applicable to zinc oxide as a photosensitizer.

If $\cdot O_2^-$ is formed by the light on the surface of the zinc oxide, and the crystal is then left deficient in electrons, both the $\cdot O_2^-$ and an oxygen atom at the point of electron deficiency would be capable of removing either a hydrogen atom or an electron from a phenol molecule, and the net result would be the rapid initiation of chains similar to those supposed to involve free radicals in autoöxidations.

We have suggested[1] that the inhibitory effect of excess phenol might be due to covering the surface to the exclusion of water or oxygen. However, detailed studies of the adsorption of these phenols on zinc oxide in the dark fail to show any positive correlation. Phenol is only very slightly adsorbed in dilute solution, but the initial oxidation reaction is rapid. It is still adsorbed to only a small extent (about $^1/_{10}$ of the surface) at the concentration where it begins to show inhibition.

Amount adsorbed on 0.1 g. of ZnO (moles × 10^6) in 25 ml.

Concn., moles/l.	Resorcinol	Catechol	Hydroquinone	Phenol	Pyrogallol
1×10^{-4}		0.5	0.75	0.2	1.75
2.5×10^{-4}	1	0.5	1.75	.25	
5×10^{-4}	2.5	2.0	2.25	.50	3.5
1×10^{-3}	2.5	6.0	4.5	.8	4.5
2×10^{-3}		6.5		1.0	
5×10^{-3}			4.0		4.5
1×10^{-2}		6.2	4.5		

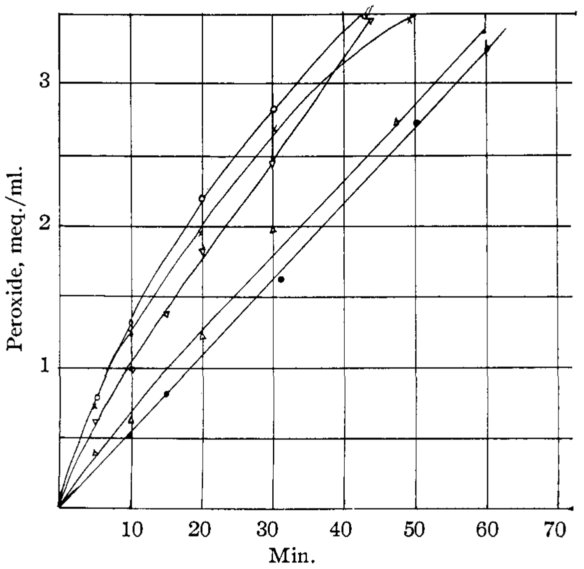

Fig. 6.—Rate of photoöxidation of resorcinol at various concentrations in aqueous suspensions of zinc oxide at 3650 Å., 20°: ○, 10^{-3} *M*; ×, 5×10^{-4} *M*; ▽, 5×10^{-3} *M*; △, 10^{-2} *M*; ●, 10^{-1} *M*.

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WEST HARTFORD, CONN.

[RESEARCH DEPARTMENT, U. S. NAVAL ORDNANCE TEST STATION]

Pyrolysis of Mixtures of Acetone and Acetone-d_6

BY J. R. MCNESBY, T. W. DAVIS[1] AND ALVIN S. GORDON

RECEIVED SEPTEMBER 4, 1953

Mixtures of acetone and acetone-d_6 were pyrolyzed at a variety of temperatures from 466–525° and the products examined. It is found that a Rice–Herzfeld mechanism is consistent with the facts, with the exception of the chain terminating reaction. Methyl ethyl ketone is not observed in the products but diacetone and ethane are present in small amounts. The activation energy difference for the abstraction of deuterium and hydrogen from acetone by methyl-d_3 radicals is 1.67 ± 0.09 kcal./mole. A brief investigation has been made of the effects of added carbon monoxide, propylene and iodine.

