PHOTOLYSIS OF *n*- AND *i*-PROPYL PROPIONATE[1]

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ABSTRACT

The photolysis of *n*- and *i*-propyl propionate has been studied in the temperature range of 30° to 170° C. The results strongly indicate that the following three primary processes may occur:

$$C_2H_5COOC_3H_7 + h\nu \rightarrow C_2H_5CO + C_3H_7O, \quad [1a]$$

$$C_2H_5COOC_3H_7 + h\nu \rightarrow C_2H_5 + CO_2 + C_3H_7, \quad [1b]$$

$$C_2H_5COOC_3H_7 + h\nu \rightarrow C_2H_5COOH + C_3H_6. \quad [1c]$$

Based on these primary steps a qualitative explanation may be given for the formation of all reaction products.

INTRODUCTION

In previous investigations of methyl acetate (1), methyl d_3-acetate (2), and ethyl propionate (3) it could be shown that the main primary step in the photolysis of these esters consisted in the break of the ester into RCO and RO radicals. It was possible to obtain information on the reactivity and thermal stability of the RO radicals thus produced.

It seemed interesting to extend these investigations to higher-boiling esters. The photolysis of *n*- and *i*-propyl propionate has therefore been studied.

EXPERIMENTAL

The experimental technique is essentially the same as described elsewhere (1). A Hanovia S-500 medium pressure arc was used as the light source. The light of the S-500 arc was not filtered, and its intensity was varied by inserting wire gauze screens between reaction cell and arc. The amount of decomposition did not exceed 5% of the compound under investigation.

As reaction products of the photolysis of *n*-propyl propionate were observed: CO, CO_2, CH_2O, C_2H_4, C_2H_6, C_3H_6, C_3H_8, *n*-C_4H_{10}, *n*-C_5H_{12}, *n*-C_3H_7OH, and CH_3CH_2CHO. *n*-Propyl alcohol was determined by mass spectrometer analysis of the residue after all other products had been removed by Toepler pump at −120° C. The total volume of these products was measured, after which analysis was carried out by mass spectrometer.

The following reaction products were observed in the photolysis of *i*-propyl propionate: CO, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, *n*-C_4H_{10}, *i*-C_4H_{10}, *i*-C_5H_{12}, $\{CH(CH_3)_2\}_2$, CH_3CHO, CH_3COCH_3, $C_2H_5COCH_3$, $C_2H_5COC_2H_5$, and *i*-C_3H_7OH. The C_1 to C_5 hydrocarbons and the carbon oxides were pumped over at −130° C., measured, and analyzed by mass spectrometer. The other products such as ketones, isopropyl alcohol, and 2,3-dimethylbutane were determined by mass spectrometer analysis of the residue.

Typical results obtained at various temperatures by photolysis of *n*-propyl propionate are given in Table I, those obtained by photolysis of *i*-propyl propionate in Table II.

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TABLE I

PHOTOLYSIS OF *n*-PROPYL PROPIONATE AT VARIOUS TEMPERATURES

	Run number:					
	1	2	3	4	5	6
n-$PrPr_0 \times 10^{-17}$ molec./sec.	9.14	8.92	8.85	8.84	8.74	9.60
Temperature, ° C.	41	41	131	131	170	170
Intensity (relative, %)	100	9	100	9	100	9
	Rate of formation of products in molec./sec. cc. $\times 10^{-12}$					
n-Propyl alcohol	2.06	0.20	—	—	—	—
Propionaldehyde	0.10	—	—	—	—	—
n-Pentane	0.64	0.04	0.67	0.04	0.60	0.02
n-Butane	6.22	0.42	8.04	0.41	7.42	0.23
Propane	1.31	0.05	1.39	0.06	0.55	0.07
Propylene	3.93	0.25	3.26	0.23	3.50	0.20
Ethane	2.68	0.29	4.69	0.48	4.50	0.39
Ethylene	0.80	0.07	0.88	0.06	1.68	0.12
Formaldehyde	2.76	0.08	1.65	0.34	5.54	0.32
Carbon monoxide	10.48	0.74	11.08	0.91	14.08	0.90
Carbon dioxide	2.60	0.20	2.60	0.22	3.50	0.21
CO/CO_2	4.0	3.7	4.2	4.1	4.0	4.3
R_{C_3}/R_{CO_2}	2.3	1.7	2.0	1.5	1.3	1.4

