suggest that an investigation of the effect of temperature on the primary process using high intensity light should provide additional information.

Hexafluoroacetone.—Ayscough and Steacie[22] recently have investigated the photolysis of hexafluoroacetone at 3130 Å. The only volatile products were hexafluoroethane and carbon monoxide in a ratio that varied from 1.00 at 27° to 0.90 at 300°. High ratios of fluoroform to hexafluoroethane were found when hexafluoroacetone was photolyzed in the presence of a hydrocarbon, proving CF_3 radicals were formed in the photolysis. The absence of tetrafluoromethane shows that trifluoromethyl radicals do not abstract a fluorine atom from the hexafluoroacetone even at 350°. Since the ratio of hexafluoroethane to carbon monoxide does not rise above one at any of the temperatures and pressures studied, and since perfluorobiacetyl is not a product, perfluoroacetyl radicals, if present, must decompose before they can take part in any other reaction. A straight line was obtained when $\Phi(CO)/(1 - \Phi(CO))$ was plotted against the reciprocal of the hexafluoroacetone pressure.

Because of the similarity between hexafluoroacetone and acetone, it is possible that the mechanism postulated here to explain the high intensity photolysis of acetone might also explain these results of Ayscough and Steacie. This mechanism, when applied to hexafluoroacetone, becomes

$$A + h\nu \longrightarrow A' \tag{21}$$

$$A' \longrightarrow CF_3CO + CF_3 \tag{22}$$

$$A' + A \longrightarrow 2CF_3 + CO + A \tag{23}$$

$$A' + A \longrightarrow 2A \tag{24}$$

$$2CF_3 \longrightarrow C_2F_6 \tag{25}$$

$$CF_3CO \longrightarrow CF_3 + CO \tag{26}$$

Here it is assumed that the perfluoroacetyl radical decomposes by reaction 26 before it can enter any other radical reactions. This is true of the acetyl radical above 100° in photolyses conducted at normal intensities and is expected to be true of the perfluoroacetyl radical at even lower temperatures.

A steady-state solution of the steps contained in this mechanism predicts the linear relationship observed by Ayscough and Steacie.

$$\Phi(CO)/(1 - \Phi(CO)) = k_{23}/k_{24} + k_{22}/k_{24}(A)$$

Hence the data are consistent with this mechanism.

Ayscough and Steacie give a mechanism that fits the data equally well. Their mechanism, however, is inapplicable to the photolysis of acetone at high intensity. This seems to be the only basis for preference of the mechanism 21–26.

Summary

The photolysis of acetone has been investigated with monochromatic light (2800 Å.) at absorbed intensities greater by about 10^6 than those normally used. The resulting predominance of reactions which are second order in radical concentrations has led to distinctly new information concerning the primary process of this much-studied reaction. Consideration of this information together with all of the earlier data leads to a mechanism which differs in several details from the previously accepted mechanism. This new set of reactions is also applicable to recent studies on the low intensity photolysis of hexafluoroacetone.

Acknowledgment.—We wish to express our thanks to Professors W. D. Gwinn, R. E. Powell and G. J. Mains for many helpful suggestions. We also wish to express our gratitude to Dr. Amos Newton for conducting and aiding in the interpretation of the mass spectrographic analyses.

BERKELEY, CAL.

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[22] P. B. Ayscough and E. W. R. Steacie, *Proc. Roy. Soc.* (*London*), **234A**, 476 (1956).

[CONTRIBUTION FROM THE U. S. NAVAL ORDNANCE TEST STATION]

Photolysis and Pyrolysis of 2-Pentanone-1,1,1-3,3-d_5

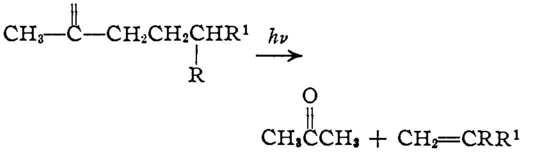
BY J. R. McNESBY AND ALVIN S. GORDON

RECEIVED JULY 12, 1957

The photolysis of $CD_3COCD_2CH_2CH_3$ was studied over a range of temperatures from 35 to 300°. In addition, some pyrolysis was done at about 500°. In the low temperature photolysis range, the ethylene/acetone ratio was found to be sensitive to the flux density of the radiation. If a γ-hydrogen shift mechanism is postulated, all the acetone formed should be -d_5. However, there was more d_6-acetone than d_5-acetone in the products. The results have been interpreted in terms of an excited molecule mechanism. In the pyrolysis region, the reaction appears to follow a free radical mechanism.