Recently[2] it was shown that the thermal decomposition of acetone at 500° proceeds almost entirely by a free radical mechanism. The Rice and Herzfeld mechanism[3] has been written as

$$CH_3COCH_3 \longrightarrow CH_3 + CH_3CO$$
$$CH_3CO \longrightarrow CH_3 + CO$$
$$CH_3 + CH_3COCH_3 \longrightarrow CH_4 + CH_2COCH_3$$
$$CH_2COCH_3 \longrightarrow CH_3 + CH_2CO$$
$$CH_3 + CH_2COCH_3 \longrightarrow CH_3CH_2COCH_3$$

There is good evidence in the literature for the first four reactions[4] but no evidence for the last. The only evidence reported for the existence of methyl ethyl ketone in the products of acetone decomposition is that of Allen[5] for the photolysis.

A quantitative study has been made of the relative rates of formation of the various methanes from the pyrolysis of mixtures of ordinary and deuterated acetones as functions of temperature from 466–525°. There is no methyl ethyl ketone in the products, but ethane and diacetone are present and are possible chain ending products.

Experimental

1. **Preparation of Materials. A. Acetone.**—Commercial acetone which had been distilled through a Widmer column was further purified by the sodium iodide method of Shipsey and Werner,[6] and again distilled through a Widmer column. The resulting material was then distilled *in vacuo* through a column of drierite and a column of P_2O_5 in tandem. Mass spectrometer analysis showed no impurity above mass 58 and no water. This acetone was used for the kinetic experiments and for the preparation of deuteroacetone.

B. **Acetone-d_6.**—A modification of the method of Halford, Anderson, Bates and Swisher[7] was used for the deu-

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(1) Professor of Chemistry, New York University. Work performed at NOTS while on leave from regular duties.

(2) J. R. McNesby, T. W. Davis and A. S. Gordon, *J. Chem. Phys.*, **21**, 956 (1953).

(3) F. O. Rice and K. F. Herzfeld, THIS JOURNAL, **56**, 284 (1934).

(4) E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publ. Corp., New York, N. Y., 1946, pp. 132–138.

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

(6) J. K. Shipsey and E. A. Werner, *J. Chem. Soc.*, **103**, 1255 (1913).

(7) J. O. Halford, L. C. Anderson, J. R. Bates and R. D. Swisher, THIS JOURNAL, **57**, 1633 (1935).

teroacetone preparation. One tenth gram of K_2CO_3 was dissolved in 10 cc. of D_2O, 25 cc. of normal acetone was added, and the mixture was shaken until homogeneous. The solution was allowed to stand three days to equilibrate. Then an excess of K_2CO_3 powder to complex the water was added until a thick slurry resulted. The acetone was then distilled *in vacuo* from the slurry into a similar vessel containing 10 cc. of D_2O and 0.1 g. of K_2CO_3. The above procedure was repeated until the sample of acetone had been cycled ten times. About 4 cc. of deuterated acetone was obtained. This material was distilled through a calcium sulfate column, and the distillate allowed to stand overnight over anhydrous calcium sulfate. The deuteroacetone so obtained was then distilled bulb to bulb *in vacuo* twice more to free it of dissolved air. The mass spectrum showed no water to be present and no peaks above mass 64, with the exception of the isotopic peaks. Mass spectrometer analysis showed that the product contained 95.7% acetone-d_6 and 4.0% acetone-d_5 with 0.3% acetone-d_4. This represents $D/(D + H) = 0.992$.

C. **Propylene.**—Commercial propylene was liquefied and pumped on for eight hours at −195°.

D. **Iodine.**—C.P. iodine was resublimed.

E. **Carbon Monoxide.**—Carbon monoxide was prepared by orthophosphoric acid dehydration of formic acid at 150–170°. It was purified by condensing the water and formic acid in a cold trap followed by a KOH trap to remove traces of formic acid and CO_2. Finally it was condensed in a trap surrounded by liquid nitrogen. About $^1/_3$ of the material was evaporated to free it of slight hydrogen impurity. About $^2/_3$ of the residual liquid was evaporated and stored. Mass spectrometric analysis failed to reveal any impurity.

