tant magnitude is $k_p/(k_t k_d)^{1/2}$, which is determined at any temperature by the nature of the monomer and the initiator.

Equations 6 and 7 may also be very useful for kinetic studies. If k_d is known, as for 2-azobisisobutyronitrile, these equations, may be used to obtain $(k_p/k_t^{1/2})f^{1/2}$. If k_d and $(k_p/k_t)^{1/2}$ are known, the efficiency f can be found. Equation 6 can readily be put into the form

$$\frac{\ln(1-x)}{\ln(1-x_\infty)} = 1 - e^{-k_d t/2} \qquad (13)$$

A determination of x as a function of time, including the asymptotic value x_∞, immediately gives a value for k_d from equation 13.

The phenomenon of dead-end polymerization can be treated in more complex cases, where the disappearance of catalyst is not simply given by equation 3 but by an equation such as

$$-\frac{d[\text{Cat}]}{dt} = k_d\,[\text{Cat}] + k_i\,[\text{Cat}]^{\nu} \qquad (14)$$

where the second term on the right-hand side refers to induced decomposition. This situation would apply to benzoyl peroxide. The mathematical treatment is obviously more complex.

The treatment is very simple if we have an activated system where destruction of catalyst is given by

$$-\frac{d[\text{Cat}]}{dt} = k_d'[\text{Cat}][\text{Act}] \qquad (15)$$

and the initiation of polymer chains is given by

$$R_i = f'k_d'[\text{Cat}][\text{Act}] \qquad (16)$$

In equations 15 and 16 [Act] represents activator concentration and f' represents initiator efficiency.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

The Photolyses of 2-Pentanone and 2-Pentanone-1,1,1,3,3-d_5[1]

BY P. AUSLOOS AND E. MURAD

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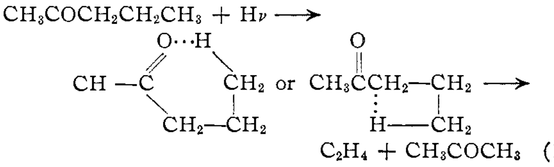
The photolyses of 2-pentanone and 2-pentanone-1,1,1,3,3-d_5 have been investigated at long wave lengths at maximum intensity of 3.7×10^{14} quanta/cc./sec. and at short wave lengths. This investigation was carried out in the temperature range 25–83°. In this study, ethylene was found to be, within experimental error, equal to the acetone yield. In the experiments with the deuterated ketone, 90% of the acetone formed was acetone-d_5. Secondary reactions are discussed and certain ratios of rate constants are deduced.

Introduction

Ketones containing at least one hydrogen atom in the γ-position dissociate photochemically into olefins and simple ketones.[2] As pointed out by Nicholson[3] the formation of 1-butene in the photolysis of methyl n-amyl ketone is evidence for the fact that a γ-hydrogen is involved in the molecular rearrangement process. This intramolecular rearrangement process has been visualized to take place *via* the formation of a ring intermediate. Taking 2-pentanone as an example, this process can be written as



(1)

However, in a recent study of the photochemical decomposition of 2-pentanone-1,1,1,3,3-d_5[4] it was found that over a wide intensity and temperature range more CD_3COCD_3 was produced than CD_3COCD_2H, and that at high intensities the ethylene/acetone ratio was higher than unity. Because these observations could not be explained by a process such as I, a different interpretation was presented, whereby, depending on the intensity, the excited ketone molecules reacted either with excited or with normal molecules.

In the present work the short and long wave length vapor phase photochemical decompositions of 2-pentanone and 2-pentanone-1,1,1,3,3-d_5 have been investigated at low temperatures and at intensities higher than those used in previous studies of these compounds. In a few photolyses oxygen was added to gain increased knowledge of the primary process.