Introduction

A considerable amount of research has been reported on the mechanism of the photolysis of methyl ketones.[1-4] Acetone and methyl ethyl ketone appear to proceed *via* free radical mechanisms. However, there is a considerable amount of evidence[1-4] that methyl *n*-propyl ketone and other methyl ketones which have a γ-hydrogen atom undergo an intramolecular photolysis with the γ-hydrogen atom migrating to the α-position.



$$CH_3\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}CH_2CH_2\underset{\underset{\displaystyle R}{|}}{C}HR^1 \xrightarrow{h\nu} CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_3 + CH_2{=}CRR^1 \tag{1}$$

The reported quantum yields of olefin and acetone are clearly independent of temperature[3,4] which

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(1) R. G. W. Norrish and M. E. S. Appleyard, *J. Chem. Soc.*, 874 (1934).

(2) C. H. Bamford and R. G. W. Norrish, *ibid.*, 1538 (1938).

(3) W. Davis, Jr., and W. A. Noyes, Jr., THIS JOURNAL, **69**, 2153 (1947).

(4) A. J. C. Nicholson, *Trans. Faraday Soc.*, **50**, 1067 (1954).

TABLE I

PRODUCT ANALYSES IN MOLE PER CENT. FOR DECOMPOSITION OF METHYL *n*-PROPYL KETONE-d_5

	84A	77	76	73B	77D	81A[a]	77C	85	79A[b]	83[c]
T, °C.	35	35	30	156	148	158	302	478	152	152
t, hr.	0.22	0.22	6.5	24	0.42	0.3	0.16	0.22	0.28	0.31
Intensity	High	High	Low	Low	High	High	High	None	High	High
CO	16.2	13.0	8.4	21.0	27.9	23.6	36.2	10.2		
Methane	8.9	9.6	3.3	11.9	4.7	2.4	18.2	41.5		
Ethylene	43.4	49.8	39.9	22.0	25.8	31.2	26.0	20.7		
Ethane	2.0	2.3	0.9	4.1	5.2	4.7	1.7	0.0		
Propane	1.6	1.4	1.7	5.9	2.1	2.9	5.6	0.0		
Propylene	....	....	....	2.7	....	....	2.2	15.6		
Butane	0.3	1.1	2.7	8.4	9.7	9.9	0.0	0.0		
Acetone	21.1	20.5	40.4	21.3	21.9	22.5	10.0	12.0		
Hexane	....	2.2	2.8	2.5	2.8	2.9	0.0	0.0		
$(k_6k_4)^{1/2}/k_5$	....	....	0.6	0.38	0.39	0.37	....	....		
$(k_7/k_6)^{1/2}$	13.5	13.8	2.1	3.9	5.2	....	....	....		
Acetone/ethylene	0.49	0.41	1.0	1.0	0.85	.72	0.38	0.58		
Acetone, No. of D's										
2	2	....	1	1	1	1	9	5	1.7	11.3
3	6	....	2	2	3	2	22	14	3.7	28.1
4	15	....	8	8	8	5	32	29	12.2	44.6
5	36	....	26	30	30	30	26	34	47.5	39.3
6	41	....	63	59	58	62	10	18	34.8	15.0
Anal. of D of the ethylene cut										
d_0	....	85	93	55	92	97	50			
d_1		5	3	35	2	3	38			
d_2		10	4	10	6		12			

[a] The products from three runs at 15 mm. pressure were measured and summed. In all other runs the pressure was 45 mm. [b] 24 mm. diethyl ketone + 24 mm. $CD_3COCD_2CH_2CH_3$. [c] 60 mm. *n*-hexane + 38 mm. $CD_3COCD_2CH_2CH_3$.

suggests an intramolecular process. In this work the mechanism of the γ-shift was studied with the aid of isotopic marking.

Experimental

The $CD_3CO-CD_2CH_2CH_3$ used in this work was prepared from synthetic $CH_3COCH_2CH_2CH_3$ obtained from the Delta Chemical Company. Examination by infrared showed that bands characteristic of diethyl ketone were absent. The ketone was deuterated in the five α-positions by gently refluxing 25 cc. of ketone with 9 cc. of D_2O containing 0.1 g. of K_2CO_3 for about eight hours. The two phase mixture was cooled and the ketone salted out of the water layer with excess K_2CO_3. The water layer was discarded and the partially deuterated ketone layer was again treated with D_2O and K_2CO_3. The procedure was repeated ten times and the ketone distilled *in vacuo* from K_2CO_3 into a reservoir isolated by a mercury cutoff. The mass 91/90 ratio of the ketone was 42.5. The only mass showing above 91 was the normal C^{13}-isotope of the d_5-ketone at mass 92. In addition, comparison of the mass spectrum of the d_5-ketone with that of the normal ketone indicated that the carbons alpha to the carbonyl group were deuterated.