2. **Procedures.**—The acetones were each frozen, pumped on and melted to expel air. This procedure was repeated about six times before any pyrolysis experiments were attempted. About 200 mm. of an equimolar mixture of acetone and acetone-d_6 was led at ambient temperature into an evacuated Pyrex reaction vessel of about 50-cc. capacity, equipped with a breakoff seal. The acetone mixture was then frozen at −195° and the reaction vessel flame sealed under vacuum. The sample was heated by plunging the reaction vessel into a stirred molten salt-bath whose temperature was controlled to ±0.1° by manually varying the voltage across the heating element. As soon as the reaction vessel was withdrawn from the salt-bath it was cooled in a blast of cold air.

3. **Analysis.**—The gases resulting from the pyrolysis were examined with a mass spectrometer. The gases were thermally fractionated prior to analysis. Volatile fractions were taken from the following refrigerants: liquid nitrogen, liquid oxygen, melting Freon "22" (−150°), melting Freon "11" (−100°), Dry Ice, boiling Freon "22" (−40°), salt-ice (−10°), and warm water (40°). In addition, a gross analysis of the pyrolyzed sample was carried out. The possibility of fractionation of the isotopic methanes when admitting them into the mass spectrometer from a liquid nitrogen bath has been investigated. The CD_3H/CD_4 ratio is the same when the sample is admitted to the mass spectrometer at −150° and at −195°. Therefore, fractionation does not occur when the methanes escape from a liquid nitrogen bath. Other experiments showed that fractionation does not occur even at solid nitrogen temperature.

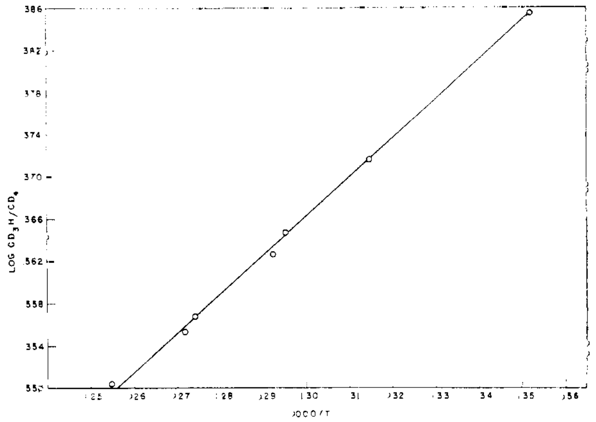

Fig. 1.—Reaction of CD_3 radicals with acetone and acetone-d_6.

Results

By means of the thermal fractionation technique it is possible to analyze the methane fraction.[8] The material volatile from liquid nitrogen consists largely of CO and the various methanes. In addition, there are smaller amounts of ethane and ethylene present.

An examination of Fig. 1 shows clearly that when the initial CD_3H/CD_4 ratio for 1:1 mixtures of ordinary and deuterated acetones is plotted as an Arrhenius relation over a temperature range, a good straight line is obtained. The situation is equally good for the CH_4/CD_4 ratio as shown in Fig. 2, but the CH_4/CH_3D ratio gives a scattered Arrhenius plot. In the evaluation of the CD_3H/CD_4 ratio, corrections were made for the small amount of exchange between the two acetones that took place in the course of the reaction. Of some interest is the observation that a mixture of the acetones suffered an almost statistical exchange at room temperature over a period of six months.

The data are plotted in Figs. 1 and 2. The isotopic methane distribution as a function of temperature is recorded in Table I. It should be noted that the CD_3H/CD_4 ratio is in excellent agreement with that of Wall and Moore[9] in the early stages of reaction at 500°. From the slope of the curve in Fig. 1 it can be calculated that the activation energy difference for the abstraction of D and H by a CD_3 radical is 1.67 ± 0.09 (standard deviation) kcal./mole if the sole source of methane is the abstraction of hydrogen from acetone by methyl radicals. It is found that the amount of CD_2H_2 formed is too large to be accounted for solely on the basis of a methyl radical reaction. For example, in a typical experiment at 513° the relative amounts of the various methanes were CD_4 = 80.5; CD_3H = 181.5; CD_2H_2 = 42.4; CH_3D = 166.8; CH_4 = 426.4. The average ratio of CD_2H to CD_3 and CH_2D to CH_3 groups is 0.05 during the run. The amount of CD_2H_2 arising from abstraction of H and D from acetone by CD_2H and

