[Contribution from the Research Department, U. S. Naval Ordnance Test Station]

The Pyrolysis and Photolysis of Acetone-d_6 in the Presence of Methane

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Mixtures of acetone-d_6 and methane were pyrolyzed in the range 475–525° and photolyzed in the temperature range 350–428°. The rate of reaction of CD_3 with CH_4 to form CD_3H relative to the rate of formation of CD_4 from CD_3 and acetone-d_6 was studied as a function of temperature. The activation energy for the reaction of CD_3 with methane to form CD_3H is 2.74 kcal./mole greater than for CD_3 with acetone-d_6 to form CD_4. From this value the activation energy for the abstraction of hydrogen from methane by CD_3 is shown to be 14.0 kcal./mole. It has been demonstrated that the CD_3H/CD_4 ratio is somewhat surface dependent; a sixfold increase in surface/volume ratio increases the CD_3H/CD_4 ratio by about 10%.

Introduction

The kinetics of reactions of methyl radicals with a number of alkanes have been studied[1] with the notable exception of methane. It is obviously impossible to measure the rate of formation of CH_4 from the reaction of CH_3 with CH_4, but a study of the reaction of CD_3 with CH_4 to give CD_3H appeared to be feasible. Such a study has been attempted by Trotman-Dickenson and Steacie[2,3] who employed a photochemical technique without success. In the present work it was noted that the reaction of methyl-d_3 radicals with methane would be much slower than with the parent acetone-d_6, and the study was made with large CH_4/acetone-d_6 ratios. This technique increased the rate of reaction of CD_3 with CH_4 relative to CD_3 with the acetone-d_5 impurity so that most of the CD_3H formed would arise from the former reaction and the blank correction would be relatively small.

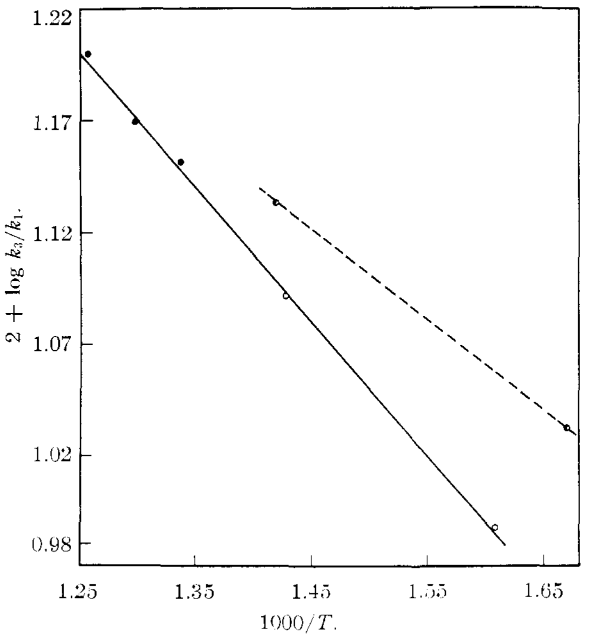

Fig. 1.—Reaction of CD_3 with methane and acetone-d_6. Dashed line is effect of 6 × increase in surface/volume ratio.

Experimental

Preparation of Materials. A. Deuterioacetone.—The preparation of this compound has been described in a previous paper.[4] It was stored in a flask equipped with a mercury cut-off valve. The composition was 95 parts acetone-d_6 and 5 parts acetone-d_5, with an unknown but small amount of acetone-d_4.

B. Methane.—The methane was obtained from the Southern California Gas Company. Mass Spectrometer analysis showed the material to be 99.6% methane and 0.4% ethane.

2. **Procedures.**—Mixtures of methane and acetone-d_6 were made up and the compositions examined mass spectrometrically. A master mixture of known composition was kept in a 2-liter flask equipped with a mercury cut-off valve. Two such mixtures were used in the course of this work. A series of pyrolyses and photolyses were run using an initial methane:deuterioacetone ratio of 5.76. A second mixture whose methane:deuterioacetone ratio was 5.34 was used for the pyrolyses at 475 and 523°, and also for the photolyses at 326 and 432°. In these photolyses the surface/volume ratio was increased by a factor of about six by inserting the appropriate amount of fused silica rod into the reaction vessel. An aluminum block furnace was used to heat the cylindrical reaction vessel which was of fused silica with plane parallel windows. The reaction vessel was 4 cm. in diameter and 4 cm. high. The maximum gradient across the vessel was 3.5° at 350° and 5° at 428°. The light source was a Hanovia SC-2537 mercury vapor lamp in the form of a flat spiral. The pyrolyses were carried out, using a technique described previously.[3] In the photolyses the system was evacuated, brought to temperature, and the lamp turned on. With the lamp shielded, a sample of the master mixture was admitted to the system until the total pressure was about 90 mm. The shield was removed and the photolysis begun. After a time the lamp was turned off and the reaction mixture allowed to expand into an evacuated Pyrex vessel equipped with a break-off seal and an Apiezon wax cut-off. The wax was melted, trapping the sample in the sampling vessel.