Experiments were carried out by permitting the ketone vapor to expand into a previously evacuated fused silica reaction vessel in an aluminum block furnace. The photolyses were performed with a medium pressure mercury arc where the 2537 Å. line is not generated. After reaction the mixture was pumped into a sample flask which facilitated the gas chromatographic analysis. A six-ft. 1.5% squalane on carbon black (Pelletex) column was employed. A synthetic blend of CO, CH_4, C_2H_4, acetone and *n*-hexane was made up and chromatographed. Areas under chromatogram peaks were considered to be proportional to the number of moles of the constituent. In this way percentage compositions in the products were estimated. Minor products were estimated by interpolation of the calibration runs. The percentage of each product reported is within 10% of the true value. Usually reactions were carried out to 1–2% decomposition.

Results and Discussion

To get direct experimental proof of the mechanism, the $CD_3COCD_2CH_2CH_3$ was photolyzed over a temperature range 25–300°. If the intramolecular mechanism is correct the ketone will produce only

$$CD_3COCD_2CH_2CH_3 \longrightarrow CD_3COCD_2H + CH_2{=}CH_2 \qquad (2)$$

Each of the products was trapped separately by means of gas chromatographic techniques[5] and analyzed for D content on the mass spectrometer.

Acetone and Ethylene.—It was originally felt that the marking of the acetone would be the most important feature of the reaction. However, it was found that acetone-d_6 exchanged on the gas chromatography column with some compounds with light H. Thus, the acetone-d_6/acetone-d_5 values found by analysis of the acetone fraction from the gas chromatography column are minimum values. The methyl *n*-propyl ketone-d_5 did not exchange on the column.

The marking of the acetone was studied over a temperature range with low and high intensity radiation, as well as in the pyrolysis region. The results are recorded in Table I.

The values at 35 and 150° are the most interesting, since the acetone exchanges rapidly during the course of the reaction at higher temperatures.

At 150°, the CD_3CO radical is unstable so that the acetone-d_6 cannot form *via*

$$CD_3 + CD_3CO \longrightarrow CD_3COCD_3 \qquad (3)$$

The following observations were made which bear on the mechanism:

1. The ethylene/acetone ratios at 35° are over 2 at high intensity and about 1 at low intensity.

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[5] C. M. Drew, J. R. McNesby, S. R. Smith and A. S. Gordon, *Anal. Chem.*, **28**, 979 (1956).

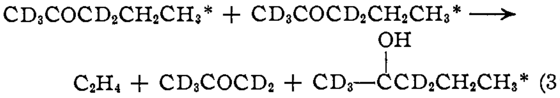
2. The ethylene/acetone ratio at high light intensity decreases to a little over 1 at about 150°, but sharply increases at temperatures above 300° where the *n*-propyl radical breaks down efficiently to CH_3 and C_2H_4.

3. The minimum acetone-d_6/acetone-d_5 ratios are always over 1, except where a light H source such as diethyl ketone, or *n*-hexane is present during photolysis. The above ratio is severely lowered under these conditions.

4. At 35° methane and ethane are minor products relative to ethylene.

5. As may be noted in Table I, at 30° most of the ethylene is light. At 150° most of the ethylene is light at high light intensity and short reaction times, but there is a very significant amount of D marking at low intensity and long reaction time. At 302° there is also a very significant amount of marking.

The ethylene/acetone ratio at 35° is intensity dependent and this indicates that part of the ethylene is formed *via* an excited molecule-excited molecule process such as



$$CD_3COCD_2CH_2CH_3^* + CD_3COCD_2CH_2CH_3^* \longrightarrow C_2H_4 + CD_3COCD_2 + CD_3\text{—}\overset{\displaystyle OH}{\overset{|}{C}}CD_2CH_2CH_3^* \quad (3')$$

The ethylene is mainly light at this temperature as may be noted in Table I. These free radicals do not decompose or abstract in this low temperature region, and are cleaned up by subsequent radical–radical processes. The stable molecules from these processes will be high boiling and are not seen by our gas chromatography techniques; they are probably buried in the peaks of the parent compounds.

At higher temperatures the steady-state concentration of excited ketone is kept down by some type of quenching process. As a result the ethylene/acetone ratio decreases with increasing temperature at equal light intensity.