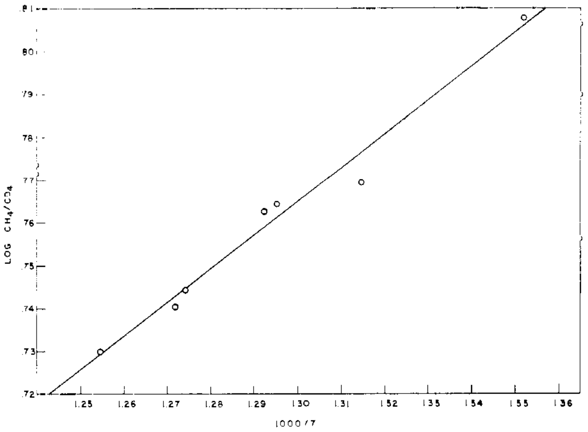

Fig. 2.—A test of the Rice–Herzfeld mechanism.

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

[9] L. A. Wall and W. J. Moore, *J. Phys. Chem.*, **55**, 965 (1951).

CH_2D, respectively, should be about 10% of the CD_3H value. Actually the amount of CD_2H_2 is about 23% of the CD_3H, more than twice as much as expected.

TABLE I

METHANE DISTRIBUTION AS A FUNCTION OF TEMPERATURE IN ACETONE PYROLYSIS

T, °C.	t, min.	CD_3H^a/CD_4	CH_4/CH_3D	CH_4/CD_4	Final[b] d_5/d_6
466.5	15	2.429	2.71	6.42	0.148
487.5	8	2.353	2.47	5.88	.140
498.9	2	2.316	2.53	5.81	.077
500.5	3	2.305	2.60	5.79	.080
511.6	2	2.274	2.50	5.55	.095
513.0	2	2.266	2.56	5.50	.084
523.8	3	2.241	2.71	5.37	.124

[a] The ratio in column 3 has been corrected to the value it would have if there were equal amounts of hydrogen and deuterium available in the acetones. Correction has also been made for CD_2H radicals as a source of CD_3H. [b] This is the ratio of acetone-d_5 to acetone-d_6 after pyrolysis.

A pressure of 26.8 mm. of iodine vapor at 90° was added to 200 mm. of the 1:1 acetone mixture at room temperature, and the pyrolysis of this system carried out at 497° for 15 minutes. The resulting CD_3H/CD_4 ratio was 4 and the unreacted acetones were almost statistically equilibrated. In view of the enormous amount of exchange which had taken place, thereby producing large quantities of CD_2H and CH_2D radicals, the magnitude of this ratio is not surprising. Total methane formation was accelerated by iodine. No organic iodides or hydrogen iodide are found in the products.

The pyrolysis in the presence of propylene was carried out in an attempt to identify the products formed in the propylene inhibited reaction. One hundred millimeters of propylene was added to 200 mm. of the 1:1 acetone mixture, and this was pyrolyzed at 500° for five minutes. A number of small mass peaks were observed in the mass region 77–84 with the largest at mass 82. This suggests the presence of di-allyl, formed by a combination of two allyl radicals. The quantity of methane in the fraction volatile at −183° showed that propylene sharply represses the pyrolysis rate. The ratio of CD_3H/CD_4 was about 7 and the acetone exchange was small.

A 1:1:1 mixture of acetone:acetone-d_6:CO was pyrolyzed at 500°. The CO acted as an inert gas. No significant change in the methane ratios was observed. Also the amount of CO_2 formed was not significantly changed.

A two-liter sample of normal acetone was pyrolyzed at 500 ± 10° in an annealing oven for 15 minutes in an effort to identify species resulting from the chain terminating reaction. In this experiment the reaction vessel was too large for the furnace normally used. In the fraction volatile from warm water, significant peaks were observed at masses 114, 100, 99, 85, 72, 71. The products of acetone pyrolysis are mainly CO, methane and ketene, with small amounts of ethylene and CO_2. Very small amounts of isobutylene, ethane, diacetone and acetylacetone are also found. No peaks appear in the spectra of the fractionated products above mass 64, except in the fraction volatile from warm water. The major peak heights from the fraction volatile from warm water are tabulated in Table II.

