[U. S. Naval Ordnance Test Station, China Lake]

Photolysis of Acetone

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The reaction between CD_3 and mixtures of deuterated and normal acetones has been studied as a function of temperature. The difference in activation energy for the abstraction of D and H from acetone by CD_3 is 1.64 ± 0.08 kcal./mole in the range 150–250°. This value is in excellent agreement with the value 1.67 ± 0.09 found for the pyrolysis in the neighborhood of 500°. Methyl ethyl ketone is a product of the photolysis, as is biacetyl up to 100°. The results indicate that there is no activation energy difference for the abstraction of H from acetone by CH_3 and CD_3. An application of the results is applied to a reported research.

Introduction

It has been shown[1] that the difference in activation energy for the abstraction of deuterium and hydrogen from acetone by methyl radicals is 1.67 ± 0.09 kcal./mole. This value was determined in the range 466–525°. In the present work the methane fraction from acetone photolysis in the range 150–250° has been examined in an effort to obtain an activation energy difference for this temperature range. At lower temperatures it would be possible to make an analysis for methane only if much lower light intensities were employed.[2]

The work of Trotman-Dickenson and Steacie[3] in the temperature range 150–250° showed that the values for the abstraction of hydrogen from acetone by methyl and for abstraction of deuterium from deutero acetone by deutero methyl are 9.7 and 10.3 kcal./mole, respectively. More recent work by Marjury and Steacie[4] has placed the activation energy for abstraction of D by CD_3 at 10.6 kcal./mole. Subsequently, Whittle and Steacie[5] found the value to be 11.6 kcal./mole, and it is the latter figure which is considered by them to be most reliable. A study of the pyrolysis of mixtures of acetone and acetone-d_6 by McNesby, Davis and Gordon[1] resulted in values which are in accord with the 11.6 kcal. figure. The energy of activation difference for CD_3 to abstract a D from acetone-d_6 and H from acetone calculated from the photolysis results of this work is 1.64 ± 0.08 kcal./mole, in excellent agreement with the value from the pyrolysis.

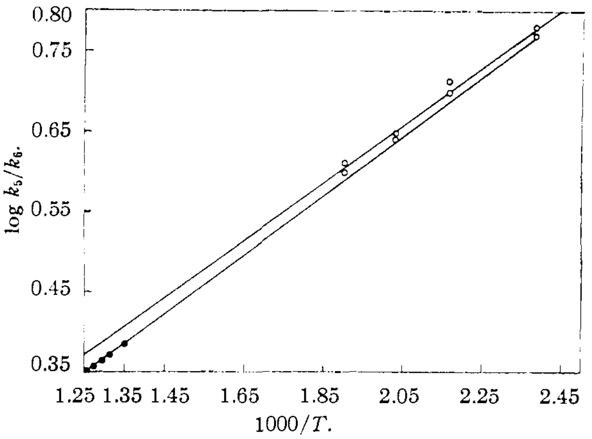

Fig. 1.—Removal of D and H from acetone by deuteromethyl radicals: open circles, photolysis; closed circles, pyrolysis.

Experimental

The preparations of acetone and acetone-d_6 have been described in a previous paper.[1]

Helium was purified by slow passage through an activated charcoal trap at −195°. Mass spectrometer analysis of the resulting helium showed greater than 99.9% helium, with a trace of nitrogen.

