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Reactions of Alkoxy Radicals. II. Photolysis of Ethyl Propionate

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The photolysis of ethyl propionate has been investigated over the temperature range 30 to 345° at different light intensities and initial pressures. As main reaction products were observed: CO, CO_2, CH_4, C_2H_6, C_2H_4, C_3H_8, C_4H_{10}, CH_2O, C_2H_5OH, CH_3CHO and $C_2H_5OC_2H_5$. These primary steps are suggested to occur in the photolysis of ethyl propionate:

$$C_2H_5COOC_2H_5 + h\nu \longrightarrow C_2H_5 + CO + C_2H_5O \qquad (1a)$$
$$\longrightarrow 2C_2H_5 + CO_2 \qquad (1b)$$

Several main reactions, involving ethoxy radicals, take place subsequently

$$C_2H_5O + C_2H_5 \longrightarrow C_2H_5OC_2H_5 \qquad (4)$$
$$\longrightarrow C_2H_6 + CH_3CHO \qquad (5)$$
$$\longrightarrow C_2H_4 + C_2H_5OH \qquad (6)$$
$$2C_2H_5O \longrightarrow C_2H_5OH + CH_3CHO \qquad (7)$$
$$C_2H_5O \longrightarrow CH_3 + CH_2O \qquad (8)$$
$$C_2H_5O + C_2H_5CO_2C_2H_5 \longrightarrow C_2H_5OH + C_4H_9CO_2 \qquad (15)$$

An activation energy difference of about 7 kcal. has been established for $E_8 - E_{15}$. Activation energies of, respectively, 8.2 and 9.8 kcal., were determined for the abstraction of a hydrogen atom from ethyl propionate by methyl and ethyl radicals.

Introduction

Little quantitative information on alkoxy radicals is available in the literature, although they are generally believed to play an important role in many combustion processes.

In a recent study[1] at this Laboratory, methoxy radicals were produced by photolysis of methyl acetate. Since methoxy radicals were thus obtained in a relatively simple system, it was possible to obtain considerable information regarding their reactivity.

This study has been extended, therefore, to the photolysis of ethyl propionate, where ethoxy radicals are produced by the main primary step.

Experimental

The apparatus has been described previously.[2] A. Hanovia S-500 medium pressure mercury arc was used as light source. As a rule the light of the S-500 arc was not filtered. Some runs were carried out using Corning filter No. 9-54 (transmitting above 2200 Å.). No difference, other than the difference due to increased light intensity, was observed when using filtered or non-filtered light. The light intensity was varied by inserting wire gauze screens between reaction cell and arc.

The reaction products and the excess ethyl propionate were cooled down to −150°. The products volatile at this temperature were pumped off by Toepler pump and their total volume was measured. This fraction was then analyzed by mass spectrometer, and quantitative measurements were obtained for these several components: H_2, CO, CO_2, CH_4, C_2H_6, C_2H_4 and C_3H_8. In addition, some C_4H_{10} was present. The residual butane and the ethanol, acetaldehyde, ethyl ether and excess ethyl propionate were determined by direct mass spectrometric analysis of the residue.

No accurate analysis could be obtained for the amount of formaldehyde produced.

The conversion was less than 5% in most experiments.

Results

The photolysis of ethyl propionate has been carried out over the temperature range 30 to 344° at different light intensities and initial pressures. The results of these experiments are given in Table I. At each temperature, the relative light intensity for the experiments may be obtained from the rate of formation of CO and/or CO_2.

Primary Steps.—Two primary steps are suggested to occur in the photolysis of ethyl propionate

$$C_2H_5COOC_2H_5 + h\nu \longrightarrow C_2H_5 + CO + C_2H_5O \qquad (1a)$$
$$\longrightarrow 2C_2H_5 + CO_2 \qquad (1b)$$

Step 1a produces carbon monoxide and ethyl and ethoxy radicals. Carbon monoxide has been observed to be the main reaction product in all experiments. The formation of ethanol and ethyl ether indicates the presence of ethoxy radicals during the reaction. Step 1a has been represented here as giving directly both C_2H_5 and CO, rather than C_2H_5CO. It is possible that C_2H_5CO radicals are formed intermediately, although their presence could not be shown under any conditions of this investigation by formation of stable products such as diethyl ketone. In this respect, it may be pointed out that the relatively high quantum yield of 0.6 to 0.7 for the production of CO in the photolysis of diethyl ketone at 25°, as reported by Kutschke, Wijnen and Steacie,[2] indicates that the C_2H_5CO radical is quite unstable. Step 1b is proposed to explain the formation of CO_2, which has been observed at all temperatures as a reaction product.

No direct evidence has been obtained in this investigation indicating any molecular rearrangement of the ester molecule in the primary process. It should be mentioned, however, that it is not unlikely that the step may occur to some extent

$$C_2H_5COOC_2H_5 + h\nu \longrightarrow C_2H_5COOH + C_2H_4 \qquad (1c)$$

Evidence for this type of primary step in esters has been first obtained by Ausloos.[3] Additional evidence for this type of decomposition also has been found in the photolysis of *n*- and *iso*propyl propionate where step 1c contributes to an extent of about 15% of the total decomposition in the primary process.[4] Careful examination of the mass spectrometer data did not yield any evidence for step 1c. This may, however, be explained by the fact that C_2H_5COOH is absorbed easily on the walls of the reaction vessel and thus was not present among the reaction products. A vague indication as to the maximum extent to which step 1c possibly

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[1] M. H. J. Wijnen, Am. Chem. Soc. 131st National Meeting, Miami, April, 1957; *J. Chem. Phys.*, **27**, 710 (1957).

[2] K. O. Kutschke, M. H. J. Wijnen and E. W. R. Steacie, THIS JOURNAL, **74**, 714 (1952).

[3] P. Ausloos, private communication.

[4] M. H. J. Wijnen, to be published.

