

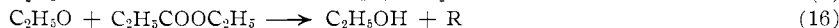
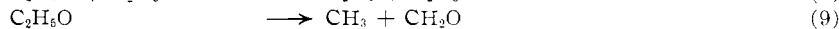
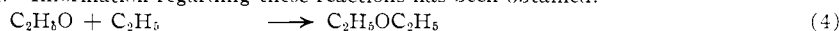
[CONTRIBUTION FROM THE RADIATION RESEARCH LABORATORIES, MELLON INSTITUTE, PITTSBURGH, PA.]

Reactions of Alkoxy Radicals. VII. The Ethoxy Radical

BY M. H. J. WIJNEN¹

RECEIVED NOVEMBER 13, 1959

The photolysis of ethyl propionate has been reinvestigated. The reactions of ethoxy radicals, produced in the primary process, have been studied in detail. Information regarding these reactions has been obtained.



At 29°, $k_5/k_4 = 1.3 \pm 0.2$ and $k_6/k_4 = 2.3 \pm 0.3$ indicating that disproportionation reactions between ethoxy and ethyl radicals are more important than their recombination reactions. Activation energies of 13 and 5.5 kcal. have been obtained for reactions 9 and 16, respectively.

Introduction

Recent investigations² of the photolysis of esters have given information on the ability of alkoxy radicals to form alcohol by hydrogen abstraction reactions. Little quantitative information is available, however, in regard to disproportionation and recombination reactions of alkoxy radicals among themselves and of alkoxy radicals with alkyl radicals.

Taking advantage of improved techniques for analysis of liquid reaction products by gas chromatography, the photolysis of ethyl propionate has been reinvestigated.

Experimental

The experimental technique is essentially the same as described previously.² 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 arc and reaction cell.

As reaction products were observed: CO, CO₂, CH₂O, CH₄, C₂H₆, C₂H₄, C₃H₈, C₄H₁₀, C₂H₅OH, CH₃CHO and C₂H₅OC₂H₅. After the exposure reaction products and excess ethyl propionate were cooled down to -145°. The products volatile at this temperature (CO, CO₂, CH₄, C₂H₆, C₂H₄, C₃H₈ and partially also C₄H₁₀) were pumped off and analyzed by gas chromatography, using a 2 m.-long silica gel column preceded by a 2½ m.-long column containing 16% (by weight) of 50 HB 660 Ucon fluid (obtained from Union Carbide Chemical Company) on firebrick. The other reaction products and the excess of ethyl propionate were sampled and analyzed by gas chromatography. In this case a 5 m.-long column containing 18% (by weight) of Reoplex 400 (obtained from Geigy Chemical Corporation) on firebrick was used. It was observed, however, that this method of separation did not give reproducible results for acetaldehyde and ethyl ether. Further investigations indicated that part of the ether and of the acetaldehyde came over in the first fraction and was lost in the silica gel column. To obtain accurate data for acetaldehyde and ether separate runs were made in which all reactions products and excess ethyl propionate were condensed together and then analyzed by gas chromatography using the Reoplex 400 column. By this procedure accurate data were obtained for acetaldehyde and ether.

No quantitative measurements were carried out to determine the amount of formaldehyde produced although its presence was observed in all experiments.

In addition to the products mentioned above we observed the formation of a compound having the empirical formula C₇H₁₄O₂. It is extremely likely that this compound is either propyl α -methylpropanoate or ethyl 2-methylbutanoate,

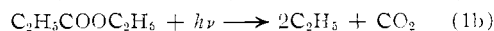
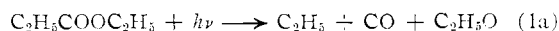
possibly a mixture of these two compounds. Determination of the amounts of C₇H₁₄O₂ formed was sometimes impossible, quite often extremely difficult since no complete separation was obtained between C₇H₁₄O₂ and the excess of undecomposed ethyl propionate. Figures given for the rate of formation of C₇H₁₄O₂ in Table I may be in error by as much as 30%.

In order to prevent, or at least minimize, secondary photolysis of acetaldehyde, the conversion was arranged such that the acetaldehyde production was less than 0.1% of the starting material. This procedure has been followed for all experiments except those at 195° where exact knowledge of acetaldehyde formation was not required.

Results

The photolysis of ethyl propionate has been carried out at 15, 29, 63, 114 and 195° at different light intensities and various 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 CO and/or CO₂ production. Single figures in column 1 of Table I indicate that only one experiment was carried out either analyzing for all products except acetaldehyde and ether, or analyzing only for butane, ether, acetaldehyde and alcohol production. Two figures in column 1 indicate that duplicate runs were carried out analyzing for all products as described under Experimental.