Acetone.—The acetone-d_6/acetone-d_5 ratios indicate that the acetonyl group from one ketone molecule can take a D atom from another ketone molecule to give acetone-d_6. In the presence of easy H sources such as diethyl ketone or *n*-hexane, acetone-d_5 is more efficiently produced, and the above ratio decreases. At 35°, the resonance stabilized acetonyl group cannot abstract H, and acetone formation must result from the reaction of an excited ketone molecule with an unexcited molecule.

Methane.—At 35° the CD_3H/CD_4 ratio is 1.51, while at 144° the ratio is 1.11, indicating that the over-all activation energy for the abstraction of D from the ketone by CD_3 is 0.7 kcal. greater than for the removal of H. The CH_4/CH_3D ratio at 144° is 1.2, in fairly good agreement with the CD_3H/CD_4 ratio. At low temperatures the abstraction from the pentanone is almost entirely from the $-CD_2-$ and $-CH_2-$ positions. The $-CH_2-$ position is probably like the secondary H in a paraffin, $E = 9.3$ kcal.[6] Thus the activation energy for abstraction from the $-CD_2-$ position is about 10.0 kcal.

However, there are reasons to suspect that the methanes may not be formed entirely *via* methyl radicals in this reaction. In the first place the ratio (rate methane)/(rate ethane)$^{1/2}$ at any temperature should depend only on the rate constant for the abstraction by methyl and the concentration of the ketone. This ratio is much higher for methyl *n*-propyl ketone-d_5 than it is for normal acetone under similar conditions. However, the over-all rate constant for methyl abstraction from normal acetone should be at least as large as for methyl *n*-propyl ketone-d_5, since the energy of activation for abstraction of D is about 1.7 kcal. higher than the corresponding H in acetone, and a secondary H is about 2 kcal. lower than a primary. In this ketone at low temperature, most of the abstraction is thus at the 2 secondary D's alpha to the carbonyl and at the two secondary H atoms. The energy of activation from these two positions will be within a few tenths of a kcal. of each other. The energy of activation for abstraction of the *six* H atoms in acetone will also be within a few tenths of a kcal. of the atoms discussed above. Secondly, the methane generated at 35° and high light intensity is much greater than would be expected from abstraction processes.

Propylene.—Propylene is formed by reaction 17 followed by reaction 18. In agreement with the mechanism, the small amount of propylene formed at 156° proved to be 95% propylene-d_2. At 478° the pyrolysis similarly gave mostly propylene-d_2.

Propane.—Propane is a minor product at low temperatures which disappears at high temperature. It is propane-d_3 and propane-d_2 in roughly equal quantities and presumably originated from the *n*-propyl-d_2 radical which abstracts H and D about equally.

Hexane.—Under conditions where the acetone is about 60% d_6, the hexane is more than 97% d_4 with less than 3% d_5 and d_6. The hexane is almost certainly formed by

$$2CH_3CH_2CD_2 \longrightarrow (CH_3CH_2CD_2)_2 \quad (4)$$

Butane.—Under the same conditions butane-d_5 is present and is formed by

$$CD_3 + CD_2CH_2CH_3 \longrightarrow CD_3CD_2CH_2CH_3 \quad (5)$$

Thus, the possibility that a primary process giving ethyl radicals is responsible for the butane is ruled out.

If ethane is formed *via*

$$2CD_3 \longrightarrow C_2D_6 \quad (6)$$

hexane *via* eq. 4, and butane *via* eq. 5, then

$$\frac{[C_2D_6]^{1/2}[CH_3CH_2CD_2CD_2CH_2CH_3]^{1/2}}{[CD_3CD_2CH_2CH_3]} = \frac{k_6^{1/2}k_4^{1/2}}{k_5} = \frac{R_E^{1/2}R_H^{1/2}}{R_B} \quad (1)$$

where R is the rate of formation[7] and k is the corresponding specific rate constant. If the areas under the chromatogram peaks are measured and reduced to a constant time of reaction, the quantity $R_E^{1/2}R_H^{1/2}/R_B$ should be independent of light intensity and of pressure. In Table I, this quantity is seen to be a constant at about 150°. The one value obtained at 30° is somewhat higher; there

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(6) J. R. McNesby and A. S. Gordon, THIS JOURNAL, **78**, 3570 (1956).

(7) The subscripts E M, H, B signify ethane, methane, hexane butane.

is no reason to suspect that k_4, k_5, or k_6 is temperature dependent.