TABLE II

PEAK HEIGHTS OF FRACTION VOLATILE FROM WARM WATER FOR ACETONE PYROLYSIS AT 500° COMPARED WITH KNOWN PATTERNS OF DIACETONE AND OF ACETYLACETONE

Mass	Peak height	Peak pattern of $(CH_3COCH_2)_2$	Peak pattern of CH_3COCH_2-$COCH_3$	Residual
71	11.0	10.5		0.5
72	4.5	2.2	2.3	0.0
85	30.2		27.6	2.6
99	18.0	18.5		−0.5
100	19.1		19.1	0.0
114	5.0	5.0		0.0

Mass spectra of acetonylacetone and acetylacetone were determined and compared with the mass peaks from the warm water fraction in Table II to complete the identification.

Acetonylacetone and ethane formation are probably the chain ending steps. Acetylacetone is probably formed from acetonyl free radicals reacting with ketene to form a free radical which stabilizes itself by abstracting hydrogen from acetone. The over-all reaction is chain continuing. Methyl ethyl ketone is not an important product since it was not identified in any fraction.

Discussion

It appears likely that rather long chains are set up in the region of 500° and that the chain terminating step is complex. The formation of ethane from two methyl radicals, and the formation of acetonylacetone both seem to occur. The results presented may be explained quantitatively according to the Rice–Herzfeld mechanism with only the chain terminating step in question. Long chains imply a high methane to CO ratio. The presence of ethylene and ketene as well as large amounts of CO indicate that ketene decomposition products are also present. In the early stages of reaction, the methane/CO ratio is of the order of 5–10, while after a few tenths per cent. of reaction the ratio drops to about two. The work of Winkler and Hinshelwood[10] shows that after a time ketene is decomposed as rapidly as it is formed.

Acetone pyrolysis has been asserted to be first order in acetone on the basis that the time for a given fraction of acetone to decompose is independent of pressure. The evidence presented by Winkler and Hinshelwood in support of this assertion shows that an apparent first-order relationship exists only from about 120–300 mm. at 602°. Below 120 mm. a plot of $1/t_{1/2}$ *vs.* initial pressure reveals two linear regions of decreasing slopes as pressure is increased. Finally at about 120 mm. the curve flattens out giving an apparent first-order relation.

It is evident that a plot of $1/t_{1/2}$ *vs.* $P_0^{1/2}$ should be linear for a 3/2-order reaction. When Winkler and Hinshelwood's data are plotted in this form a good straight line results from 3.5 mm. to about 120 mm. at 602°. Further, their data show that the $t_{3/4}/t_{1/2}$

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[10] C. A. Winkler and C. N. Hinshelwood, *Proc. Roy. Soc.* (*London*), **A149**, 340 (1935).

ratio of about 2.7 is actually more in harmony with a 3/2-order reaction than with a first-order reaction. In the light of this information and of the absence of methyl ethyl ketone in the pyrolysis products, there is good reason to doubt that acetone pyrolysis is cleanly first order.

With ethane formation as the chain ending step in a Rice–Herzfeld mechanism, the rate of acetone disappearance should be 3/2 order while diacetone formation gives an order between 1/2 and 1 depending on the relative values of the rate constants for the elementary steps. In addition, the possibility of methylene radicals from decomposing ketene may further complicate the picture. In view of the above it is not surprising that Winkler and Hinshelwood's data can reflect such peculiar behavior with pressure. The Rice–Herzfeld mechanism for mixtures of acetone and acetone-d_6 may be written