3. **Analysis.**—A gross analysis of the sample was performed in order to ascertain the relative amounts of methane and acetone-d_6 remaining at the end of the reaction. A sample volatile from liquid nitrogen was admitted into the mass spectrometer and the ratio of the $^{19}/_{20}$ mass peaks (CD_3H/CD_4) was recorded. This procedure was followed for all the experiments reported in this paper.

Results and Discussion

The results are given in Tables I and II, and the Arrhenius plot is shown in Fig. 1. The experiments without added surface are designated by open circles for photolyses and filled circles for pyrolyses. Experiments with added surface are denoted by half filled circles. Considerable difficulty was encountered in obtaining reproducible results in the photolyses but not in the pyrolyses. In the latter cases methane was formed almost to the exclusion of ethane, while in the photolyses at low temperatures, ethane is the major hydrocarbon product.

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(1) A. F. Trotman-Dickenson, J. R. Birchard and E. W. R. Steacie, *J. Chem. Phys.*, **10**, 163 (1951).

(2) A. F. Trotman-Dickenson and E. W. R. Steacie, *ibid.*, **19**, 335 (1951).

(3) A. F. Trotman-Dickenson and E. W. R. Steacie, *ibid.*, **19**, 919 (1951).

(4) J. R. McNesby, T. W. Davis and A. S. Gordon, This Journal, **76**, 823 (1954).

TABLE I

REACTION OF CD_3 RADICALS WITH METHANE

Run no.	T, °C.	t, min.	$\frac{CD_3H}{CD_4}$	$\frac{k_3M}{k_1(A\text{-}d_6 + A\text{-}d_5)}$	$\frac{M}{(A\text{-}d_6 + A\text{-}d_5)}$	k_3/k_1	$2 + \log k_3/k_1$	$1000/T$
1	348	4	0.688	0.614	5.76			
2	347	8	.753	.682				
3	350	16	.862	.792				
4	351	4	.074		0			
5	349	8	.071		0			
6	348	16	.069		0			
	348	0		.560	5.76	0.0972	0.9877	1.608
7	428	3	.800	.738				
8	428	6	.830	.769				
9	428	10	.864	.802				
10	428	3	.062		0			
11	429	6	.061		0			
12	429	10	.062		0			
	428	0		.711	5.76	.1234	1.0913	1.427
13	475	10	.851					
14	475	20	.837					
15	475	30	.834					
16	475	30	.085		0			
	475	0		.756	5.34	.1416	1.1511	1.337
17	499	5	.940					
18	496	15	.930					
19	498	15	.085		0			
20	498	30	.085		0			
	498	0		.850	5.76	.1476	1.1691	1.297
21	523	2	.945					
22	523	4	.928					
23	523	6	.938					
24	524	5	.091		0			
	523	0		.847	5.34	.1586	1.2003	1.256

TABLE II

INFLUENCE OF 6× INCREASE IN SURFACE ON REACTION OF CD_3 WITH METHANE

Run no.	T, °C.	t, min.	$\frac{CD_3H}{CD_4}$	$\frac{k_3M}{k_1(A\text{-}d_6 + A\text{-}d_5)}$	$\frac{M}{(A\text{-}d_6 + A\text{-}d_5)}$	k_3/k_1	$2 + \log k_3/k_1$	$1000/T$
25	326	3.0	0.654	0.586				
26	326	5.0	.661	.593				
27	326	4.0	.066		0			
	326	0		.575	0.534	0.1077	1.0322	1.669
28	431	1.1	.796	.733				
29	432	3.0	.808	.745				
30	433	1.0	.063		0			
31	434	3.0	.062		0			
	432	0		.726	0.534	0.1360	1.1335	1.418

In order to obtain enough methane for analysis, the low temperature (150–250°) photolyses had to be carried out to large percentage conversions of acetone-d_6. This caused large variations in the CD_3H/CD_4 ratio when runs were made to different percentage conversions. The photochemical study was done in the range 350 to 428° in order to increase the proportion of methane in the products. In Tables I and II runs 4, 5, 6, 10, 11, 12, 16, 19, 20, 24, 27, 30 and 31 were made with acetone-d_6 alone. The CD_3H arises from the reactions 2 and 3, while CD_4 comes from reaction 1.