TABLE I

PHOTOLYSIS OF ETHYL PROPIONATE[a]

Run no.	Reaction time, sec.	[EP]i, molec./cc. × 10^{-17}	Rate of formation of products in molecules/(sec. cc.) × 10^{-13}										
			Ethanol	Acetaldehyde	Ethyl ether	Methane	Ethane	Ethylene	Propane	Butane	Carbon monoxide	Carbon dioxide	Hydrogen
Temperature 30°													
31	1680	7.76	6.55	4.82	1.44	0.09	1.68	3.09	0.94	7.77	12.92	3.44	..
32	5160	7.80	2.51	0.71	0.33	.03	0.47	0.88	.28	2.43	3.94	1.04	..
33	1620	5.84	6.68	3.96	.70	.09	1.53	3.00	.86	6.34	11.29	3.11	..
40	16740	8.75	0.81	0.46	.03	Trace	0.14	0.28	.07	0.83	0.97	0.28	..
41	4380	8.98	5.29	2.45	Not detd.	0.03	0.92	1.72	.46	3.58	6.64	1.98	..
55	5820	8.23	2.54	0.82	0.14	.02	0.50	1.00	.26	1.82	3.54	1.01	..
56	1560	5.90	6.64	2.23	.38	.06	1.60	2.98	.80	5.48	10.47	3.17	..
57	5640	9.07	2.30	0.84	.11	.02	0.48	0.92	.26	1.67	3.68	0.99	..
Temperature 72°													
17	9600	7.64	1.69	0.41	..	0.07	0.45	0.41	0.34	2.88	2.12	0.57	..
18	1560	7.67	8.75	3.00	..	.22	2.29	3.70	1.76	11.85	15.50	3.62	..
19	9180	5.10	1.01	0.34	..	.07	0.28	0.32	0.25	1.18	1.79	0.45	..
20	5080	5.22	2.15	1.06	..	.15	0.56	0.64	0.49	2.62	3.82	0.94	..
21	1500	7.15	8.25	1.26	..	.24	3.29	3.14	2.26	10.40	14.74	4.09	..
22	1500	7.87	8.38	...	1.02	.19	2.14	3.02	1.92	16.00	14.60	3.74	..
23	1500	4.83	5.05	0.15	0.43	.18	2.37	2.60	1.79	5.62	11.21	3.08	..
Temperature 108°													
2	2460	7.87	7.02	2.22	..	0.80	3.31	3.54	3.14	5.58	15.88	3.74	..
3	1860	8.76	6.40	1.16	..	.81	4.41	3.11	3.74	8.71	18.71	4.50	..
4	1800	5.37	5.90	3.47	..	.60	2.56	3.14	2.78	6.99	13.52	3.22	..
5	1800	8.64	6.54	1.87	..	.77	3.74	3.50	3.47	6.27	16.62	4.57	..
6	3900	4.61	2.48	0.61	..	.26	1.28	1.27	1.22	2.76	5.65	1.48	..
7	11520	6.95	0.82	0.40	..	.21	0.50	0.35	0.37	1.39	2.42	0.61	..
8	4080	7.01	3.64	1.16	0.08	.48	1.55	1.63	1.63	6.73	7.94	2.00	..
9	5280	6.91	1.65	0.52	.08	.34	1.03	1.01	1.01	3.30	4.88	1.24	..
10	1620	7.00	6.92	4.04	.29	.75	4.02	3.36	3.96	10.80	16.94	4.63	..
Temperature 152°													
11	1680	6.82	3.48	0.86	..	2.77	5.86	2.56	5.22	9.82	14.85	4.29	..
12	10260	6.47	0.44	0.13	..	0.67	0.89	0.37	0.50	1.24	2.11	0.61	..
13	4800	6.40	0.89	0.20	..	1.04	1.41	0.91	1.16	3.66	4.48	1.25	..
14	1680	6.25	3.37	1.11	0.21	2.22	3.96	2.36	4.47	9.29	16.52	4.08	..
15	4500	4.57	0.79	0.26	..	0.75	1.13	0.81	1.11	2.52	3.88	0.99	..
16	8100	4.12	0.28	...	..	0.51	1.46	...	0.65	1.04	1.29	0.50	..
Temperature 202°													
27	8040	4.90	0.12	0.53	..	0.97	0.95	0.38	0.30	0.58	1.90	0.53	0.47
28	1500	3.75	.99	1.82	..	3.39	4.18	2.84	3.55	6.02	11.95	3.47	.73
29	4980	5.23	.31	0.31	..	1.72	1.85	0.71	0.76	1.94	3.86	1.13	.45
30	7560	5.16	.19	0.91	..	1.32	1.52	0.56	0.53	1.21	3.56	0.82	.29
36	1560	6.02	.68	3.04	..	6.03	5.72	3.06	3.69	7.88	14.90	3.88	1.40
37	7380	5.55	.32	0.96	..	1.56	1.77	0.59	0.37	1.46	3.23	0.74	0.32
Temperature 239°													
45	4320	5.17	..	1.21	..	2.50	2.95	1.01	0.47	1.12	4.65	1.28	0.50
46	2820	5.17	..	1.71	..	3.92	5.35	1.58	.87	1.60	7.36	2.16	.87
47	7380	5.63	0.08	0.38	..	0.77	1.00	0.25	.09	0.58	1.23	0.38	.21
49	4260	5.58	0.40	2.68	..	3.32	3.82	1.08	.38	1.29	5.94	1.34	.90
50	1200	5.67	..	3.92	..	7.13	7.32	4.02	2.58	4.97	14.93	4.82	1.51
Temperature 272°													
35	1080	4.90	..	12.18	..	9.40	12.00	4.49	1.92	4.70	20.27	4.49	2.48
42	1800	4.82	..	5.67	..	5.03	7.20	2.54	0.78	2.30	10.48	2.31	0.92
43	7200	4.88	..	6.40	..	4.68	6.45	2.33	.74	2.46	10.01	2.16	0.85
44	2340	5.17	..	4.35	..	4.21	6.40	1.88	.46	1.27	9.05	2.24	1.16
Temperature 344°													
52	720	4.82	..	52.70	..	18.60	46.20	38.20	2.44	6.50	66.00	11.20	4.10
53	240	4.82	..	60.20	..	14.86	47.20	54.70	2.24	9.16	60.00	11.68	4.92
54	240	4.92	..	62.70	..	16.40	51.60	57.20	2.42	14.63	66.20	12.77	5.37