$$CH_3COCH_3 \longrightarrow 2CH_3 + CO \tag{1}$$
$$CD_3COCD_3 \longrightarrow 2CD_3 + CO \tag{2}$$
$$CH_3 + CH_3COCH_3 \longrightarrow CH_4 + CH_3COCH_2 \tag{3}$$
$$CH_3 + CD_3COCD_3 \longrightarrow CH_3D + CD_3COCD_2 \tag{4}$$
$$CD_3 + CH_3COCH_3 \longrightarrow CD_3H + CH_2COCH_3 \tag{5}$$
$$CD_3 + CD_3COCD_3 \longrightarrow CD_4 + CD_2COCD_3 \tag{6}$$
$$CH_3COCH_2 \longrightarrow CH_3 + CH_2CO \tag{7}$$
$$CD_3COCD_2 \longrightarrow CD_3 + CD_2CO \tag{8}$$
$$2CH_2COCH_3 \longrightarrow (CH_3COCH_2)_2 \tag{9}$$
$$2CD_2COCD_3 \longrightarrow (CD_3COCD_2)_2 \tag{10}$$
$$CH_3COCH_2 + CD_2COCD_3 \longrightarrow CH_3COCH_2CD_2COCD_3 \tag{11}$$
$$CH_3 + CH_3 \longrightarrow C_2H_6 \tag{12a}$$
$$CD_3 + CD_3 \longrightarrow C_2D_6 \tag{12b}$$
$$CH_3 + CD_3 \longrightarrow CH_3CD_3 \tag{12c}$$

It follows from 5 and 6 that

$$CD_3H/CD_4 = \sigma_5/\sigma_6 e^{(E_6 - E_5)/RT} \tag{13}$$

The following assumptions are made in solving the usually steady state equations: (a) $k_7 = k_8$; (b) $k_3/k_5 = k_4/k_6$: (c) for a long chain reaction k_1A, $k_2\text{A}_\text{D}$, $k_9(\text{A}_\text{D}')^2$, $k_{10}(\text{A}')^2$, $k_{11}(\text{A}')(\text{A}_\text{D}')$, $k_{12a}(CH_3)^2$, $k_{12b}(CD_3)^2$, $k_{12c}(CD_3)(CH_3)$ are all small, where A represents acetone, A_D is deuteroacetone, A′ is acetonyl, and A_D' is deuteroacetonyl.

From the steady state relations and from assumptions (a), (b) and (c)

$$CH_3/CD_3 = k_5/k_4$$

From 3 and 6

$$CH_4/CD_4 = k_3CH_3/k_6CD_3 = k_5/k_6 \times k_3/k_4$$
$$CH_4/CD_4 = \sigma_5/\sigma_6 e^{(E_6 - E_5)/RT}\ \sigma_3/\sigma_4\ e^{(E_4 - E_3)/RT}$$

As shown in Fig. 2, the plot of log CH_4/CD_4 *vs.* $1/T$ gives a slope of 3.60 kcal./mole. The above treatment shows this slope to equal $E_6 - E_5 + E_4 - E_3$. From the plot in Fig. 1, $E_6 - E_5 =$ 1.7 kcal./mole and therefore $E_4 - E_3 = 1.9$ kcal./mole. This value is fairly close to the value of $E_6 - E_5$, which is more accurate and indicates that $E_6 - E_5 = E_4 - E_3 = 1.7$ kcal./mole. All the above slopes were obtained from least square treatment of the data.

The assumption (b) $k_3/k_5 = k_4/k_6$ requires that $k_3/k_4 = k_5/k_6$ and that the CH_4/CH_3D ratio should be equal to the CD_3H/CD_4 ratio. An inspection of the data indicates that the CH_4/CH_3D ratio is about 15% too high.

Also, as has been noted, the CH_2D_2 cannot all be accounted for on the basis of hydrogen abstraction by CD_2H radicals and deuterium abstractions by CH_2D radicals formed from the acetone or acetonyl decomposition. There are two possibilities for these observations: 1. Ketene or methylene may react with acetone. 2. There may be an error in the methane spectral pattern. This would have no effect on the CD_3H/CD_4 ratio since the mass 19 and mass 20 peaks are uncontaminated. CH_4 is also quite reliable since it is present in relatively large concentrations and errors in subtraction of the mass 16 peak arising from other methanes are not serious.

To check the possibility of ketene or methylene contributions, the photolysis of acetone–acetone-d_6 mixtures is being studied over a temperature range where no ketene is formed.