The following reactions are important

$$CD_3COCD_3 \xrightarrow{h\nu} 2CD_3 + CO \qquad (ia)$$

$$CD_3COCD_3 \longrightarrow 2CD_3 + CO \qquad (ib)$$

$$CD_3 + CD_3COCD_3 \longrightarrow CD_4 + CD_2COCD_3 \qquad (1a)$$

$$CD_3 + CD_2HCOCD_3 \longrightarrow CD_4 + CDHCOCD_3 \qquad (1b)$$

$$CD_3 + CHD_2COCD_3 \longrightarrow CD_3H + CD_2COCD_3 \qquad (2a)$$

$$CD_2H + CD_3COCD_3 \longrightarrow CD_3H + CD_2COCD_3 \qquad (2b)$$

$$CD_2H + CD_2HCOCD_3 \longrightarrow CD_3H + CDHCOCD_3 \qquad (2c)$$

$$CD_3 + CH_4 \longrightarrow CD_3H + CH_3 \qquad (3)$$

$$CD_2H + CD_2HCOCD_3 \longrightarrow CD_2H_2 + CD_2COCD_3 \qquad (4)$$

$$CD_2H + CH_4 \longrightarrow CD_2H_2 + CH_3 \qquad (5)$$

$$\frac{CD_3H}{CD_4} = \frac{k_{2a}(CD_3)(A\text{-}d_5) + k_{2b}(CD_2H)(A\text{-}d_6) + k_{2c}(CD_2H)(A\text{-}d_5) + k_3(CD_3)M}{k_{1a}(CD_3)(A\text{-}d_6) + k_{1b}(CD_3)(A\text{-}d_5)} \qquad (I)$$

$$\frac{CD_3H}{CD_4} = \frac{k_{2a}(CD_3)(A\text{-}d_5) + (k_{2b}(A\text{-}d_6) + k_{2c}(A\text{-}d_5))CD_2H}{(k_{1a}(A\text{-}d_6) + k_{1b}(A\text{-}d_5))CD_3} + \frac{k_3M}{(k_{1a}(A\text{-}d_6) + k_{1b}(A\text{-}d_5))} \qquad (II)$$

where A-d_5 and A-d_6 represent the concentrations of acetone-d_5 and acetone-d_6, respectively.

Early in the reaction $CD_2H/CD_3 = \alpha =$ constant.

Since α is initially independent of the amount of added CH_4, the first fraction on the right-hand side of equation II can be obtained to a close approximation as the CD_3H/CD_4 ratio in the absence of added CH_4. If the reasonable assumption $k_{1a} \approx k_{1b}$ is made, equation II becomes

$$CD_3H/CD_4 = (CD_3H/CD_4)_0 + (k_3/k_1)(M/[(\text{A-}d_6) + (\text{A-}d_5)]) \quad \text{(III)}$$

where $(CD_3H/CD_4)_0$ is the ratio in the absence of added methane. Thus k_3/k_1 can be obtained from the initial ratio of mass 19/mass 20, $(CD_3H/CD_4)_0$ and a knowledge of the composition of the initial mixture. In the temperature range 350–428° the CD_3H/CD_4 ratio was dependent upon the time of photolysis for methane:acetone-d_6 mixtures. Since this ratio was found to be almost linear with time, a short extrapolation to zero time was applied to the ratio after correction for $(CD_3H/CD_4)_0$. This gave $(k_3/k_1)(M/[(\text{A-}d_6) + (\text{A-}d_5)])$. In contrast to the photolysis, the $M/[(\text{A-}d_6) + (\text{A-}d_5)]$ ratio did not change appreciably in the course of pyrolysis, so that it was not necessary to extrapolate to zero time. The constancy of this ratio was reflected in the constancy with time of the CD_3H/CD_4 ratio in the pyrolyses. In the case of the photolyses, the smaller percentage of methane in the products made it necessary to carry out the reactions to greater percentage conversions of deuterioacetone in order to obtain enough products for analysis. Hence extrapolation of CD_3H/CD_4 to zero time was necessary in the photolyses. The line drawn through the points in Fig. 1 was drawn by the method of least squares. Since