[a] Open spaces indicate that under the given conditions this compound was not formed or formed in too small amounts to allow detection by mass spectrometer analysis.

may occur may be obtained by assuming that in the low temperature runs all ethylene, not produced by disproportionation of the ethyl radicals, is due to step 1c. Such calculations indicate that step 1c may be responsible for about 10% of the decomposition occurring in the primary steps.

Steps 1a and 1b are similar to the primary steps in the photolysis of CH_3COOCH_3[2] and CH_3COOCD_3,[5] where in the case of CH_3COOCD_3 the following steps could be shown to occur

$$
\begin{aligned}
CH_3COOCD_3 + h\nu &\longrightarrow CH_3CO + CD_3O \\
&\longrightarrow CH_3 + CD_3 + CO_2
\end{aligned}
$$

The ratio R_{CO}/R_{CO_2} was found to be 3.8 ± 0.3 in the temperature range 30 to 157°. This indicates that step 1a occurs about 4 times as frequently as step 1b. At higher temperatures this ratio of R_{CO}/R_{CO_2} increases somewhat. It seems likely that this is caused by secondary reactions such as decomposition of the $CH_3CHCOOC_2H_5$ and $C_2H_5COOCHCH_3$ radicals rather than by a temperature effect on the relative occurrence of steps 1a and 1b.

Reaction Mechanism.—Accepting reactions 1a and 1b as primary steps, these main reactions are proposed to explain the observed results

$$
\begin{array}{lll}
2C_2H_5 & \longrightarrow C_4H_{10} & (2) \\
 & \longrightarrow C_2H_4 + C_2H_6 & (3) \\
C_2H_5 + C_2H_5O & \longrightarrow C_2H_5OC_2H_5 & (4) \\
 & \longrightarrow C_2H_6 + CH_3CHO & (5) \\
 & \longrightarrow C_2H_4 + C_2H_5OH & (6) \\
2C_2H_5O & \longrightarrow C_2H_5OH + CH_3CHO & (7) \\
C_2H_5O & \longrightarrow CH_3 + CH_2O & (8) \\
 & \longrightarrow CH_3CHO + H & (9) \\
2CH_3 & \longrightarrow C_2H_6 & (10) \\
CH_3 + C_2H_5 & \longrightarrow C_3H_8 & (11) \\
 & \longrightarrow CH_4 + C_2H_4 & (12) \\
CH_3 + C_2H_5COOC_2H_5 & \longrightarrow CH_4 + C_4H_9CO_2 & (13) \\
C_2H_5 + C_2H_5COOC_2H_5 & \longrightarrow C_2H_6 + C_4H_9CO_2 & (14) \\
C_2H_5O + C_2H_5COOC_2H_5 & \longrightarrow C_2H_5OH + C_4H_9CO_2 & (15) \\
H + C_2H_5COOC_2H_5 & \longrightarrow H_2 + C_4H_9CO_2 & (16)
\end{array}
$$

Reactions 2, 3, 10, 11 and 12 are generally accepted recombination and disproportionation reactions of ethyl and methyl radicals and do not warrant any discussion. Reaction 4 explains the formation of ethyl ether, especially observed at low temperatures. Reactions 5 and 6 are possible disproportionation reactions between ethyl and ethoxy radicals. Disproportionation reactions of alkoxy radicals, such as reaction 7, have been suggested frequently[6-8] to explain alcohol and aldehyde formation. Not included in the reaction mechanism is the recombination reaction of two ethoxy radicals to form diethyl peroxide. The mass spectrum of diethyl peroxide shows considerable peaks at m/e 90 and m/e 62. Total absence of these peaks proved the absence of diethyl peroxide as a reaction product. Reactions 8 and 9 have been shown to occur by several investigations.[9-11] Reaction 8 produces formaldehyde and methyl radicals. The results show clearly an increase in methyl radicals with increasing temperature as might be expected by the thermal decomposition of ethoxy radicals according to reaction 8. Not included in the reaction mechanism are the reactions of methyl radicals with ethoxy radicals to form methyl ethyl ether and/or methane and acetaldehyde. The main reason for this is that, in the low temperature region where such reactions preferably occur, the amount of decomposition of the ethoxy radical is too small to allow these radical–radical reactions to occur to any marked extent. It may be mentioned that methyl ethyl ether never was observed among the reaction products. Reactions 13, 14, 15 and 16 represent the hydrogen abstraction reactions from ethyl propionate by methyl, ethyl and ethoxy radicals and by H atoms produced by reaction 9. The radicals formed by these abstraction reactions are given as $C_4H_9CO_2$, rather than expressing an opinion whether the abstraction would occur at the propionyl or ethoxy group of the ester molecule.