Experimental

Irradiation.—The long wave length runs were made with an unfiltered Hanovia S-100 medium pressure mercury lamp. The light was collimated into the cell with one short focus lens. The distance between the lamp and the front window of the cell was approximately 6 cm. In most experiments the intensity was increased by irradiating the opposite end of the cell with a second Hanovia S-100 lamp. The volume of the cell was 195 ml. (10 cm. long and 5 cm. in diameter). The temperature of the cell was controlled by a constant temperature bath provided with double quartz windows and filled with distilled water. The number of quanta absorbed was determined by measuring the carbon monoxide yield in the photolysis of diethyl ketone at 90°.

The short wave length runs were carried out with a Hanovia hydrogen discharge lamp. The cell was placed at a distance of about 2 cm. from the lamp. At the low pressures used in these experiments, practically all of the absorbed radiation lies near 1900 Å. No attempt was made to determine the absorbed light intensity.

Analysis.—The carbon monoxide–methane fraction was removed at liquid nitrogen temperature and analyzed over hot CuO. The C_2 fraction was removed at −157°. The C_3 and C_4 fractions were separated at −135° and at −110°, respectively. All fractions were analyzed mass spectrometrically. Hexane, acetone, biacetyl and the parent compound were separated on a Perkin–Elmer Vapor Frac-

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[1] This research was supported in part by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under contract No. AF(600)-1528. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] For a review see: J. N. Pitts, Jr., *J. Chem. Educ.*, **34**, 112 (1957).

[3] A. J. C. Nicholson, *Trans. Faraday Soc.*, **50**, 1067 (1954).

[4] J. R. McNesby and A. S. Gordon, THIS JOURNAL, **80**, 261 (1958).

tometer, Model 154. The first two were subsequently determined mass spectrometrically. Biacetyl was determined only when appreciable quantities were present. In the earlier part of the investigation a 2-meter column A from the Perkin–Elmer Corp. was used for this analysis; however, this did not separate the acetone from the hexane. In the latter part of the study a 1-meter column of polyethylene glycol was used in series with another 1-meter column of polyoxyethylene sorbitan monostearate (both column materials were supplied by the Burrell Corp.). This combination permitted a separation of acetone from hexane. The amounts of acetone and hexane were determined in two ways: (1) from the peak areas of the vapor chromatograms and (2) from the peak heights of the mass spectra. On a few occasions, acetone and hexane were partially separated from the parent ketone in the vacuum line at $-90°$ and analyzed directly with the mass spectrometer.

Materials.—The 2-pentanone for this work has been purified by Dr. Guenther of this Department. Examination by vapor phase chromatography showed no detectable impurities. The 2-pentanone-1,1,1,3,3-d_5 was prepared from the light ketone by refluxing 15 ml. of the ketone with 6 ml. of D_2O in the presence of 80 mg. of K_2CO_3 in a nitrogen (dry nitrogen from Air Reduction Co.) atmosphere for 12 hours. The water layer was salted out with K_2CO_3. This procedure was repeated nine times; all of the work was carried out in a dark room, and, when necessary, a red light was used. The ketone was finally fractionally distilled in a dry nitrogen atmosphere and was separated into three fractions, the middle fraction being used. Final analysis showed this sample to contain no impurities. The height of the 90 peak was 2.5% of the 91 peak. The 92 peak could be attributed entirely to the C^{13} isotope of the ketone.

Results and Discussion

Photolysis of 2-Pentanone.—The photochemical decomposition of 2-pentanone was studied at high intensities and low temperatures to find out whether the previously[4] suggested excited molecule–excited molecule reaction

$$2CH_3COC_3H_7^* \longrightarrow C_2H_4 + CH_3COCH_2 + CH_3COHC_3H_7$$

takes place under these conditions.

The results given in Table I indicate that at both low and high intensities the ethylene yields are roughly equal to the acetone yields, although the absorbed intensities for the first two runs were approximately ten times higher than in the work of McNesby and Gordon.[5] From the equality of the ethylene and acetone it may be concluded that under the experimental conditions specified in this work, the above-mentioned process does not occur. The results of the two high intensity oxygen–2-pentanone runs given in Table I indicate that in agreement with recent experiments carried out in this Laboratory,[6] oxygen does not inhibit the olefin or acetone formation. This indicates that an upper singlet state probably is responsible for the formation of these products.