Equimolar mixtures of acetone and acetone-d_6 were led into an evacuated 50-cc. cylindrical fused silica vessel with plane windows. The vessel was heated in an air-bath which maintained a 2° gradient over the entire vessel. The air-bath was heated by means of a surrounding silicone oil-bath equipped with a thermostat. A Hanovia SC-2537 lamp in the form of a flat spiral was placed in the air-bath about 4 inches from the top plane window of the reaction vessel. The air-bath was heated to temperature, the lamp turned on for 15–20 minutes, and then 180 mm. of the acetone mixture was placed in the reaction vessel. A trap containing gold wire was inserted between the reaction vessel and the mercury in the system. Although the efficiency of a gold trap in removing mercury vapor is questionable, any photosensitization would not affect any of our results or arguments. After the photolysis the contents of the reaction vessel were expanded into a Pyrex vessel equipped with a breakoff seal and cooled in liquid nitrogen. Some Apiezon W wax was placed in the shell tubing of this collection vessel prior to sealing it to the system. The wax was now warmed so that it would run down, isolating the gas collection vessel from the rest of the system. This technique was used instead of fusing the Pyrex in order to prevent pyrolysis of gases volatile at −195°. The photolyses were carried out for 5–30 minutes, depending upon the temperature. In all cases the acetone was less than 4% reacted, and exchange was almost negligibly small. The mass spectrometric analyses were carried out using the same technique previously reported.[1]

Results and Discussion

Figure 1 shows the CD_3H/CD_4 ratios in an Arrhenius plot; the slope was calculated by the method of least squares and gives an activation energy difference for the abstraction of D and H from acetone by deutero methyl radicals of 1.64 ± 0.08. The pyrolysis points are also shown in the same figure. The straight line shown in Fig. 1 was drawn by the method of least squares applied to the photolysis data (open circles). Photolyses were also carried out with 1:1:1 mixtures of helium, acetone and acetone-d_6 at 252 and 145°. At the higher temperature the CD_3H/CD_4 ratio was the same as without helium, and at 145° the ratio was slightly lower. The data are presented in Table I.

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

[2] L. M. Dorfman and W. A. Noyes, Jr., *J. Chem. Phys.*, **16**, 557 (1948).

[3] A. F. Trotman-Dickenson and E. W. R. Steacie, *ibid.*, **18**, 1097 (1950).

[4] T. G. Marjury and E. W. R. Steacie, *Can. J. Chem.*, **30**, 800 (1952).

[5] E. Whittle and E. W. R. Steacie, *J. Chem. Phys.*, **21**, 993 (1953).

TABLE I

PHOTOLYSIS OF 1:1 MIXTURES OF ACETONE AND ACETONE-d_6

T°C.	t, min.	$\frac{CD_3H}{CD_4}$	$\frac{CH_4}{CH_3D}$	$\frac{CD_3H^a}{CD_4}$	$\frac{CH_4^a}{CD_3H}$	$\frac{CH_4^b}{CH_3D}$	Final d_5/d_6	d_0/d_6
146.2	15	6.09	...	5.88	...	...	0.049	1.021
146.2	60	5.97	...	6.04	...	...	.049	0.983
188.4	10	5.035	12.8	5.16	0.98	5.6	.049	.971
188.2	5	5.03	11.3	5.00	1.01	5.5	.051	1.000
219.0	6	4.52	9.7	4.46	1.00	5.1	.050	1.010
219.0	3	4.50	8.8	4.38	0.95	4.8	.050	1.022
252.5	5	4.20	7.0	4.09	1.04	4.3	.052	1.021
252.5	3	3.91	7.1	3.97	1.01	4.2	.052	0.981
252.5[c]	5	3.92	...	4.07	...	4.2	.050	.962
145.5[c]	20	7.907	...	5.71	...	...	.052	1.392
145.5[c]	20	5.49	...	5.64	...	...	.051	0.973

[a] Corrected for CD_3H formed from CD_2H which is generated from acetone-d_5. The methane ratios are corrected for the deviation of acetone/acetone-d_6 from unity. The column headed d_0/d_6 represents acetone/acetone-d_6. The column headed Final d_5/d_6 represents acetone-d_5/acetone-d_6 after the reaction is over. [b] These values are computed from a private communication which quotes the latest mass spectrum of Dibeler and Mohler[7] for CD_3H. The mass peaks for CD_3H have essentially the same values as the published values,[6] with the exception that mass 18 is 43.3% of mass 19 in the mass spectrum. [c] Contained 33.3% helium.