In the suggested reaction mechanism, methane is formed by reactions 12 and 13. According to Ausloos and Steacie,[12] $R_{CH_4(12)} = 0.04R_{C_3H_8}$, where $R_{CH_4(12)}$ indicates the rate of production of methane by reaction 12 only. Equation I is therefore obtained

$$(R_{CH_4\,total} - 0.04R_{C_3H_8})/(R^{1/2}{}_{C_2H_6(10)}\,[EP]) = k_{13}/k_{10}{}^{1/2} \tag{I}$$

$R_{C_2H_6(10)}$—the rate of ethane production by reaction 10—may be calculated from data obtained by Ausloos and Steacie[12] and by Wijnen,[13] which indicate that $R_{C_2H_6(10)} = 0.29R^2{}_{C_3H_8}/R_{C_4H_{10}}$. Values calculated *via* equation I for $k_{13}/k_{10}{}^{1/2}$ are given in Table II. By plotting log $k_{13}/k_{10}{}^{1/2}$ against $1/T$ (Fig. 4), an activation energy of about 8.2 kcal. is obtained for reaction 10.

TABLE II

RATIO OF RATE CONSTANTS

Temp., °C.	10^{13} $k_{13}/k_{10}{}^{1/2}$, molec.$^{1/2}$/cc.$^{1/2}$ sec.$^{1/2}$	10^{13} $k_{14}/k_2{}^{1/2}$, molec.$^{1/2}$/cc.$^{1/2}$ sec.$^{1/2}$	10^{19} k_{15}/k_8[a]	10^{13} $k_7/k_8{}^2$, molec.$^{-1}$ sec. cc.
30	..	..	97	~50
72	7	..	45; 37(V)	
108	13	3	9.2(V)	
152	46	8	3.1	~0.2
202	115	22	2.1	
239	251	43	...	
277	397	105	...	
344	817	289	...	

[a] Values given for k_{15}/k_8 marked by (V) were obtained *via* equation V, all other data for k_{15}/k_8 were obtained from equation IV.

According to the given reaction mechanism, ethane is produced by reactions 3, 5, 10 and 14. $R_{C_2H_6(10)}$ may be calculated as indicated above, and previous investigations have shown that $R_{C_2H_6(3)} = 0.12R_{C_4H_{10}}$.[2,14] The results in Table I indicate that

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(13) M. H. J. Wijnen, *J. Chem. Phys.*, **22**, 1631 (1954).

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from 239° upward in most experiments no ethanol could be detected. This proves that reaction 6 and therefore in all probability also reaction 5 do not occur at these temperatures.

It may be added here that the formation of acetaldehyde may be explained easily by other reactions as will be pointed out later.

At 239° and higher, the ethane formation by abstraction of a hydrogen atom from ethyl propionate may therefore be given by the equation

$$(R_{\mathrm{C_2H_6\,total}} - 0.12R_{\mathrm{C_4H_{10}}} - R_{\mathrm{C_2H_6(10)}})/(R^{1/2}{}_{\mathrm{C_4H_{10}}}\,[\mathrm{EP}]) = k_{14}/k_2{}^{1/2} \quad \mathrm{(II)}$$

Values for $k_{14}/k_2{}^{1/2}$, thus calculated, are given in Table II for the temperatures 239 to 344°. At temperatures below 239°, reaction 5, producing ethane *via* disproportionation of ethyl and ethoxy radicals, may become more important. Therefore, equation (III) is derived, which includes possible C_2H_6 production *via* reaction 5.

$$(R_{\mathrm{C_2H_6\,total}} - R_{\mathrm{C_2H_6(10)}} - 0.12R_{\mathrm{C_4H_{10}}})/(R_{\mathrm{CH_3}}R^{1/2}{}_{\mathrm{C_4H_{10}}}) = k_{14}/k_2{}^{1/2}[\mathrm{EP}]/R_{\mathrm{CH_3}} + k_5/k_8k_2{}^{1/2} \quad \mathrm{(III)}$$

In equation III, $R_{\mathrm{CH_3}}$ represents the rate of production of CH_3 radicals. In the proposed reaction mechanism CH_3 radicals are produced only by thermal decomposition of C_2H_5O radicals. If this is correct, $R_{\mathrm{CH_3}}$ will be a measure of the concentration of ethoxy radicals. To calculate $R_{\mathrm{CH_3}}$, it has been assumed that CH_3 radicals will only react to form ethane (reaction 10), propane (reaction 11) and methane (reactions 12 and 13), in which case $R_{\mathrm{CH_3}}$ is given by $R_{\mathrm{CH_3}} = 2R_{\mathrm{C_2H_6\,(10)}} + R_{\mathrm{CH_4}} + R_{\mathrm{C_3H_8}}$. Some CH_3 radicals undoubtedly may have disappeared undetected, possibly by addition to $C_4H_9CO_2$ radicals. As will be pointed out later, the extent to which CH_3 radicals disappear by addition or other, not given, reactions, seems to be small and the evidence indicates, therefore, that $R_{\mathrm{CH_3}}$ is a good approximation of the C_2H_5O radical concentration.

Equation III is plotted in Fig. 1 for the temperatures 108, 152 and 202°. Values thus obtained for $k_{14}/k_2{}^{1/2}$ are given in Table II. Figure 1 shows clearly that the results are less accurate at lower temperatures. Considering that $R_{\mathrm{C_2H_6(14)}}$ is calculated from $R_{\mathrm{C_2H_6\,total}} - R_{\mathrm{C_2H_6(10)}} - 0.12R_{\mathrm{C_4H_{10}}}$, this is not surprising. With increasing temperature, $R_{\mathrm{C_2H_6(14)}}$ approaches $R_{\mathrm{C_2H_6\,total}}$, and errors in the determination of $R_{\mathrm{C_2H_6(10)}}$ and $0.12R_{\mathrm{C_4H_{10}}}$ become, therefore, negligible compared to $R_{\mathrm{C_2H_6\,total}}$.

Log $k_{14}/k_2{}^{1/2}$ is plotted against $1/T$ in Fig. 4, and an activation energy of 9.8 kcal. is obtained for E_{14}, the energy required to abstract a hydrogen atom from ethyl propionate by ethyl radicals.

In plotting equation III, small intercepts were observed at 108 and 152° which, if real, indicate that reaction 5 occurs. The results are, however, not accurate enough to give reliable data for $k_5/k_8k_2{}^{1/2}$.