At this point it may be mentioned that at the intensities used in this work the probability for the occurrence of an excited molecule–excited molecule process should be low. Using the same lifetimes as those for acetone, namely, 8×10^{-6} and 5×10^{-4} sec. for the upper singlet and upper triplet states, respectively, it can be deduced that the probability for a singlet excited molecule to collide with another ketone molecule in the upper triplet or singlet state is about 10^{-3} and 10^{-5}, respectively.

Photolysis of 2-Pentanone-1,1,1,3,3-d_5.—Because a difference in lifetime between the electronically excited 2-pentanone and 2-pentanone-1,1,1,3,3-d_5 might explain the discrepancy between McNesby and Gordon's work and the results presented in this paper, it was decided to carry out analogous experiments to those given in Table I with the partially deuterated compound.[7]

The data of the experiments performed with the mercury lamp, presented in Table II, can be best explained by the mechanism

$$CD_3COCD_2CH_2CH_3 + h\nu$$
$$\longrightarrow CD_3COCD_2H + C_2H_4 \qquad (I)$$
$$\longrightarrow CD_3 + COCD_2CH_2CH_3 \qquad (II)$$
$$\longrightarrow CD_3CO + CD_2CH_2CH_3 \qquad (III)$$
$$CH_3CH_2CD_2CO \longrightarrow CH_3CH_2CD_2 + CO \qquad (1)$$
$$CD_3CO \longrightarrow CD_3 + CO \qquad (2)$$
$$CD_3CO + CD_2CH_2CH_3$$
$$\longrightarrow CD_3COCD_2CH_2CH_3 \qquad (3)$$
$$\longrightarrow CD_3CHO + CD_2{=}CHCH_3 \qquad (4)$$
$$\longrightarrow CD_2CO + CD_3CH_2CH_3 \qquad (5)$$
$$2CD_2CH_2CH_3 \longrightarrow (CH_3CH_2CD_2)_2 \qquad (6)$$
$$\longrightarrow CH_3CH_2CD_2H + CD_2CHCH_3 \qquad (7)$$
$$2CD_3CO \longrightarrow (CD_3CO)_2 \qquad (8)$$
$$\longrightarrow CD_3CDO + CD_2CO \qquad (9)$$
$$CD_3 + CH_3CH_2CD_2 \longrightarrow CD_3CD_2CH_2CH_3 \qquad (10)$$
$$\longrightarrow CD_3H + CD_2CHCH_3 \qquad (11)$$
$$CD_3 + CD_3CO \longrightarrow CD_3COCD_3 \qquad (12)$$
$$\longrightarrow CD_4 + CD_2CO \qquad (13)$$
$$2CD_3 \longrightarrow C_2D_6 \qquad (14)$$

It can be seen that the products given in Table II are in accordance with this mechanism, and that, consequently, only the α-carbons of 2-pentanone were deuterated. Abstraction reactions are of minor importance at the intensities and temperatures used in this work and have not been included in the reactions scheme. Also, reactions involving the $CH_3CH_2CD_2CO$ radicals have not been taken into account because it can be deduced from a comparison of the ethane and hexane yields that primary process II is at most 10% of primary process III.

Primary Process I.—The fact that at high intensities the ethylene yields are, within experimental error, equal to the acetone-d_5 yields indicates that in agreement with the light 2-pentanone photolysis data of Table I, excited molecule–excited molecule reactions do not occur under these conditions. Addition of oxygen did not affect the ethylene and acetone yields to any appreciable extent, which again indicates that both compounds are formed from an upper singlet excited molecule.

