated $[M^1]^{-1}$, the third body concentration is taken as $[D_2] + [CH_4] + [Xe]$. On the abscissa designated as $[M]^{-1}$, the third body concentration is taken as $[D_2] + [CH_4]$. This latter plot yields a linear relationship as predicted and is surely the more reasonable interpretation of the third body concentration. The excitation in the deuteriomethanes is purely vibrational and xenon would be expected to be a much poorer deactivator than either D_2 or CH_4. From the intercept and slope and taking k_8[15] as 7.5 × 10^{-11} cm.^{3}-molecule^{-1}-sec.$^{-1}$ we arrive at the values

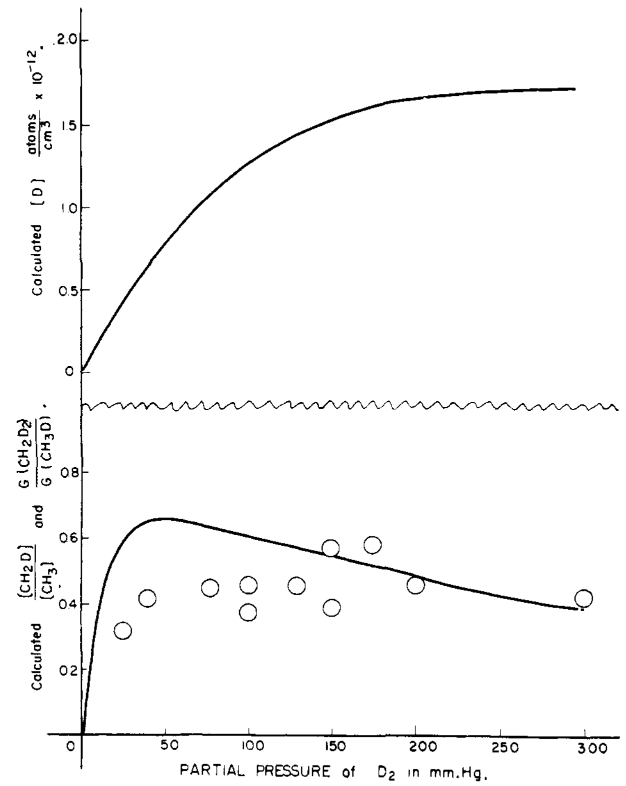

Fig. 6.—Calculated [D] and product ratio as a function of deuterium pressure: ———, calculated; ○, observed.

$$k_1/k_2 = 1.46 \times 10^{-7} \quad \text{(E14)}$$

$$k_d/k_3 = 9.12 \times 10^{18} \text{ molecules/cm.}^3 \quad \text{(E15)}$$

Whittle and Steacie[16] have measured the rate constant for the reaction

$$CH_3 + HD \longrightarrow CH_4 + D \quad (9)$$

If we combine their rate constant at 300°K. with the calculated equilibrium constant[17] for this reaction, we calculate for k_1 (which refers to the reverse of 9) the value k_1 = 3.66 × 10^{-17} cm.^{3}-molecule^{-1}-sec.$^{-1}$. Combining with E14 gives

$$k_2 = 2.60 \times 10^{-10} \text{ cm.}^3\text{-molecule}^{-1}\text{-sec.}^{-1}$$

It is of interest that the collision rate constant for CH_3 and D, assuming a collision diameter of 2.6 Å., is 4.0 × 10^{-10} cm.^{3}-molecule^{-1}-sec.$^{-1}$.

If we now consider the recombination of CH_3 with D to be a third-order reaction we can write for the third-order rate constant, k'

$$k' = \frac{k_2}{[\mathrm{M}] + (k_d/k_3)} \quad \text{(E16)}$$

and the limiting third-order rate constant is

$$k' = k_2k_3/k_d = 2.9 \times 10^{-29} \text{ cm.}^6\text{-molecule}^{-2}\text{-sec.}^{-1} \quad \text{(E17)}$$

Self-Consistency of Treatment.—If the treatment just described is to have any validity it must explain the saturation effect of G(HD) observed in Fig. 1. Secondly, as [M] is increased it would seem evident that more and more of the exchange should stop at CH_3D. This would mean that the ratio $G(CH_2D_2)/G(CH_3D)$ should decrease with increasing $[D_2]$ and this is not borne out by the data in Fig. 1.

For the first point it may be shown from a steady-state treatment of deuterium atom concentration, the rate constants just derived, and the third-order recombination rate constant for deuterium atoms[18]

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[15] R. Gomer and G. B. Kistiakowsky, *J. Chem. Phys.*, **19**, 85 (1951).

[16] E. Whittle and E. W. R. Steacie, *ibid.*, **21**, 993 (1953).

[17] A. F. Trotman-Dickenson, *ibid.*, **21**, 211 (1953).

[18] W. Steiner, *Trans. Faraday Soc.*, **31**, 623 (1935).

that the steady-state deuterium atom concentration depends on deuterium pressure as shown in the upper part of Fig. 6. Over the range of deuterium pressure covered, G(HD) is essentially proportional to [D] so that the similarity of the curves of G(HD) and [D] (Fig. 1 and 6) demonstrate the self-consistency of the treatment in regard to saturation of G(HD).