The results show a considerable acetaldehyde production at temperatures above 239°. Since at these temperatures no ethanol is observed, it is obvious that acetaldehyde cannot be produced by disproportionation of ethoxy radicals. A possible explanation for this increased acetaldehyde production might be given by reaction 9—the thermal decomposition of ethoxy radicals into acetaldehyde and hydrogen atoms. However, if this were the case, then it might be expected that, especially at high temperatures, the hydrogen production would closely parallel the acetaldehyde production. This is not the case. The possibility that acetaldehyde may be produced by some other reaction(s) should therefore be considered. The $C_4H_9CO_2$ radical, produced by abstraction of a hydrogen atom from ethyl propionate, may well be a source for acetaldehyde production. Accepting that mainly a secondary hydrogen atom is abstracted from ethyl propionate, these two $C_4H_9CO_2$ radicals may be formed: $CH_3CHCOOC_2H_5$ and $C_2H_5COOCHCH_3$. Little speculation seems involved in suggesting that the $CH_3CHCO_2C_2H_5$ radical may thermally decompose into C_2H_4, CO and C_2H_5O, into C_2H_4, CO_2 and C_2H_5, or possibly even into CH_3CHCO and C_2H_5O, although methyl ketene was not observed among the reaction products. The $C_2H_5CO_2CHCH_3$ radical on the other hand may decompose into C_2H_5, CO_2 and C_2H_4 or into CH_3CHO, CO and C_2H_5. Either radical, in decomposing, produces a C_2H_5 or C_2H_5O radical and thus starts a chain reaction. Indication for such a chain reaction is obtained by comparing the product yields at 344° with those obtained at lower temperatures. The fact that $R_{\mathrm{C_2H_4}}$ total $>>> (0.12R_{\mathrm{C_4H_{10}}} + 0.04R_{\mathrm{C_3H_8}})$ is added proof for the decomposition of the $C_4H_9CO_2$ radical. In addition, acetone was photolyzed in presence of ethyl propionate at wave lengths above 3000 Å., where ethyl propionate does not absorb. Both ethylene and acetaldehyde were formed at temperatures above 152°, proving that at these temperatures ethylene and acetaldehyde are formed by decomposition of the $C_4H_9CO_2$ radicals.

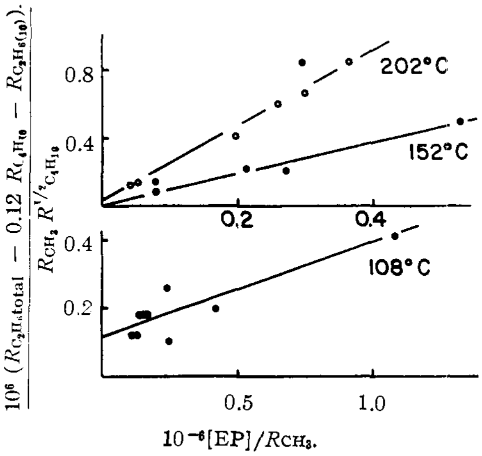

Fig. 1.—Plots of $10^6\,(R_{\mathrm{C_2H_6\,total}} - R_{\mathrm{C_2H_6(10)}} - 0.12R_{\mathrm{C_4H_{10}}})/(R_{\mathrm{CH_3}}R^{1/2}{}_{\mathrm{C_4H_{10}}})$ ***versus*** $10^{-6}\,[\mathrm{EP}]/R_{\mathrm{CH_3}}$ at 108, 152 and 202°.

No appreciable ethylene and acetaldehyde production was observed when acetone was photolyzed in presence of ethyl propionate at 152°. It may therefore be assumed that at this and lower temperatures, the $C_4H_9CO_2$ radical will not decompose. Equations (IV) and (V) may be derived under this condition

$$\frac{R_{\mathrm{C_2H_5OH}} - R_{\mathrm{C_2H_4(6)}}}{R^2{}_{\mathrm{CH_3}}} = \frac{k_7}{k_8{}^2} + \frac{k_{15}}{k_8}\frac{[\mathrm{EP}]}{R_{\mathrm{CH_3}}} \quad \mathrm{(IV)}$$

and

$$\frac{R_{C_2H_5OH} - R_{CH_3CHO}}{R^{1/2}_{C_4H_{10}}R_{CH_3}} = \frac{k_6 - k_5}{k_8k_2^{1/2}} + \frac{k_{15}}{k_8}\frac{[EP]}{R^{1/2}_{C_4H_{10}}} \quad (V)$$

In equation IV, $R_{C_2H_4(6)}$ is the rate of ethylene production by reaction 6 only and is given by $R_{C_2H_4(6)} = R_{C_2H_4\ total} - 0.12R_{C_4H_{10}} - 0.04R_{C_3H_8}$, disregarding possible ethylene production by primary step 1c. The maximum extent to which primary step 1c may take part is 10% of the total decomposition occurring in the primary steps. Taking this ethylene production by step 1c into account, data obtained for k_{15}/k_8 *via* equation IV will increase by not more than 15% at 30 and at 72°. At 152° the value of $10^{19}\ k_{15}/k_8$ is 3.1, disregarding primary step 1c and 5.4 if it is accepted that step 1c occurs to an extent of 10% of the total decomposition in the primary steps. Equation IV is plotted in Fig. 2 for the temperatures 30, 72 and 152°.