The results also indicated that the excited molecule–normal molecule reaction postulated by McNesby and Gordon to explain their high acetone-d_6/acetone-d_5 ratios does not necessarily have to be considered in this work, because acetone-d_5 accounts for at least 90% of the acetone, while the

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[5] A 1–2% conversion in the work of McNesby and Gordon was reached after 13 minutes, while in the present work a 2-minute photolysis led to a conversion of over 2%.

[6] V. Brunet and W. A. Noyes, Jr., *Bull. soc. chim. France*, 121 (1958).

[7] That the lifetime of an excited deuterated ketone may (but not necessarily so) differ considerably from that of the light molecule was demonstrated by a few phosphorescence measurements of acetone and acetone-d_6 in which it was found that the phosphorescence yield of acetone-d_6 was approximately $^1/_6$ that of acetone. Of course, a difference in the quantum yields would also have the same effect.

TABLE I

PHOTOLYSIS OF $CH_3COCH_2CH_2CH_3$[a]

Ketone concn., 1.75 × 10^{-6} mole/cc.

Temp., °C.	25	25	26	26	25	25	83
Time, min.	2	2	4	140	2	2	5
$I_{abs.}$, quanta/cc./sec. × 10^{-14}	3.75	3.75	2.15	0.09	3.75	2.15	2.15
O_2 moles/cc. × 10^{-6}					0.06	0.12	
Products in moles/cc./sec. × 10^{11}							
CO	1.56	1.5	0.93	0.0474	1.36	0.9	5.7
CH_4	0.083	0.082	.04	.0042			0.42
C_2H_6	0.12	0.12	.07	.0028			0.575
C_2H_4	24.0	24.7	14.3	.572	22.8	12.0	13.6
C_3H_8	0.74	0.82	0.40	.0266			0.94
C_3H_6	0.78	0.82	.46	.02			0.52
C_4H_{10}	1.22	1.26	.72	.028			2.2
C_6H_{14}	4.05	4.1	2.4	.095			2.27
$CH_3COCOCH_3$	5.0	n.d.	3.1	.12			n.d.
CH_3COCH_3	26.0	24.0	15.0	.60	24.0	11.0	14.5
$\frac{(C_4H_{10})}{(C_2H_6)^{1/2}(C_6H_{14})^{1/2}}$	1.75	1.80	1.78	1.71			1.92

[a] Blank spaces indicate product was not formed. n.d. stands for not determined.

TABLE II

PHOTOLYSIS OF $CD_3COCD_2CH_2CH_3$

Temp., °C.	25	25	25	82	26	28[a]	28[a]
Time, min.	6	3	3	3	67	84	103
I_{abs}, quanta/cc./sec. × 10^{-14}	1.75	3.05	3.05	3.05	0.915		
K, moles/cc. × 10^{+6}	1.75	1.75	1.75	1.70	1.75	0.5	0.5
O_2, moles/cc. × 10^{+6}			0.08				.08
Products in moles/cc./sec. × 10^{11}							
CO	0.75	1.4	1.4	8.1	0.088	0.245	.243
CD_4	.012	0.019		0.075	.013	.00085	
CD_3H	.029	.050		0.2	.0032	.00445	
CH_4						.0010	
CH_3D						.002	
C_2D_6	0.0485	.080		1.33	.0065	.037	
CD_3CH_3						.017	
C_2H_6						.008	
C_2H_4	11.2	19.4	18.6	18.5	1.245	.11	.105
CH_2CD_2						.034	.033
CH_3CHCD_2	0.295	0.528		0.62	0.035	.016	.008
$CH_3CH_2CD_3$	.024	.047		.164	.004	.0148	
$CH_3CH_2CD_2H$	.275	.485		.735	.036	.013	
$CH_3CH_2CD_2CD_3$	.57	.95		3.6	.063	.0875	
$CH_3CH_2CD_2CH_3$						.0152	
$(CH_3CH_2CD_2)_2$	1.85	3.2		3.33	.206	.0695	
$CD_3COCOCD_3$	2.40	n.d.		n.d.	n.d.	n.d.	
CD_3COCD_3	0.68	1.4	<1.0	2.2	0.08	0.0145	<0.006
CD_3COCD_2H	11.0	19.0	17.6	18.2	1.20	0.125	0.11
$k_{10}/k_6^{1/2}k_{14}^{1/2}$	1.89	1.86		1.72	1.72	1.8	
k_{11}/k_{10}	0.051	0.0525			0.051	0.051	
k_7/k_6	0.148	0.152			0.155	0.187	