Similarly, for

$$CD_3 + XR \longrightarrow CD_3X + R \qquad (7)$$

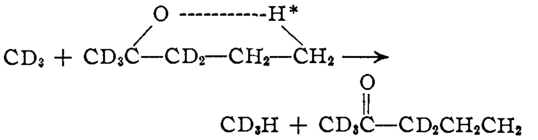
where X is H or D and

$$2CD_3 \longrightarrow C_2D_6 \qquad (6)$$

the ratio $R_M/R_E^{1/2} = k_7/k_6^{1/2}$ should be independent of intensity. Table I shows, however, that this ratio rises sharply at high light intensity at 35°. It seems likely that at high intensity a new source of readily available hydrogen appears, *e.g.*

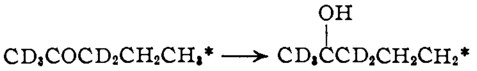
$$CD_3 + CD_3CO \longrightarrow CD_4 + CD_2CO \qquad (8)$$

or



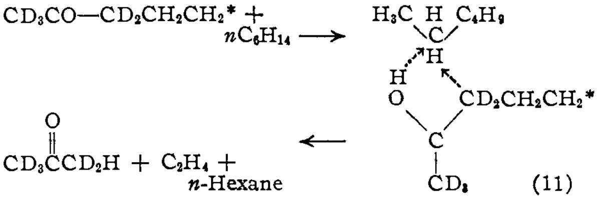
(9)

The mechanism for acetone production at low temperatures probably involves an excited ketone molecule and an unexcited molecule. One possibility is



$$CD_3COCD_2CH_2CH_3^* \longrightarrow CD_3\overset{OH}{C}CD_2CH_2CH_2^* \qquad (10)$$

If a labile H atom is introduced into the system



(11)

If the second molecule contains an easily extracted D atom, acetone-d_6 would be one of the products. Such is the case when the second molecule is the original ketone.

In the pyrolysis region at 478° carbon monoxide, methane, ethylene, propylene and acetone are the major products, as may be seen in Table I.

An experiment at 522° using the undeuterated ketone showed CO_2, as well as the above products. The pyrolysis of methyl *n*-propyl ketone in the temperature region 500–570° has been studied by Waring and Garik.[8] They found ethylene, propylene, methane and carbon monoxide and CO_2 to be the main products of the decomposition. They do not report any acetone in the products. Their free radical mechanism involves short chains. They state that by considering abstraction only from the α-methylene, the products can be predicted. If abstraction from all the H positions is considered, they claim that the product distribution is not shifted appreciably.

$$CH_3 + CH_3COCH_2CH_2CH_3 \longrightarrow CH_4 + CH_3COHCH_2CH_3 \qquad (12)$$

Acetone cannot be accounted for with their mechanism. We believe that all the H atoms can be abstracted from the parent ketone with relative rates determined by the energies of activation and number of H atoms on the C atom. At low temperatures, the α-methylene hydrogen would be favored by a considerable margin. In the pyrolysis range hydrogen abstraction at other positions would be competitive.

$$CD_3 + CD_3COCD_2CH_2CH_3 \longrightarrow CD_4 + CD_2COCD_2CH_2CH_3 \qquad (13)$$

$$CD_2COCD_2CH_2CH_3 \longrightarrow CD_2CO + C_2H_2D_2 + CH_3 \qquad (14)$$

$$CD_3 + CD_3COCD_2CH_2CH_3 \longrightarrow CD_4 + CD_3COCDCH_2CH_3 \qquad (15)$$

$$CD_3COCDCH_2CH_3 \longrightarrow CD_3 + COCDC_2H_5 \qquad (16)$$

$$CD_3 + CD_3COCD_2CH_2CH_3 \longrightarrow CD_3H + CD_3COCD_2CHCH_3 \qquad (17)$$

$$CD_3COCD_2CHCH_3 \longrightarrow CD_3 + CO + CH_3CHCD_2 \qquad (18)$$

$$CD_3 + CD_3COCD_2CH_2CH_3 \longrightarrow CD_3COCD_2CH_2CH_2 + CD_3H \qquad (19)$$

$$CD_3COCD_2CH_2CH_2 \longrightarrow C_2H_4 + CD_3COCD_2 \qquad (20)$$

$$CD_3COCD_2 + CD_3COCD_2CH_2CH_3 \longrightarrow CD_3COCD_3 + CD_3COCDCH_2CH_3 \qquad (21)$$

The above free radical mechanism accounts for all the pyrolysis products, except that we do not find ketenes in our gas chromatograms. Ketenes polymerize on the column material of a gas chromatographic unit. However, ketene has been observed in the pyrolysis products of acetone in this and other laboratories using mass spectrometer identification. At high temperatures it is one of the major products of acetone decomposition. Ethyl ketene is formed by a reaction analogous to the formation of ketene in the mechanism for acetone pyrolysis.

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[8] C. E. Waring and V. L. Garik, THIS JOURNAL, **78**, 5198 (1956).