TABLE II

PHOTOLYSIS OF *i*-PROPYL PROPIONATE AT VARIOUS TEMPERATURES

	Run number:					
	7	8	9	10	11	12
i-$PrPr_0 \times 10^{-17}$ molec./sec.	7.74	7.14	6.67	6.85	5.31	5.31
Temperature, ° C.	33	33	109	109	176	176
Intensity (relative, %)	100	9	100	9	100	9
	Rate of formation of products in molec./sec. cc. $\times 10^{-12}$					
i-Propyl alcohol	6.65	0.27	0.44	0.03	0.21	0.02
Acetaldehyde	7.58	0.29	10.66	0.69	7.12	0.55
Methyl ethyl ketone	1.04	0.06	—	—	—	—
Diethyl ketone	0.34	0.03	—	—	—	—
Methyl isopropyl ether	0.39	—	—	—	—	—
i-Pentane	2.23	0.13	2.63	0.19	2.18	0.15
2,3-Dimethylbutane	0.60	—	0.41	0.05	0.96	—
n-Butane	2.25	0.17	2.72	0.17	2.04	0.11
i-Butane	0.28	0.03	0.82	0.06	0.70	0.02
Propane	3.14	0.22	4.14	0.32	4.15	0.22
Propylene	5.66	0.41	6.32	0.43	5.75	0.42
Ethane	1.40	0.10	2.54	0.23	3.32	0.37
Ethylene	0.65	0.05	0.75	0.06	0.81	0.04
Methane	0.27	0.02	1.21	0.22	3.22	0.51
Carbon monoxide	9.56	0.70	10.20	0.98	10.28	0.82
Carbon dioxide	4.12	0.29	4.34	0.35	4.42	0.34
CO/CO_2	2.2	2.4	2.4	2.8	2.3	2.4

DISCUSSION OF RESULTS

n-Propyl Propionate

To explain the formation of products in the photolysis of *n*-propyl propionate the following primary steps are suggested:

$$n\text{-}C_2H_5COOC_3H_7 + h\nu \rightarrow C_2H_5CO + n\text{-}C_3H_7O, \quad [1a]$$

$$\rightarrow C_2H_5 + CO_2 + n\text{-}C_3H_7, \quad [1b]$$

$$\rightarrow C_2H_5COOH + C_3H_6. \quad [1c]$$

Steps [1*a*] and [1*b*] have been shown to occur in the photolysis of methyl acetate and ethyl propionate. Step [1*a*] produces *n*-propoxy and propionyl radicals. Propionyl radicals are known (4) to be quite unstable and decompose readily into ethyl radicals and carbon monoxide. The possibility that at 40° C. some C_2H_5CO radicals survive long enough to form diethyl ketone and possibly propyl ethyl ketone as has been observed in the case of isopropyl propionate may, however, not be excluded. Carbon monoxide is observed at all temperatures as the main reaction product. The presence of *n*-propoxy radicals is confirmed by the formation of *n*-propyl alcohol and of propionaldehyde at 40° C. Step [1*b*] produces ethyl and propyl radicals in addition to carbon dioxide. Accepting that practically all C_2H_5CO radicals decompose into C_2H_5 and CO, it would be expected that at any given temperature the ratio CO/CO_2 would be constant. This is confirmed by the results, as shown in Table I, which indicate that step [1*a*] occurs about four times as frequently as step [1*b*]. The presence of propyl radicals during the photolysis of *n*-propyl propionate is confirmed by reaction products such as propane, propylene, and pentane. The formation of butane, ethane, and ethylene confirms the presence of ethyl radicals, suggested to be formed by step [1*b*] and by step [1*a*] via the C_2H_5CO radical.