[a] Short wave length run. Blank spaces indicate product was not formed. n.d. indicates product was not determined.

small amount of acetone-d_6 can largely be accounted for by the occurrence of reaction 12. It is to be expected that for the first two experiments in Table II, where the biacetyl yield is roughly equal to the hexane yield, the rate of formation of acetone-d_6 should be comparable to the rate of formation of butane.

The authors do not see any obvious explanation for the difference between this work and that of McNesby and Gordon.[8] It may be pointed out that exchange on the vapor phase chromatographic column (v.p.c.) of the acetone-d_6 to acetone-d_5 did not occur in the course of this work, because the acetone, which in a few experiments was distilled directly from 2-pentanone at −90° and analyzed with the mass spectrometer, showed the same distribution as the sample collected from the v.p.c. Also, the amount of acetone-d_4 was not higher than might be expected from the isotopic purity of the sample.

(8) Although an impurity of about 1% acetone-d_6 in the 2-pentanone used by McNesby and Gordon might have explained the origin of the large amounts of acetone-d_6 in that work, Dr. McNesby has pointed out to the authors that the maximum content of acetone-d_6 was a few hundredths of a per cent.

Secondary Reactions.—Contrary to McNesby and Gordon's results, methane is a minor product for all the runs included in Tables I and II. From this it follows that reaction between a methyl radical and an excited ketone molecule does not have to be considered. Considering reactions 3 to 14 only, these relationships can be deduced

$$k_{10}/k_6^{1/2}k_{14}^{1/2} = (\mathrm{CD_3CD_2CH_2CH_3})/((\mathrm{CH_3CH_2CD_2})_2)^{1/2}(\mathrm{C_2D_6})^{1/2}$$

$$k_{12}/k_8^{1/2}k_{14}^{1/2} = (\mathrm{CD_3COCD_3})/((\mathrm{CD_3CO})_2)^{1/2}(\mathrm{C_2D_6})^{1/2}$$

$$k_{11}/k_{10} = (\mathrm{CD_3H})/\mathrm{CD_3CD_2CH_2CH_3}$$

$$k_7/k_6 = (\mathrm{CD_2HCH_2CH_3})/((\mathrm{CH_3CH_2CD_2})_2)$$

The quantities $k_{10}/k_6^{1/2}k_{14}^{1/2}$ are presented in Table II and correspond to an average value of 1.8. The analogous relationship for the undeuterated ketone leads to the same figure.

From the first run in Table II a value of 1.99 can be deduced for $k_{12}/k_8^{1/2}k_{14}^{1/2}$. This is the only experiment for which a quantitative determination of $(\mathrm{CD_3CO})_2$ was carried out. Recently, Wijnen[9] and Calvert[10] obtained values of 1.65 and 2.2, respectively.

The k_{11}/k_{10} and k_7/k_6 ratios given in Table II for the room temperature runs lie in the neighborhood of 0.05 and 0.15, respectively. These values may be compared with 0.04 and 0.12 obtained[11] for the ratios of disproportionation to recombination of methyl–ethyl and ethyl–ethyl, respectively. Earlier values for k_7/k_6 for the undeuterated compound were in the range 0.1 to 0.17.[12,13]

Due to the very small $\mathrm{CD_4}$ yields, k_{13}/k_{12} values are not very reproducible and lie in the range 0.014 and 0.055.

