

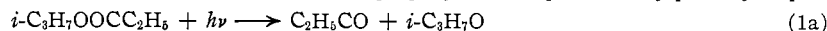
[CONTRIBUTION FROM THE RADIATION RESEARCH LABORATORIES, MELLON INSTITUTE]

Reactions of Alkoxy Radicals. VI. Photolysis of Isopropyl Propionate¹

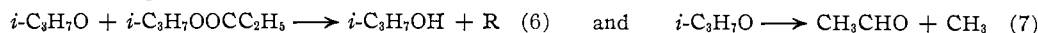
BY M. J. H. WIJNEN

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The photolysis of isopropyl propionate has been investigated over the temperature range 28 to 65° at various intensities and at different initial pressures. The results indicate that part of the isopropoxy radicals produced by primary step

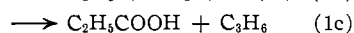
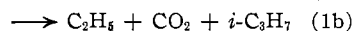
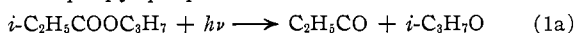


are excited and decompose before being able to take part in further reactions. The fraction of excited isopropoxy radicals thus produced increases with increasing temperatures. A maximum value of $E_7 - E_3 = 6$ kcal. is suggested for the difference in activation energies of the reactions



Introduction

Previous investigations of the photolysis of isopropyl propionate² and of alkyl esters³ indicate that the primary steps occurring in the photolysis of isopropyl propionate are



Due to the many different radicals produced in the primary process, the resulting reaction mechanism is obviously complex and no quantitative interpretation of the data has been given so far. In the present investigation an attempt has been made to study in detail the reactions of the isopropoxy radical produced by step 1a.

Experimental

The experimental technique is essentially the same as described elsewhere.⁴ A Hanovia S-500 medium pressure mercury arc was used as the light source. The light of the S-500 arc was not filtered; its intensity was varied by inserting wire gauze screens between reaction cell and arc. The amount of conversion was in the order of 1 to 2% of the starting material.

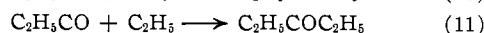
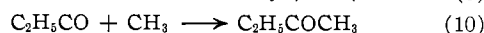
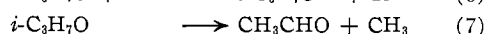
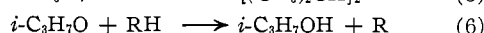
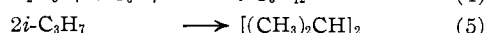
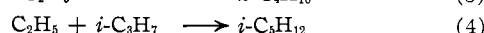
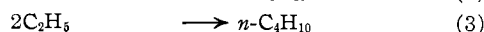
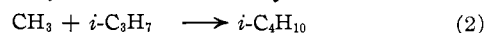
The reaction products observed were: CO, CO₂, CH₄, C₂H₆, C₂H₄, C₃H₈, C₃H₆, *n*-C₄H₁₀, *i*-C₄H₁₀, *i*-C₃H₁₂, [(CH₃)₂CH]₂, CH₃CHO, CH₃COCH₃, C₂H₅COCH₃ and *i*-C₃H₇-OH. CO, CO₂, CH₄, C₂H₆, C₂H₄ and CH₃COC₂H₅ were not measured. The last compound was observed only in the lower temperature region. All other reaction products were analyzed by gas chromatography. A 5-m. long column containing 16% (by weight) of 50 HB 660 Ucon fluid on fire brick was employed for routine analysis. No separation was obtained under these conditions between acetaldehyde and 2,3-dimethylbutane. However, using different columns yielding good separation between acetaldehyde and 2,3-dimethylbutane, it was possible to show that not only the production of 2,3-dimethylbutane was negligible compared to the amount of acetaldehyde produced but also that within experimental error $R_{2,3} \text{ dimethylbutane} = R^2 \text{ } i\text{-pentane} / 4R_{n\text{-butane}}$ (where R_x is the rate of production of the compound *x*).

It was thus possible to calculate the amount of 2,3-dimethylbutane produced from the amounts of *i*-pentane and *n*-butane produced. Subsequently accurate values could be obtained for the rate of acetaldehyde production.

Results and Discussion

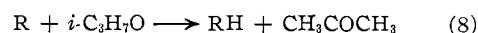
The results obtained are given in Table I. Accepting the primary steps suggested in the introduction, these reactions are proposed to explain the formation of *i*-butane, *n*-butane, *i*-pentane, 2,3-di-

methylbutane, 1-propanol, acetaldehyde, acetone, methyl ethyl ketone and diethyl ketone.