Steacie and his collaborators[11-13] have reported three values; 10.3, 10.6 and 11.6 kcal./mole for the activation energy for abstraction of D from acetone-d_6 by CD_3 radicals. As will be seen in the following presentation, the results of this work argue for the last value. A plot of log CH_4/CD_3H *vs.* $1/T$ on the assumption that $CH_3/CD_3 = \Delta E/RT$ shows that the activation energy for CD_3 and CH_3 abstracting a hydrogen atom from acetone is negligible. From this information and the knowledge that the activation energy difference for abstraction of D and H from acetone by CD_3 radicals is 1.7 kcal./mole, it would be expected that the difference in activation energy for the reactions

$$CD_3 + CD_3COCD_3 \longrightarrow CD_4 + CD_2COCD_3$$
$$CH_3 + CH_3COCH_3 \longrightarrow CH_4 + CH_2COCH_3$$

should be $\Delta E = 1.7$ kcal./mole. Results of recent work[11-15] are in excellent agreement that the activation energy for the latter reaction is 9.6 kcal./mole. The activation energy for the former reaction should thus be 11.3 kcal./mole, a value very close to that recently reported by Whittle and Steacie.[13]

The greatly accelerated rate of exchange between D and H brought about by the introduction of iodine into the system, as well as the absence of any compounds of iodine in the products, is worthy of comment. A possible explanation for the increased rate of exchange is that iodine atoms react with acetone[16] more rapidly than do methyl radicals, and the following reactions occur

$$I + CH_3COCH_3 \longrightarrow HI + CH_2COCH_3$$
$$HI + CD_2COCD_3 \longrightarrow CD_2HCOCD_3 + I$$
$$CH_2COCH_3 + CD_3COCD_3 \longrightarrow CH_2DCOCH_3 + CD_2COCD_3$$

The HI or DI may be removed rapidly by the reaction[17,18]

$$HI + CH_3 \longrightarrow CH_4 + I$$

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

(12) A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **18**, 1097 (1950).

(13) E. Whittle and E. W. R. Steacie, *ibid.*, **21**, 993 (1953).

(14) A. J. C. Nicholson, This Journal, **73**, 3981 (1951).

(15) M. Szwarc, *ibid.*, **74**, 6005 (1952).

(16) G. M. Gantz and W. D. Walters, *ibid.*, **63**, 3412 (1941)

(17) H. M. Chadwell and J. Titani, *ibid.*, **55**, 1363 (1933).

(18) R. A. Ogg, Jr., *ibid.*, **56**, 526 (1934).

and any methyl iodide formed may react with HI[18]

$$CH_3I + HI \longrightarrow CH_4 + I_2$$

so that the resulting HI is below the sensitivity of the mass spectrometer.

The evidence from the reaction in the presence of propylene sheds some light on the question of whether the propylene reacts with CH_3 or with CH_3COCH_2 to inhibit the decomposition. Since the CD_3H/CD_4 ratio is elevated in the presence of propylene, the CD_3 prefers to react with propylene rather than with acetone. The residual allyl radical apparently is unreactive and reacts only with another allyl radical. This picture appears to explain propylene inhibition if it is noted that acetonyl radicals and methyl radicals act to propagate the chains. If the methyl radicals preferentially abstract hydrogen from propylene, some chains are broken and the average chain length is shortened.

The percentage of CO_2 is not appreciably changed when as much as 33% CO is present during pyrolysis. CO_2 is thus probably formed from the decomposition of ketene.[19]

Acknowledgment.—The authors wish to thank Dr. S. R. Smith for development of mass spectrometer techniques employed in this research, and Professor Milton Burton for many stimulating discussions. The authors also wish to thank Mr. E. A. Fay for his assistance in the statistical analysis of the data.

[19] W. D. Walters, private communication.

CHINA LAKE, CALIF.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE GEORGIA INSTITUTE OF TECHNOLOGY]

The Kinetics of the Base-catalyzed Deuterium Exchange of Chloroform in Aqueous Solution[1,2]

BY JACK HINE, ROY C. PEEK, JR., AND BILLY D. OAKES

RECEIVED OCTOBER 8, 1953

The kinetics of the reaction of deuterochloroform with sodium hydroxide in homogeneous aqueous solution has been studied by infrared measurements of the isotopic content of the haloform. Rate constants at 0, 20.1 and 35° and values of the heat and entropy of activation have been determined. The reaction appears to be only slightly subject to general base catalysis and has been found to proceed very nearly half as fast as the analogous reaction of chloroform with sodium deuteroxide in deuterium oxide solution.