The CH_4/CH_3D ratio was also obtained. It was up to 100% greater than CD_3H/CD_4 at the same temperature. It has previously been noted that the CH_4/CH_3D ratio was larger than the CD_3H/CD_4 ratio in the pyrolyses by about 10–15%.

The unexpectedly large amount of CD_2H_2 found in the pyrolyses[1] might indicate that methylene radicals generated from decomposing ketene abstract two H or D atoms at a time from acetone. However, CD_2H_2 is formed in even larger relative amounts in the photolysis where no ketene is produced. There is one possibility which explains both the excessive amounts of CD_2H_2 and the extremely high values for CH_4/CH_3D relative to CD_3H/CD_4. If the height of the mass 18 peak in CD_3H is about 40% of the parent 19 peak instead of the reported 27%,[6] the residual 18 peak in the methane fraction for both pyrolysis and photolysis is reduced nearly to zero and consequently the amount of CD_2H_2 approaches zero. As a result of the absence of appreciable amounts of CD_2H_2, a large part of the mass 17 peak which had formerly been attributed to CD_2H_2 now must be interpreted as being the contribution of CH_3D. It is evident, then, that the amount of CH_3D is increased and the CH_4/CH_3D ratio decreased. The CH_4/CH_3D ratios computed on the basis that for CD_3H the height of the mass 18 peak is 43.3% of the parent mass 19 peak are recorded in the last column of Table I. The figure 43.3 is used as a result of work done recently by Dibeler and Mohler[7] in which our predicted value of about 40% for mass 18 was confirmed.

The new spectrum for CD_3H thus brings the CH_4/CH_3D and CD_3H/CD_4 ratios into rather good agreement. The change in the CH_4/CD_3H ratio introduced by the new CD_3H spectrum is not significant.

If the absorption coefficients of acetone and acetone-d_6 are about equal, then the CH_4/CD_3H ratio should be about unity if there is no significant difference in the hydrogen abstracting ability of CH_3 and CD_3. As may be seen in Table I, CH_4/CD_3H is about unity independent of temperature. This ratio should also be quite reliable since the deuterated methanes contribute relatively little to the large mass 16 peak, and as has been previously noted, the mass 19 peak is uncontaminated. The ratios in Table I are consistent with the following concepts.

1. Methyl radicals abstract D and H from acetone with an activation energy difference of 1.7 kcal./mole. Methyl-d_3 radicals also abstract D and H from acetone with about the same activation energy difference. The CH_4/CH_3D ratio is not as accurate as the CD_3H/CD_4 ratio.
2. CH_3 and CD_3 radicals abstract hydrogen from acetone with equal facility and no measurable activation energy difference. This fact, in conjunction with concept (1), implies that CH_3 and CD_3 radicals also abstract D from acetone-d_6 with equal facility and no activation energy difference.

It is pertinent to note that Wall and Moore[8] observed no CH_3D initially in pyrolysis of acetone and acetone-d_6 mixtures of 500°. If the new value for the mass 18 peak[7] in the CD_3H spectrum is applied to their data, CH_3D appears in the products. Using purer starting material, we have shown that CH_3D is present from the start.

The gross analysis of the products of the photolysis of acetone-d_6 at 100° showed only 80 and 92 mass peaks above the reactant acetone peaks. These masses correspond to fully deuterated methyl ethyl ketone and biacetyl-d_6, respectively. Allen[9] had previously reported finding methyl ethyl ketone in the products of acetone photolysis. The photolysis of 1:1 mixtures of acetone and acetone-d_6 at 100° produces biacetyl with zero, one and two deutero methyl groups in the proportion 1:2:1. W. Davis, Jr.[10] states that below 160° biacetyl must be formed since $C_2H_6/CO > 1$. Although the presence of biacetyl is evident at 100° none appears in the photolysis at 146° or higher temperatures. For photolyses of 1:1 mixtures of acetone and acetone-d_6, methyl ethyl ketone appears at all temperatures from 100–250°, but only masses 72 and 75 of approximately equal magnitudes are observed.