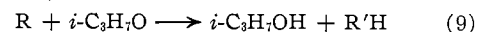


In addition to the reactions given above methyl, ethyl and *i*-propyl radicals will react to form methane, ethane, ethylene, propane and propylene *via* abstraction disproportionation, and partially, even recombination reactions.

The production of acetone has been suggested to occur *via* the reaction



where R may be an alkyl or even an isopropoxy radical. The possibility that acetone may be produced *via* thermal decomposition of the isopropoxy radical into acetone and H atoms has been discarded since in that case acetone formation would be expected to increase rather than decrease with increasing temperatures. Disproportionation reactions such as 8 between alkoxy and alkyl radicals have been observed previously.⁵ If reaction 8 occurs then it is of course quite likely that reaction 9 may also occur.



Unfortunately it is not possible to get any indication of the extent to which this reaction may occur. The fact that reaction 8 does not occur at 65° (no acetone is observed) leads us to assume that at this temperature little or no 2-propanol is produced *via* reaction 9. Equation (I) may be derived in this case.

$$R_{i\text{-C}_3\text{H}_7\text{OH}} / (R_{\text{AcH}} \times V_0) = k_6/k_7 \quad (I)$$

In equation I V_0 indicates the amount of propyl propionate initially present. Data obtained for $R_{i\text{-C}_3\text{H}_7\text{OH}} / (R_{\text{AcH}} \times V_0)$ are given in Table II for the temperatures 28, 53 and 65°. It should be repeated that equation I is not completely correct for the lower temperatures since possible 2-propanol produc-

(1) This work was supported in part by the U. S. Atomic Energy Commission.

(2) M. H. J. Wijnen, *Can. J. Chem.*, **36**, 691 (1958).

(3) P. Ausloos, *ibid.*, **36**, 383 (1958).

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(5) M. H. J. Wijnen, *ibid.*, **28**, 271 (1958).

TABLE I
 PHOTOLYSIS OF ISOPROPYL PROPIONATE^a

Run no.	Intensity relat. %	V_0 , molec./cc. $\times 10^{-17}$	Rate of formation of products in molec./ (sec. cc.) $\times 10^{-10}$							
			C_3H_8	C_3H_6	$i-C_4H_{10}$	$n-C_4H_{10}$	$i-C_3H_{12}$	CH_3CHO	CH_3COCH_3	$i-C_3H_7OH$
Temperature 28°										
19	15	6.94	18.1	37.5	3.1	16.8	6.1	12.0	5.1	16.3
20	4.5	1.90	2.9	7.0	0.7	2.3	0.8	1.8	?	1.7
21	100	1.96	76.2	207.0	16.9	65.0	25.0	59.0	12.4	45.3
22	30	3.92	45.2	69.5	8.3	39.4	13.7	26.8	5.7	34.0
23	4.5	6.80	9.5	18.6	2.0	9.2	3.3	6.4	1.3	8.9
Temperature 53°										
24	100	3.33	44.2	84.0	9.2	30.9	10.0	42.2	..	27.2
25	100	13.98	261.0	363.1	45.0	242.0	87.1	242.2	19.9	164.5
26	4.5	6.00	11.2	17.6	2.2	8.0	2.6	9.7	tr.	4.0
27	50	4.55	89.8	148.3	16.0	66.9	23.5	72.9	8.8	50.0
28	50	11.18	136.8	203.0	23.2	108.2	36.9	116.5	12.0	67.3
29	50	2.78	65.0	121.1	15.9	47.3	16.2	57.9	..	22.1
30	30	12.93	99.2	142.5	18.2	86.7	28.2	85.0	?	53.5
Temperature 65°										
8	16	6.73	19.1	25.6	3.8	15.6	5.5	20.1	..	5.4
9	100	4.34	228.1	358.2	41.4	154.5	51.1	193.2	..	50.5
10	100	4.48	226.2	337.3	39.6	144.2	50.1	162.2	..	54.5
11	100	4.47	208.0	312.1	39.4	122.4	45.0	175.0	..	32.4
12	100	4.45	207.0	341.0	47.3	143.5	51.5	173.0	..	55.2
14	25	7.25	65.5	93.5	12.9	48.2	17.8	61.0	..	17.9
15	4.5	5.37	11.1	17.7	2.2	7.6	2.6	10.5	..	3.2
16	50	15.32	128.1	162.0	27.8	92.5	34.7	129.0	..	29.5
17	4.5	18.00	13.1	19.8	2.0	11.7	4.2	17.2	..	6.7
18	30	12.66	98.7	138.1	20.3	86.9	28.5	119.0	..	45.0

^a Open spaces indicate that the compound was not observed under the given conditions.