As part of a study of the relative importance of inductive and resonance effects on acidity, and also in relation to the mechanism of the basic hydrolysis of chloroform,[3] we became interested in studying the rate of the base-catalyzed deuterium exchange of chloroform. By use of a heterogeneous mixture of chloroform and alkaline heavy water, Horiuti and Sakamoto have shown that the reaction is rapid compared to the basic hydrolysis.[4] However, we were interested in learning the rate constants and heat and entropy of activation in homogeneous solutions, and something about the kinetic isotope effect and existence of general base catalysis. For economy we have in most cases used deuterochloroform as the reactant and "ordinary" water as the solvent.

Experimental

Reagents.—Deuterochloroform was prepared from chloral and 99.8% deuterium oxide (obtained from the D. A. Stuart Oxygen Co. on allocation from the Atomic Energy Commission) by a modification of the method of Boyer, Bernstein, Brown and Dibeler,[5] fractionated through a 30-in. column packed with glass helices and stored in a number of small sealed glass tubes under nitrogen until used. The material used had a boiling point range of less than 0.2° and an isotopic purity of 98.5% as determined by the spectroscopic method described in the next section.

Carbonate-free sodium hydroxide solutions and "isoöctane" (2,2,4-trimethylpentane) of greater than 99 mole per cent. purity were used. The methylamine was freshly distilled from a 25% aqueous solution of the C.P. material into distilled water.

Analysis.—The chloroform-deuterochloroform mixtures were analyzed by infrared measurements using a Perkin-Elmer Model 21 instrument. The deuterochloroform was analyzed for chloroform by measurements on the 8.233 μ band in carbon disulfide solution and on the 13.085 μ band in isoöctane solution. If it is assumed that pure deuterochloroform has no absorption at either of these wave lengths, these analyses show the presence of 1.6 ± 0.1% and 1.4 ± 0.1% chloroform, respectively, and the material was therefore taken to be 98.5% isotopically pure.[6]

The analyses for kinetic runs were made on isoöctane solutions at two absorption maxima for deuterochloroform and one for chloroform. The Beer-Lambert law was shown to hold in all cases, and the following molecular extinction coefficients (and average deviations), determined with the resolution control set at 960 (corresponding to slit schedule 3 for earlier machines), were used[7]

$$\epsilon^{CDCl_3}_{11.005} = 376 \pm 2 \quad \epsilon^{CDCl_3}_{13.085} = -0.006 \pm 0.002 \quad \epsilon^{CDCl_3}_{13.536} = 731 \pm 4$$

$$\epsilon^{CHCl_3}_{11.005} = -0.010 \pm 0.003 \quad \epsilon^{CHCl_3}_{13.085} = 915 \pm 8 \quad \epsilon^{CHCl_3}_{13.536} = 25.3 \pm 0.4$$

The deuterochloroform concentration was the average of that determined at its two maxima, the average deviation being about 1%. All measurements were made in the same cell, the solutions being diluted if necessary to bring the optical density in the range 0.2–0.6.

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(1) This study was carried out as part of a project sponsored by the Atomic Energy Commission.

(2) Paper II in the series "The Mechanism of the Base Catalyzed Decomposition of Haloforms." For Paper I see ref. (3).

(3) J. Hine, THIS JOURNAL, **72**, 2438 (1950).

(4) Y. Sakamoto, *J. Chem. Soc. Japan*, **57**, 1169 (1936); J. Horiuti and Y. Sakamoto, *Bull. Chem. Soc. Japan*, 11, 627 (1936).

(5) W. M. Boyer, R. B. Bernstein, T. L. Brown and V. H. Dibeler, THIS JOURNAL, **73**, 770 (1951).

(6) If the assumption is incorrect the isotopic purity is even higher.

(7) The extinction coefficients listed for deuterochloroform are for the isotopically pure material. All extinction coefficients were determined from the optical density of a standard solution compared with pure solvent in the same cell and are therefore "apparent" extinction coefficients, the negative values corresponding to wave lengths at which the solvent absorbs more strongly than the haloform.