$$k_3/k_1 = (A_3/A_1)e^{(E_1-E_3)/RT} \quad \text{(IV)}$$

where A_3 and A_1 are the Arrhenius pre-exponential factors for reactions 3 and 1, respectively, a plot of log k_3/k_1 *vs.* $1/T$ should give a straight line of slope $(E_1 - E_3)/4.576$ and intercept log A_3/A_1. Using this treatment and applying the method of least squares, $E_3 - E_1 = 2.74$ kcal./mole and $A_3/A_1 = 0.48$. It has been shown[4,5] that $E_1 = 11.3$ kcal./mole, and therefore $E_3 = 14.0$ kcal./mole. These activation energies are based upon an energy of activation of 9.6 kcal./mole for the abstraction of H from acetone by CD_3 and an activation energy of zero for the methyl–methyl combination. Since CH_3 and CD_3 have previously been shown[5] to take a hydrogen atom from normal acetone with equal facility, it is reasonable that CD_3 and CH_3 abstract a hydrogen atom from methane with equal facility.

Figure 1 demonstrates that it is entirely practical to study reactions of methyl radicals using both photochemical and pyrolytic techniques concurrently. In addition to giving results in harmony with photolysis, the pyrolytic technique can be used, as it has been here, to establish the presence or absence of hot radicals. In the present case it is evident that hot radicals cannot be present in the photolysis since they are absent in the pyrolysis and the two techniques give consistent results.

Table II and Fig. 1 show clearly that the reaction of CD_3 radicals with CH_4 is partly heterogeneous relative to the reaction of CD_3 with CD_3COCD_3. A sixfold increase in the surface area caused a ten per cent. increase in the ratio k_3/k_1. If the reaction of CD_3 with acetone-d_6 is homogeneous, it may be concluded that the rate of the homogeneous reaction between CD_3 and methane is at least 98% of the observed rate. Therefore, if the CD_3–acetone-d_6 reaction is homogeneous, the data obtained without added surface represent the homogeneous reaction of CD_3 with methane within the limits of experimental error. If homogeneity of acetone decomposition were established beyond any doubt, the relative heterogeneity of methyl radical reactions could be studied conveniently and quantitatively using the technique outlined here.

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[5] J. R. McNesby and Alvin S. Gordon, THIS JOURNAL, **76**, 1416 (1954).

INYOKERN, CHINA LAKE, CALIF.

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

γ-Ray-Induced Oxidation of Aqueous Formic Acid–Oxygen Solutions. Effect of *p*H

BY EDWIN J. HART

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Radiation yields of carbon dioxide, hydrogen and hydrogen peroxide formed and oxygen reacted have been measured at 0.01 *M* formic acid concentration over the *p*H range from 0.32 to 11.58. In the *p*H range above 3, molecular hydrogen and hydrogen peroxide are formed in equimolar amounts. Below this range of *p*H, an excess of hydrogen peroxide is formed. The results are interpreted in terms of number of water molecules dissociated in three primary reactions: (1) $H_2O = H + OH$, (2) $H_2O = {}^1/_2H_2O_2 + {}^1/_2H_2$, and (3) $H_2O = H + {}^1/_2H_2O_2$. Each of these three reactions is *p*H dependent. However, the total number of water molecules decomposed/100 e.v. is substantially constant in the *p*H range 0.32 to 11.58 and equals 3.99 ± 0.14.

The formic acid–oxygen system has been employed to measure the radical pair and molecular product yields of ionizing radiations in aqueous solutions.[1] Specifically, the yield of oxygen consumption, $G_{(-O_2)}$, provides a measure of free radicals available, whereas the yield of hydrogen extrapolated to infinite oxygen concentration, $G_{(H_2)}$, is a measure of reaction 2.

$$H_2O = H + OH \quad (1)$$

$$H_2O = {}^1/_2H_2 + {}^1/_2H_2O_2 \quad (2)$$

Recently Allen[2] has been led to postulate a third

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[1] (a) E. J. Hart, *J. Phys. Chem.*, **56**, 594 (1952); (b) THIS JOURNAL, **76**, Sept. (1954); (c) *Rad. Research*, **1**, 53 (1954).

[2] A. O. Allen, Brookhaven National Laboratory report BNL-1498 (1953); *Rad. Research*, **1**, 85 (1954).