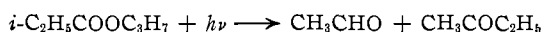
TABLE II

Run no.	In-tensity, relat. %	V_0 , molec./cc. $\times 10^{-17}$	10^{19}	10^{17}	10^{17}
			$\frac{R_{i-PrOH}}{R_{AcH}V_0}$	$\frac{R_{AcH} \cdot V_0}{R_{i-PrOH}}$	$\frac{R_{tot i-C_3H_7O} \cdot V_0}{R_{PrOH}}$
Temperature 28°					
19	15	6.94	19.6	5.1	14.2
20	4.5	1.90	49.5	2.0	3.9
21	100	1.96	39.2	2.6	5.0
22	30	3.92	32.4	3.1	7.7
23	4.5	6.80	20.4	4.9	12.7
Temperature 53°					
24	100	3.33	19.4	5.2	8.5
25	100	13.98	4.9	20.5	36.1
26	4.5	6.00	6.9	14.4	20.8
27	50	4.55	15.1	6.6	11.9
28	50	11.18	5.2	19.4	30.6
29	50	2.78	13.7	7.3	10.0
30	30	12.93	4.9	20.6	33.5
Temperature 65°					
8	16	6.73	4.0	25.0	33.7
9-12	100	4.44	6.5	15.4	20.2
14	25	7.25	4.1	24.4	31.9
15	4.5	5.37	5.6	17.8	23.0
16	50	15.32	1.5	66.6	82.5
17	4.5	18.00	2.2	46.4	64.2
18	30	12.66	3.0	33.3	46.0

tion *via* reaction 9 has been neglected. The following observation seems to indicate that even at 29° reaction 9 is only of minor importance. If reaction 9 were important then 2-propanol production *via* reaction 9 would be most important at high radical concentrations, where disproportionation reactions are favored. It would thus be expected that $R_{i-C_3H_7OH}/(R_{AcH} \times V_0)$ would in-

crease with increasing intensity and increasing isopropyl propionate pressure. Table II clearly indicates that the opposite effect is observed at all temperatures.

From the discussion above it is clear that reactions 6, 7 and 9 do not represent correctly the data obtained. It was first believed that added 2-propanol and/or acetaldehyde might be formed *via* molecular rearrangement reactions. However, no 2-propanol is observed under present experimental conditions at temperatures above 100° indicating that no 2-propanol is formed by such a reaction. If acetaldehyde were formed *via* a molecular re-arrangement reaction, it should be possible to detect the compound formed simultaneously. For example, the reaction



does not occur since methyl ethyl ketone has not been observed at 53 and 65°. At 29° the presence of methyl ethyl ketone is readily explained by reaction 10.

The rather large amount of acetaldehyde produced even at 29°, seems to indicate that additional acetaldehyde is produced by a reaction (or reactions) other than 7. Additional acetaldehyde might well be produced *via* an excited $i-C_3H_7O$ radical which would decompose before being able to take part in any reactions. If this is the case the rate of acetaldehyde production is given by

$$R_{CH_3CHO} = k_7(i-C_3H_7O) + \alpha R_{tot i-C_3H_7O}$$

where $R_{tot i-C_3H_7O}$ is the rate of total (excited and thermal) isopropoxy radical production. This quantity may be calculated from the resulting products: $R_{tot i-C_3H_7O} = R_{CH_3COCH_3} + R_{CH_3CHO} +$

$R_{i-C_3H_7OH}$. The fraction of excited isopropoxyl radicals is given by α . Equation (II) may now be derived

$$R_{CH_3CHO} \times V_0/R_{i-C_3H_7OH} = \frac{k_7}{k_6} + R_{tot. i-C_3H_7O} \times V_0/R_{i-C_3H_7OH} \quad (II)$$

The data plotted in Fig. 1 for the temperatures 28, 53 and 65° show a good agreement with equation II. It may be pointed out here that the formation of excited radicals, which decompose before further reaction, has been suggested previously for CH_3CO^{5-7} and $C_2H_5CO^8$ radicals. Both in the case of CH_3CO^5 and in the case of $C_2H_5CO^8$ radicals, it has been observed that the fraction of excited radicals increases with increasing temperatures. Similar results are obtained in the present investigation where α (fraction of C_3H_7O radicals inevitably decomposing) increases from 0.3 at 28° to 0.7 at 65°.

It is also interesting to compare the results regarding primary step 1a with those obtained in the photolysis of other esters. In the case of $CH_3COOCD_3^4$ the results gave clear evidence of the production of an excited CH_3CO radical which decomposed before being able to take part in recombination and disproportionation reactions.