At 150–250° where enough methane is produced for quantitative analysis on the mass spectrometer, the acetyl radical is unstable enough so that the mechanism of acetone photolysis may be written

$$CH_3COCH_3 \xrightarrow{h\nu} 2CH_3 + CO \quad (1)$$

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

$$CH_3 + CH_3COCH_3 \longrightarrow CH_4 + CH_3COCH_2 \quad (3)$$

$$CH_3 + CD_3COCD_3 \longrightarrow CH_3D + CD_3COCD_2 \quad (4)$$

$$CD_3 + CH_3COCH_3 \longrightarrow CD_3H + CH_3COCH_2 \quad (5)$$

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(6) V. H. Dibeler and F. L. Mohler, *J. Research Natl. Bur. Standards*, **45**, 441 (1950).

(7) V. H. Dibeler and F. L. Mohler, communicated through R. E. Varnerin.

(8) L. A. Wall and W. J. Moore, *J. Phys. Colloid Chem.*, **55**, 965 (1951).

(9) A. O. Allen, THIS JOURNAL, **63**, 708 (1941).

(10) W. Davis, Jr., *Chem. Revs.*, **40**, 201 (1947).

$$\mathrm{CD_3 + CD_3COCD_3 \longrightarrow CD_4 + CD_3COCD_2} \quad (6)$$
$$\mathrm{2CH_3 \longrightarrow C_2H_6} \quad (7)$$
$$\mathrm{CH_3 + CD_3 \longrightarrow CH_3CD_3} \quad (8)$$
$$\mathrm{2CD_3 \longrightarrow C_2D_6} \quad (9)$$
$$\mathrm{CH_3 + CH_2COCH_3 \longrightarrow CH_3CH_2COCH_3} \quad (10)$$
$$\mathrm{CD_3 + CH_2COCH_3 \longrightarrow CD_3CH_2COCH_3} \quad (11)$$
$$\mathrm{CH_3 + CD_2COCD_3 \longrightarrow CH_3CD_2COCD_3} \quad (12)$$
$$\mathrm{CD_3 + CD_2COCD_3 \longrightarrow CD_3CD_2COCD_3} \quad (13)$$

It should be borne in mind in the following analysis that 1:1 mixtures of acetone and acetone-d_6 are employed. It is assumed that the absorption coefficients for these acetones are equal.

Reactions 10, 11, 12 and 13 indicate that four methyl ethyl ketones should be observed in the products. Application of the steady state equations and the two previously mentioned concepts leads to the conclusion that $\mathrm{CH_3} \backsimeq \mathrm{CD_3}$ and $\mathrm{CH_2COCH_3/CD_2COCD_3} \backsimeq 6$. Consequently if $k_{10} = k_{11} = k_{12} = k_{13}$, it should be expected that the concentrations of $\mathrm{CH_3CH_2COCH_3}$ and $\mathrm{CD_3CH_2COCH_3}$ will be about equal and approximately six times as large as the concentration of each of the species $\mathrm{CH_3CD_2COCD_3}$ and $\mathrm{CD_3CD_2COCD_3}$. This is in harmony with the experimental finding that only 72 and 75 mass peaks in about equal amounts are evident in the spectra. These peaks are of the order of 1–2 peak height divisions and hence we would not expect to find peaks corresponding to masses 77 and 80 of observable magnitude.