If reactions [1*a*] and [1*b*] were the only primary steps, then it would be expected that $R_{CO_2} = R_{C_3}$, where R_{C_3} is the rate of production of all compounds containing *n*-propyl radicals so that $R_{C_3} = R_{C_5H_{12}} + R_{C_3H_8} + R_{C_3H_6}$. Table I shows $R_{C_3} \gg R_{CO_2}$. This indicates that more products, containing propyl radicals, are formed than can be accounted for by step [1*b*]. To explain this, step [1*c*] has been suggested. Propionic acid in trace amounts is not detected by mass spectrometer analysis, as could be shown by adding small amounts of propionic acid to the *n*-propyl propionate residue of the photolysis before analysis. Confirmation for step [1*c*] may, however, be found (1) in the rather large amounts of propylene produced, especially if compared to the amounts of propane formed, and (2) in the fact that chemical analysis indicated the presence of an acid among the reaction products.

This investigation was mainly undertaken to obtain information regarding the *n*-propoxy radical. However, neither propyl alcohol nor propionaldehyde could be detected at 130° C. and higher temperatures. This seems to indicate that the *n*-propoxy radical is not very stable thermally. Since no hydrogen was observed among the reaction products, the results indicate that the *n*-propoxy radical decomposes into ethyl radicals and formaldehyde according to the reaction

$$n\text{-}C_3H_7O \rightarrow C_2H_5 + CH_2O. \qquad [2]$$

This type of decomposition reaction for the alkoxy radical has been suggested previously by other authors (5, 6). It is important to point out that relatively large amounts of formaldehyde were produced. In the extreme case where all *n*-propoxy radicals would decompose according to reaction [2], it would be expected that $R_{CO} = R_{CH_2O}$. This has not been observed. Since formaldehyde polymerizes easily it is probable that part of the formaldehyde was left behind in the apparatus as polymer and thus was not available for analysis.

The fact that no ethers were formed even at 40° C., which could conceivably be produced by recombination between alkyl and propoxy radicals, indicates that the concentration of propoxy radicals must be small. This is also confirmed by the fact that propionaldehyde, possibly a product of disproportionation reactions involving the propoxy radical, has only been observed in trace amounts at low temperatures.

i-Propyl Propionate

Primary steps similar to those suggested in the photolysis of *n*-propyl propionate will produce ethyl, *i*-propoxy, *i*-propyl, and propionyl radicals in addition to carbon oxides and propionic acid.

The isopropoxy radical has been suggested (6) to decompose according to the following reactions:

$$(CH_3)_2CHO \rightarrow CH_3 + CH_3CHO \quad [3]$$

and

$$(CH_3)_2CHO \rightarrow CH_3COCH_3 + H. \quad [4]$$

Reaction [3] is confirmed by the fact that large amounts of acetaldehyde were observed among the reaction products. The presence of methyl radicals is shown by the formation of methane and isobutane. Since it is not possible to decide to what extent methyl radicals are involved in the production of ethane and propane, it is difficult to draw a comparison between the amounts of acetaldehyde and methyl radicals produced by reaction [3]. No reliable data were obtained for the production of acetone although it could be established that some acetone was produced, especially at low temperatures. Since no hydrogen was observed, it is unlikely that acetone was formed by reaction [4]. More probable is the formation of acetone via disproportionation reactions involving the isopropoxy radical. Accepting primary steps [1*a*], [1*b*], [1*c*], and reaction [3], all other reaction products may be explained by abstraction, recombination, and disproportionation reactions of the radicals thus produced.

The fact that methyl ethyl ketone and diethyl ketone are found at 33° C. indicates some stability for the C_2H_5CO radical. This is in agreement with previous results for the photolysis of diethyl ketone, where a quantum yield of 0.6 (7) was observed for the production of CO at 25° C. The ratio R_{CO}/R_{CO_2} indicates that step [1*a*] occurs about 2.4 times as frequently as step [1*b*]. Comparison with the similar ratio for *n*-propyl propionate indicates that step [1*a*] is relatively more important for normal propyl propionate than it is for isopropyl propionate.

The sharp decrease of isopropyl alcohol formation with increasing temperature seems to indicate that the isopropoxy radical is not very stable thermally. In all respects our results indicate that both *n*- and *i*-propoxy radicals react very similarly and decompose readily by breakage of the carbon–carbon bond rather than by splitting off of hydrogen atoms.

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