The absence of any products containing C_2H_5CO in the photolysis of ethyl propionate⁹ at 28° might well indicate that here also at least part of the propionyl radicals produced are excited and decompose immediately into C_2H_5 and CO. This suggestion is not contradicted by the fact that recently some evidence has been obtained for the formation of a thermal C_2H_5CO radical at 15° in the photolysis of ethyl propionate¹⁰ since, as observed here and elsewhere,^{5,8} the fraction of excited radicals seems to decrease with decreasing temperatures. The results seem therefore to indicate, as observed previously by Ausloos,⁵ that in ester photolysis excess energy is carried over from the primary process thus causing one of the fractions to decompose immediately. It is however noteworthy that the excited fraction in the photolysis of methyl acetate and ethyl propionate is the RCO radical while in the photolysis of isopropyl propionate the RO radical carries the excess energy. It is of course possible that before decomposing, the excited molecule may live long enough to allow distribution of the absorbed energy over the entire molecule thus causing an excitation of the heavier fraction. In this respect it might be interesting to photolyse propyl or butyl acetates. From the results reported here it might be expected that the RO radical would be hot rather than the CH_3CO radical which carries excess energy in the photolysis of methyl acetate.

(6) G. F. Sheats and W. A. Noyes, Jr., *THIS JOURNAL*, **77**, 1421 (1955).

(7) F. P. Lossing, *Can. J. Chem.*, **35**, 305 (1957).

(8) J. E. Jolley, *THIS JOURNAL*, **79**, 1537 (1957).

(9) M. H. J. Wijnen, *ibid.*, **80**, 2394 (1958).

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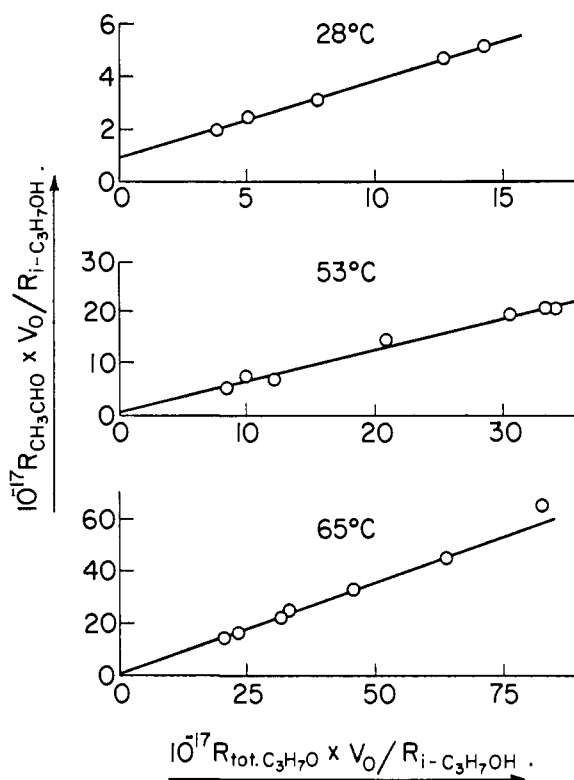
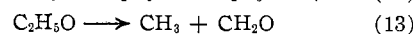
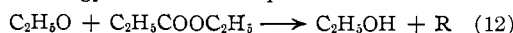
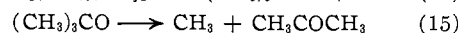
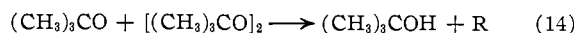


Fig. 1.—Plots of $10^{-17}R_{CH_3CHO} \times V_0/R_{i-C_3H_7OH}$ versus $10^{-17}R_{tot. C_3H_7O} \times V_0/R_{i-C_3H_7OH}$ at various temperatures.

From the intercepts in Fig. 1 we obtain $k_7/k_6 = 1.0 \times 10^{-17}$ at 28°. While it is not possible to obtain reliable values for k_7/k_6 at higher temperatures, our data nevertheless indicate that k_7/k_6 will not exceed the value of 5×10^{-17} at 65°. From this it is possible to obtain a maximum value for $E_7 - E_6$ indicating $E_7 - E_6 < 6$ kcal. No other data are reported in the literature for $E_7 - E_6$. A comparison is possible, however, with the activation energy differences reported for the reactions



and for the reactions



The values $E_{13} - E_{12} = 7$ kcal.⁹ and $E_{15} - E_{14} = 3$ kcal. have been reported.¹¹ The present results therefore seem to fit in well with those obtained on other alkoxy radicals.

Acknowledgment.—The author wishes to express his sincere thanks to Mr. J. A. Guercione for carrying out the experiments described in this paper.

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(11) G. McMillan and M. H. J. Wijnen, *Can. J. Chem.*, **36**, 1227 (1958).