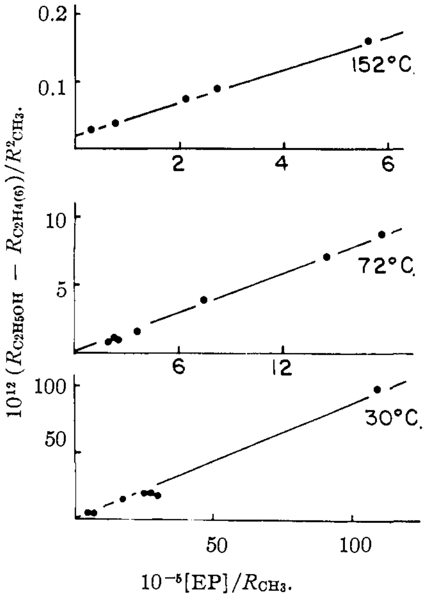

Fig. 2.– Plots of $10^{12}\ (R_{C_2H_5OH} - R_{C_2H_4(6)})/R^2_{CH_3}$ *versus* $10^{-5}\ [EP]/R_{CH_3}$ at 30, 72 and 152°.

Except for the results at 152°, no intercepts were observed, indicating that k_7/k_8^2 is small compared to the units in which the ordinate of Fig. 2 is expressed. Values of k_{15}/k_8, obtained from Fig. 2, are given in Table II. No accurate results were obtained at 108°, although there was a general agreement of the data with equation IV.

Equation V is plotted in Fig. 3 for the temperatures 72 and 108°. The intercepts are not pronounced enough to allow an accurate determination of $(k_6 - k_5)/(k_8k_2^{1/2})$. Values of k_{15}/k_8 obtained *via* equation V are given in Table II. No plot was possible for equation V at 30 and at 152°. In this respect, it should be mentioned that acetaldehyde is probably the compound most subject to analytical error. An explanation for the failure to be able to plot equation V at 152° may in addition be given by the possibility that at this temperature some acetaldehyde is produced by reaction 9—the thermal decomposition of ethoxy radicals producing CH_3CHO and H atoms.

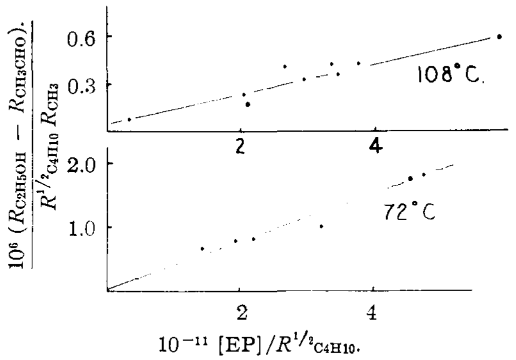

Fig. 3.– Plots of $10^6\,(R_{C_2H_5OH} - R_{CH_3CHO})/(R^{1/2}_{C_4H_{10}}R_{CH_3})$ *versus* $10^{-11}\ [EP]/R^{1/2}_{C_4H_{10}}$ at 72 and 108°.

Equations IV and V are not applicable to the results obtained at 202° and higher, since at those temperatures additional acetaldehyde and ethylene are produced by the thermal decomposition of the $C_4H_9CO_2$ radicals at 202°, k_{15}/k_8 therefore was calculated *via* equation VI.

$$\frac{R_{C_2H_5OH}}{R_{CH_3}[EP]} = \frac{k_{15}}{k_8} \quad (VI)$$

Equation VI is valid only if reactions 6 and 7 do not occur at 202° which is difficult to prove. Some justifications for equation VI may be found in the following considerations. Plots of equation IV at different temperatures gave no or small intercepts, indicating that k_7/k_8^2 is small compared to $k_{15}/k_8 \times [EP]/R_{CH_3}$. Secondly the fact that no ethyl ether is found at high temperatures proves that no recombination—and therefore probably also no disproportionation—reactions occur between ethyl and ethoxy radicals at these temperatures. Table II gives the value obtained for k_{15}/k_8 at 202° by equation VI. No calculations have been carried out to determine k_{15}/k_8 at 239° since the amount of ethanol produced at this temperature is too small to allow its accurate determination.

In Fig. 4, log k_{15}/k_8 is plotted against $1/T$. From this plot an activation energy difference of $E_8 - E_{15} \simeq 7$ kcal. is obtained.

Since disproportionation and recombination reactions usually have a low activation energy, they will be most important in the lower temperature region. As an example of this may be given the production of ethyl ether, formed by recombination of ethyl and ethoxy radicals, which decreases rapidly with increasing temperature. By extrapolation of the data obtained for $k_{14}/k_2^{1/2}$, it may be shown that at 30° the amount of ethane, produced by reaction 14, is negligible compared to the total ethane production. At this temperature $R_{C_2H_6(5)}$ therefore is given by

$$R_{C_2H_6(5)} = R_{C_2H_6\ total} - 0.12R_{C_4H_{10}} - R_{C_2H_6(10)}$$

Equation (VII) is thus obtained

$$(R_{CH_3CHO} - R_{C_2H_6(5)})/R^2_{CH_3} = k_7/k_8^2 \quad (VII)$$

It is obvious from the derivatives made to obtain $R_{C_2H_6(5)}$ that large errors are almost unavoidable. The results nevertheless indicate that at 30° $10^{12}\ k_7/k_8^2 = 5 \pm 2$ molec.$^{-1}$ sec. cc.

Material Balance.—Since CO and C_2H_5O are both produced by the primary step 1a only, it is evident that $R_{CO}/R_{C_2H_5O}$ should be equal to unity. In the above expression $R_{C_2H_5O}$ indicates the rate of production of C_2H_5O radicals and is given by $R_{C_2H_5O} = R_{C_2H_5OC_2H_5} + R_{CH_3CHO} + R_{C_2H_5OH} + R_{CH_3}$. These calculations have been carried out, although they are not reported in order to save space. Within experimental error $R_{CO}/R_{C_2H_5O}$ was found to be equal to unity—largest observed deviations were -0.2 and $+0.3$. The fact that experimentally $R_{CO}/R_{C_2H_5O}$ equals unity indicates also that R_{CH_3}, as suggested earlier, is a good approximation for the rate of disappearance of ethoxy radicals by thermal decomposition into CH_3 and CH_2O.