For the second point it is easily shown from a steady-state treatment for CH_2D radicals that

$$\frac{[CH_3]}{[CH_2D]} = \frac{4}{3}\left[\frac{1}{2} + \frac{k_3[M]}{k_d} + \frac{2k_8{}^{1/2}R°_{C_2H_6}{}^{1/2}}{k_2[D]}\left(1 + \frac{k_3[M]}{k_d}\right)\right] \tag{E18}$$

Using E18 and E8 and our values for the pertinent rate constants, we have calculated the lower curve in Fig. 6 for the ratio $[CH_2D]/[CH_3]$. The agreement of the experimental points, particularly above 100 mm. where the treatment is expected to be more valid and where experimental error in determining the product CH_2D_2 is lessened, is evidence of the self-consistency of our treatment.

As a final check on the validity of our assumed mechanism we now consider the isotopic distribution of ethanes. As mentioned previously, we carried out a mass spectral analysis, using parent peaks, of the deuterated ethanes for the irradiations at 150 mm. of deuterium. Only analyses above ethane-d_0 are considered at all accurate because of sizable contributions from deuterated propane, the net result of which is to make the ethane d_0 value too small. The mass spectrometrically determined values normalized to unity at ethane-d_3 are shown in column 3 of Table I. In column 2 of Table I, also normalized to unity at ethane-d_3, are values calculated using eq. E8–E10, the assumption that all ethane arises by methyl recombination, and the assumption that the recombination rate constant for like radicals is one-half that for unlike. We consider the degree of agreement, for deuteration above d_0, to be evidence of the validity of our mechanism.

TABLE I

ISOTOPIC ETHANE DISTRIBUTION

Species	Calcd.	Obsd.	Species	Calcd.	Obsd.
C_2H_6	3.4	0.7	$C_2H_2D_4$	0.34	0.40
C_2H_5D	2.1	2.0	C_2HD_5	.12	0.09
$C_2H_4D_2$	2.0	1.5	C_2D_6	.02	..
$C_2H_3D_4$	1.0	1.0			

We are somewhat at a loss to explain the discrepancies between this work and that of Firestone, *et al.*[8] These authors, working at much higher deuterium pressures, found no ethane, so that we are limited in using our eq. E18 to calculate the theoretical $G(CH_3D)/G(CH_2D_2)$. If we use their estimated upper limit to ethane formation and their estimate of the steady-state deuterium atom concentration in eq. E18, we calculate that they should have observed a minimum value of 0.23 for $G(CH_2D_2)/G(CH_3D)$. As this should have been within their capability of detection, the much higher pressure of deuterium cannot be the explanation. The only explanation left to us at the moment is that Firestone, *et al.*,[8] used no ionic scavenger and that hence a major part of their exchange may be due to ionic intermediates. The ionic paths, which are presumably absent in our work, lead by reasonable mechanistic schemes only to CH_3D as a primary product.

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The Crystal Structure of Bis-(*m*-chlorobenzoyl)-methane[1a]

BY GORDON R. ENGEBRETSON AND R. E. RUNDLE[1b]

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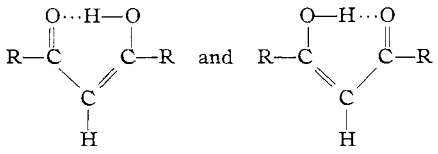
The crystal structure of bis-(*m*-chlorobenzoyl)-methane has been determined by three-dimensional anisotropic least squares refinement of scintillation counter data. The molecule was found to be nearly planar with a maximum deviation from the least squares molecular plane of 0.068 Å. and an average deviation of 0.023 Å. Fourier transform techniques to locate phenyl rings provided the key to the structure determination. The intramolecular bond distances and thermal parameters of the oxygen atoms support a resonant, enol ring with a symmetric, intramolecular hydrogen bond. The structure confirms conclusions from the structure of bis-(*m*-bromobenzoyl)-methane where the symmetry of the molecule was forced by the crystal symmetry.

Introduction

Interest in short, strong, intramolecular hydrogen bonds has prompted structural investigations of β-diketones and other intramolecular, hydrogen-bonded compounds. It has been established that the β-diketones exist almost completely in the enol form, but the question has been whether the structure is a statistical distribution of the two enol forms



or a symmetric resonance hybrid of the two.

In the one previous structural investigation of β-diketones the hydrogen atom was required to lie on a symmetry element.[2] There is the possibility, in such a case, that the observed symmetry results from averaging the results of two orientations of somewhat asymmetric molecules. The present investigation was undertaken to see if the apparent symmetry of a β-diketone persists in an asymmetric, crystalline environment.

Preparation and Properties of the Crystals.—Crystals of bis-*m*-(chlorobenzoyl)-methane were prepared

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(1) (a) Taken in part from a thesis by Gordon Engebretson submitted November 7, 1962, to Iowa State University, Ames, Iowa, in partial fulfillment of the requirements for the Ph.D. degree. This work was performed under contract with the Atomic Energy Commission. (b) Deceased, October 9, 1963.

(2) D. Williams, R. Rundle, and W. Dumke, *Acta Cryst.*, **15**, 627 (1962).