No saturated hydrocarbons were formed in the 2-pentanone–oxygen experiments. Carbon dioxide, formaldehyde and propionaldehyde were the major products. Formaldehyde was at least 95% $\mathrm{CD_2O}$, while the propionaldehyde consisted mainly of $\mathrm{C_2H_5CDO}$. The 64 peak was higher than might have been expected from the isotopic distribution of acetone-d_5. However, several other unidentified peaks were present at lower and higher masses, and, hence, this peak could not be ascribed to acetone-d_6 with certainty.

Short Wave Length Photolysis of $\mathrm{CD_3COCD_2CH_2CH_3}$.—From the products of the two short wave length runs of Table II it can be deduced that under these conditions the acetyl and butyryl radicals are mostly decomposed by energy carried over from the primary processes II and III. The fact that the CO yield is not suppressed by the presence of oxygen excludes any appreciable thermal decomposition of the acetyl radicals at 28°.

The $\mathrm{C_2H_4}$ is roughly equal to the acetone-d_5 yield, both in absence and in presence of oxygen, while acetone-d_6 was a minor product in both cases.

Besides processes I, II and III a few other primary steps have to be considered

$$\mathrm{CD_3COCD_2CH_2CH_3} + h\nu \longrightarrow$$

$$\mathrm{CD_3COCD_2CH_2} + \mathrm{CH_3} \quad \text{(IV)}$$

$$\mathrm{CD_3COCD_2} + \mathrm{C_2H_5} \quad \text{(V)}$$

$$\mathrm{CD_2CHCH_3} + \text{Products} \quad \text{(VI)}$$

The presence of $\mathrm{CH_4}$, $\mathrm{CH_3D}$, $\mathrm{C_2H_6}$, $\mathrm{CH_3CD_3}$ and $\mathrm{CH_3CH_2CD_2CH_3}$ is evidence for process IV. An alternative explanation such as process II followed by a decomposition of a hot propyl radical into $\mathrm{CH_3}$ and $\mathrm{CD_2CH_2}$ may be considered as another possible source of $\mathrm{CH_3}$ but cannot be the only way by which $\mathrm{CH_3}$ is produced because $(\mathrm{CH_3}) > \mathrm{CH_2CD_2}$. The $\mathrm{CH_2CD_2}$ found among the products may also come from the decomposition of a hot $\mathrm{CD_5COCD_2CH_2}$ formed in primary process IV.

The presence of small amounts of pentane-d_2 and the high $\mathrm{CH_3CH_2CD_3}/\mathrm{CH_3CH_2CD_2H}$ ratio as compared to the long wave length runs can best be explained by the recombination of the $\mathrm{C_2H_5}$ radicals produced in process V with $\mathrm{CH_3CH_2CD_2}$ and $\mathrm{CD_3}$.

That some propylene may be formed in the primary process follows from the fact that it is a product in the experiments done in the presence of oxygen. Besides an intramolecular rearrangement into propylene and acetaldehyde, other ways of forming propylene may have to be considered, *e.g.*, decomposition of a hot propyl radical produced in process II into propylene and a hydrogen atom. Hydrogen was present as a minor product.

The low $\mathrm{CD_4}$ and $\mathrm{CD_3H}$ yields indicate that hot methyl abstraction reactions are of minor importance. This is corroborated by the fact that methane and propane were absent among the products of the short wave length photolysis of $\mathrm{CD_3COCD_2CH_2CD_3}$ in the presence of oxygen.

Conclusion

The results given in this paper are in agreement with an intramolecular rearrangement process *via* a six-membered ring as visualized by Davis and Noyes[14] or by a direct transfer of a γ-hydrogen atom to the α-carbon atom as proposed by Pitts.[2] It may be added that the correlation between the photochemical primary act and the mass spectrometric cracking pattern which has been discussed before[3,15] is supported by the fact that the cracking pattern of the partially deuterated ketone showed a large 63 peak which corresponds to $\mathrm{CD_3COCD_2H^+}$. The small 64 and 62 peaks could be entirely attributed to the contributions of the $\mathrm{C^{13}}$ isotope and 2.5% 2-pentanone-d_4 present in the sample.

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