Combining the reaction products of steps 1a and 1b, it may also be shown that $2(R_{CO} + R_{CO_2})/(R_{C_2H_5} + R_{C_2H_5O})$ should equal unity, which has, within experimental error, been observed to be true.

Discussion

An activation energy of 8.2 kcal. was obtained for E_{13}, the energy required for the abstraction of a hydrogen atom from ethyl propionate by methyl radicals. No other data are reported in the literature for E_{13}. An activation energy of 10 kcal.[4] has been reported for the reaction

$$CH_3 + CH_3COOCH_3 \longrightarrow CH_4 + CH_2COOCH_3$$

These values seem to be in good agreement since in methyl acetate a primary—and in ethyl propionate a secondary—hydrogen is abstracted. A similar difference in activation energy for the abstractions of primary and secondary hydrogen has been observed in acetone and methyl ethyl ketone.

$$CH_3 + CH_3COCH_3 \longrightarrow CH_4 + CH_2COCH_3 \quad (A)$$

$$CH_3 + C_2H_5COCH_3 \longrightarrow CH_4 + C_2H_4COCH_3 \quad (B)$$

The activation energies have been reported as 9.7 kcal.[15] for reaction A, and 7.4 kcal.[10] for reaction B.

As activation energy for the hydrogen abstraction from ethyl propionate a value of $E_{14} = 9.8$ kcal. was obtained. Since the C_2H_5–H bond is somewhat weaker than the CH_3–H bond, it might be expected that the hydrogen abstraction by ethyl radicals needs a higher activation energy than the similar reaction by methyl radicals.

The ratios of the steric factors $P_{13}/P_{10}^{1/2}$ and $P_{14}/P_2^{1/2}$ is in the order of 10^{-3}, as generally observed in abstraction reactions by methyl and ethyl radicals.

Information obtained from this work indicates that with increasing temperature the ethoxy radical decomposes rather than forming ethanol by hydrogen abstraction or by disproportionation. It is interesting to compare these data with those obtained by Rebbert and Laidler,[7] who studied the thermal decomposition of ethyl peroxide in a flow system in presence of a large excess of toluene. As main reaction products were observed ethane and formaldehyde and in much smaller amounts, methane and dibenzyl. They suggested the following reaction mechanism to explain their data

$$C_2H_5OOC_2H_5 \longrightarrow 2C_2H_5O \quad (16)$$

$$C_2H_5O \longrightarrow CH_3 + CH_2O \quad (8)$$

$$2CH_3 \longrightarrow C_2H_6 \quad (10)$$

$$CH_3 + C_6H_5CH_3 \longrightarrow CH_4 + C_6H_5CH_2 \quad (17)$$

$$2C_6H_5CH_2 \longrightarrow (C_6H_5CH_2)_2 \quad (18)$$

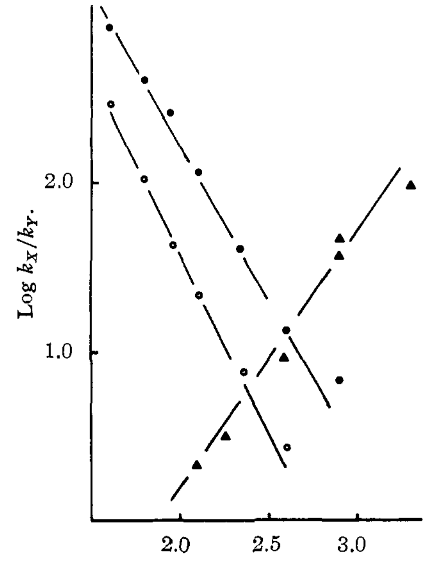

Fig. 4.—Plots of $13 + \log k_{13}/k_{10}^{1/2}$ (●); $13 + \log k_{14}/k_2^{1/2}$ (○); and $19 + \log k_{15}/k_8$ (▲) *versus* $10^3 \times 1/T$.

Because of the lack of any appreciable peak at 17 *m/e* in the mass spectrometric analysis of the reaction products, they concluded that reaction 8 would be much faster than reaction 19.

$$C_2H_5\dot{O} + C_6H_5CH_3 \longrightarrow C_2H_5OH + C_6H_5CH_2 \quad (19)$$

These results were obtained in the temperature range 200 to 245°. Our data show that small amounts of ethanol were observed at 200°, but within experimental error no ethanol was found in four of the five runs at 239°. Qualitatively speaking, these data are in excellent agreement and indicate, as pointed out by Rebbert and Laidler, that at these temperatures the thermal decomposition of the ethoxy radical proceeds much more rapidly than the hydrogen abstraction reaction by ethoxy radicals.

Evidence for the occurrence of a disproportionation reaction between ethoxy radicals to form ethanol and acetaldehyde has been obtained at 30 and at 152°. Ethanol formation by disproportionation of ethoxy radicals seems to be mainly important in the low temperature region. A similar observation was made regarding methoxy radicals.[1,3]

As difference in activation energy between reactions 8 and 15 was obtained $E_8 - E_{15} \simeq 7$ kcal. The heat of dissociation of ethoxy radicals into CH_3 and CH_2O has been reported as 10.4 kcal. by Rebbert and Laidler[7] and as 12.8 kcal. by Gray.[16] In his calculations Gray accepted $\Delta H = -9.0$ kcal. as enthalpy of formation for the C_2H_5O radical. Recent investigations by Pollard, Marshall and Pedler[9] place $\Delta H = -6.7$ kcal., in which case the heat of dissociation of the C_2H_5O radical into CH_3 and CH_2O would become 10.5 kcal. as reported by Rebbert and Laidler. Accepting therefore ΔH ($C_2H_5O \rightarrow CH_3 + CH_2O$) as 10.5 kcal., it is obvious that $E_8 \geqslant 10.5$ kcal.; from this a minimum value of 3.5 kcal. is obtained for E_{15}.