The ratio of the steric factors for the formation of $\mathrm{CD_3H}$ and $\mathrm{CD_4}$ is 0.84 ± 0.07. This is to be compared with the value 0.77 ± 0.05 obtained from the pyrolysis data. Considering the precision of the measurement of the $\mathrm{CD_3H/CD_4}$ ratios, it is significant that the ratio of pre-exponential factors σ_5/σ_6 is less than unity. According to collision theory

$$k = \sigma^2{}_{\mathrm{AB}}[8\pi kT\mu]^{1/2}e^{-E/RT}$$

It follows that

$$k_5/k_6 = P_5\sigma^2{}_{\mathrm{AB}}/P_6\sigma^2{}_{\mathrm{AC}}\,(1.01)e^{\Delta E/RT}$$

where σ_{AB} is the mean collision diameter for the acetone–methyl-d_3, and σ_{AC} is the value for the acetone-d_6–methyl-d_3 reaction. The fact that the pre-exponential factor has an experimental value of about 0.8 for both pyrolysis and photolysis indicates that σ_{AB} is about 90% of σ_{AC} if the P factors are equal.

Table I includes the ratio $\mathrm{CH_4/CD_3H}$ as a function of temperature. It should be noted that there are no chains in this temperature range because the $\mathrm{CH_3COCH_2}$ radical does not break down easily. With 1:1 mixtures of acetone and acetone-d_6, and equal absorption coefficients, the $\mathrm{CH_3}$ and $\mathrm{CD_3}$ stationary concentrations are probably about the same. The small amount of methane formed at 146° makes the $\mathrm{CH_4}$ very uncertain and the $\mathrm{CH_4/CD_3H}$ at this temperature was not determined.

The results provide evidence that there is no measurable activation energy difference for the abstraction of H from acetone by $\mathrm{CH_3}$ and $\mathrm{CD_3}$.

Kenyon[11] assumes that there is no activation energy difference for the abstraction of H and D from acetone by $\mathrm{CD_3}$ radicals.

Analyzing his data on this assumption, he concludes that in an approximate 4:1 acetone–*sec*-butyl chloride mixture, one methyl in nine abstracts hydrogen from acetone, while the other eight abstract hydrogen from *sec*-butyl chloride at 122°.

If Kenyon's data are re-analyzed on the basis of the experimental findings in this paper then

$$\mathrm{CD_3 + CH_3COCH_3 \longrightarrow CD_3H + CH_2COCH_3} \quad (14)$$
$$\mathrm{CD_3 + C_4H_9Cl \longrightarrow CD_3H + C_4H_8Cl} \quad (15)$$
$$\mathrm{CD_3 + CD_3COCD_3 \longrightarrow CD_4 + CD_2COCD_3} \quad (16)$$
$$\mathrm{CD_3H/CD_4} = [(\mathrm{CD_3H})_{\mathrm{A}} + (\mathrm{CD_3H})_{\mathrm{SB}}]/\mathrm{CD_4}$$

where A and SB signify acetone and *sec*-butyl chloride, respectively.

$$\mathrm{CD_3H/CD_4} = (A/A_{\mathrm{d}})0.8e^{1700/RT} + (\mathrm{CD_3H})_{\mathrm{SB}}/\mathrm{CD_4}$$

Kenyon reports a $\mathrm{CD_3H/CD_4}$ ratio of 11.2 at 122° for a mixture of acetone-d_6, acetone and *sec*-butyl chloride of 0.38, 0.80 and 0.96 ml., respectively. From the results of the work reported in this paper, a mixture of acetone-d_6 and acetone in the above proportions at 122° would result in a $\mathrm{CD_3H/CD_4}$ ratio of 13.3 so that no hydrogen has to be abstracted from the *sec*-butyl chloride. It is quite apparent that $k_{14} \gg k_{15}$, a conclusion opposite to that reached by Kenyon.

The problem of hot radicals has been investigated by photolyzing the mixture of acetones in the presence of helium. The process requiring the higher activation energy should proceed relatively faster with hot radicals and slower in their absence. Consequently if helium reduces the hot radical concentration, the $\mathrm{CD_3H/CD_4}$ ratio should rise.

The observation that the ratio is not raised in the presence of helium demonstrates that hot radicals are not a factor in the present study.

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