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

[16] P. Gray, *Proc. Roy. Soc.* (*London*), **A221**, 462 (1954).

The author of this investigation feels that E_8 and E_{15} are close to the minimum values given above and bases his opinion on the following considerations. Granting that the values reported for k_7/k_8^2 are not very accurate, since they were mainly determined from intercepts, they nevertheless indicate that E_8 is small. In an investigation of methyl acetate,[1] an activation energy of about 4.5 kcal. was obtained for reaction 20.

$$CH_3O + CH_3COOCH_3 \longrightarrow CH_3OH + CH_2COOCH_3 \quad (20)$$

Although the RO–H bond has been reported[17] as 100 kcal. for $CH_3O–H$ and as 99 kcal. for $C_2H_5O–H$, it seems logical that E_{15} should not exceed E_{20} to any great extent, if at all. This is even more so if we consider that a primary hydrogen is abstracted in reaction 20 while a secondary hydrogen is abstracted from ethyl propionate.

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CLARKWOOD, TEXAS

[17] P. Gray, *Trans. Faraday Soc.*, **52**, 344 (1956).

[CONTRIBUTION FROM THE MINERALS THERMODYNAMICS EXPERIMENT STATION, REGION II, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Low Temperature Heat Capacities and Entropies at 298.15°K. of Lead Sesquioxide and Red and Yellow Lead Monoxide

BY E. G. KING[1]

RECEIVED JANUARY 10, 1958

The heat capacities of lead sesquioxide and the red and yellow forms of lead monoxide were measured over the temperature range 51–298°K. All three substances behaved in a regular manner. Entropies at 298.15°K. were obtained, as shown (cal./deg. mole): sesquioxide, 36.3 ± 0.7; red monoxide, 15.6 ± 0.2; and yellow monoxide, 16.1 ± 0.2.

This paper reports heat capacity measurements over the temperature range 51–298°K., together with entropy evaluations at 298.15°K., for lead sesquioxide, red lead monoxide (tetragonal) and yellow lead monoxide (rhombic). No previous similar data have been published for these compounds except the few results of Nernst and Schwers[2] for the yellow monoxide in the temperature range 21–93°K. Data for lead dioxide and minium (Pb_3O_4) have been reported by Millar.[3]

Materials.—Lead sesquioxide was prepared by the following procedure. A solution of reagent grade lead nitrate was treated with a slight excess of ammonium carbonate solution. The precipitated lead carbonate was washed free of ammonium salts and dried at 140°. It then was converted to sesquioxide by heating in air, 40 hr. at 290°, 64 hr. at 310° and 10 days at 320°. Analysis of the product gave 89.64% lead, as compared with the theoretical 89.62%. The X-ray diffraction pattern agreed with the ASTM catalog.

Red lead monoxide was prepared by heating electrolytic lead dioxide *in vacuo* at 430–480° for about 8 weeks. (The long heating period was required to eliminate yellow monoxide which is very slow to convert to red.) The product gave no test for higher oxides when treated with strong sodium hydroxide solution. It analyzed 92.69% lead (theory, 92.83%). The X-ray diffraction pattern indicated the presence of only a small amount of the yellow variety.

Yellow lead monoxide was made by heating lead carbonate (obtained by the method mentioned above). The first heating, 80 hr. at 560–580°, was insufficient to decompose the carbonate completely or to prevent the formation of some red monoxide. The substance finally was split into small portions, heated for 10 hr. at 725° and quenched to room temperature. No reconversion to the red form occurred during this treatment. Analysis of the product gave 92.84% lead (theory, 92.83%). The X-ray diffraction pattern agreed with the ASTM catalog.

TABLE I

HEAT CAPACITIES (CAL./DEG. MOLE)

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
Pb_2O_3 (mol. wt., 462.42)					
53.36	8.891	114.88	15.90	216.45	22.80
58.06	9.524	124.78	16.81	226.13	23.25
62.66	10.12	136.53	17.82	235.97	23.64
67.03	10.70	145.90	18.58	245.91	24.04
71.50	11.24	155.87	19.33	256.50	24.44
75.95	11.77	166.02	20.02	266.45	24.81
81.00	12.38	175.85	20.62	276.38	25.09
85.48	12.87	186.19	21.25	287.09	25.40
94.96	13.91	196.05	21.78	296.56	25.70
104.75	14.92	206.42	22.33	298.15	(25.74)
PbO (red, mol. wt., 223.21)					
53.40	4.095	114.78	7.039	216.27	9.878
58.07	4.354	124.89	7.440	226.09	10.05
62.71	4.608	135.91	7.841	236.73	10.21
67.26	4.851	145.79	8.183	245.91	10.32
71.67	5.088	155.84	8.494	256.39	10.47
76.13	5.311	165.83	8.773	266.62	10.60
81.30	5.559	176.34	9.039	276.58	10.71
85.97	5.777	186.35	9.283	286.79	10.82
94.64	6.179	195.99	9.479	296.27	10.94
104.71	6.627	206.38	9.702	298.15	(10.95)
PbO (yellow, mol. wt., 223.21)					
54.13	4.353	114.74	7.184	216.48	9.915
58.39	4.590	124.80	7.568	226.22	10.08
62.59	4.806	135.95	7.958	236.04	10.24
66.82	5.041	145.71	8.292	245.94	10.37
71.12	5.260	155.95	8.599	256.39	10.50
75.57	5.472	165.87	8.868	266.26	10.61
81.03	5.734	176.28	9.118	276.22	10.72
85.21	5.924	185.83	9.337	286.42	10.82
94.91	6.363	196.21	9.547	296.11	10.94
105.01	6.793	206.23	9.747	298.15	(10.95)

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[1] Bureau of Mines, U. S. Department of the Interior, Berkeley, California.

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[3] R. W. Millar, THIS JOURNAL, **51**, 207 (1929).