Primary Steps.—These primary steps have been suggested previously³ to explain the results



The formation of reaction products such as CO, CO₂, C₂H₅OH, C₂H₅OC₂H₅, C₂H₆, C₂H₄ and C₄H₁₀ presents sufficient evidence for the occurrence of these steps. No further discussion of steps 1a and 1b seems therefore warranted, except to note that the ratio $R_{\text{CO}}/R_{\text{CO}_2} = 3.4 \pm 0.2$ in the temperature range 29 to 114°. This value is in reasonable agreement with the previous estimate of $R_{\text{CO}}/R_{\text{CO}_2} = 3.8 \pm 0.3$.³ The fact that at 15° the ratio $R_{\text{CO}}/R_{\text{CO}_2}$ is considerably smaller than 3.4 may be taken as evidence that the formation of CO by step 1a occurs through the C₂H₅CO radical as intermediate. Results obtained in the photolysis of diethyl ketone⁴ indicate that at 15° the C₂H₅CO radical may be stable enough to react with other radicals forming CO containing compounds such

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

(2) M. H. J. Wijnen, *J. Chem. Phys.*, **27**, 710 (1957); **28**, 271, 939 (1958); *This Journal*, **80**, 2394 (1958); *Can. J. Chem.*, **36**, 691 (1958).

(3) M. H. J. Wijnen, *This Journal*, **80**, 2394 (1958).

(4) K. O. Kutselike, M. H. J. Wijnen and E. W. R. Steacie, *ibid.*, **74**, 713 (1952).

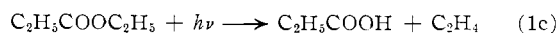
TABLE I
PHOTOLYSIS OF ETHYL PROPIONATE^a
Rate of formation of reaction products in molec./ (sec. cc.) $\times 10^{-12}$

Run no.	10^{-17} [EP] molec./ cc.	CO	CO ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₄ H ₁₀	C ₂ H ₅ OH	C ₂ H ₅ OC ₂ H ₅	CH ₃ CHO	C ₇ H ₁₄ O ₂
Temp. 15°												
29	6.35	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	3.92	9.64	1.45	2.09	..
30	1.77	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.32	4.02	0.48	0.64	..
31-32	4.32	0.94	0.40	..	0.13	0.40	..	0.36	0.80	.043	.046	..
33	6.06	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.54	4.38	.51	.52	..
34	6.06	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.23	0.52	.022	?	..
35	6.24	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	.10	.21	.006	.007	..
36	5.37	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	.24	.44	.029	.035	..
37	3.50	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	.07	.17	.007	?	..
38-39	6.18	11.20	4.43	..	2.14	3.53	..	3.34	10.41	1.36	1.61	..
Temp. 29°												
1-2	3.36	0.75	0.21	0.03	0.23	0.24	0.06	0.22	0.55	0.019	0.025	0.09
3-4	9.20	1.38	0.42	0.02	0.24	0.40	0.08	.49	1.37	.030	.047	0.20
5	3.52	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	.17	0.48	.015	.020	n.d.
6-7	3.56	2.64	0.80	0.11	0.69	0.89	0.12	.73	2.04	.120	.160	0.32
8-9	9.74	4.99	1.54	.07	.80	1.52	.20	1.80	4.86	.177	.181	0.72
10-11	6.50	4.55	1.37	.07	.83	1.50	.31	1.49	3.49	.160	.201	n.d.
12	9.10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.69	1.47	.037	.049	n.d.
13	9.30	1.49	0.45	0.03	0.21	0.43	0.07	0.70	1.43	.033	.043	0.24
28	{ 8.45EP 0.07I ₂	6.32	4.82	..	Trace	3.31	4.28	..	1.741	..
Temp. 63.5°												
18	8.80	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.12	2.75	0.045	0.080	n.d.
19	8.82	3.52	0.92	0.02	0.76	0.91	0.27	0.96	2.12	n.d.	n.d.	0.51
20	8.58	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	.83	1.88	0.024	0.061	n.d.
21	8.50	3.16	0.87	0.13	0.69	0.85	0.24	.93	2.22	n.d.	n.d.	0.64
22	5.86	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	.73	1.88	0.033	0.057	.43
23	5.86	2.30	0.69	0.09	0.48	0.71	0.22	.76	1.64	n.d.	n.d.	.41
Temp. 114°												
14	5.15	3.00	0.84	0.51	0.98	0.81	0.69	0.61	0.85	0.50
15	2.70	1.61	.46	.26	0.53	.54	.33	0.38	0.3214
16	7.22	3.55	.97	.48	1.04	.94	.75	1.00	1.4551
17	5.10	0.93	.33	.16	0.30	.28	.20	0.23	0.2716
Temp. 195°												
24	6.55	2.62	0.97	1.56	1.59	0.75	0.35	0.43	0.36	..	n.d.	n.d.
25	6.37	2.66	.87	1.45	1.64	.78	.42	.38	.31	..	n.d.	0.47
26	4.22	2.06	.78	1.05	1.14	.80	.36	.27	.19	..	n.d.	.34
27	6.37	0.97	.28	0.56	0.71	.21	.06	.10	.09	..	n.d.	.13

^a Open spaces indicate that under the given conditions this compound was not formed or formed in too small amounts to allow its determination by gas chromatography; n.d. indicates that no analysis was carried out for the given compound.

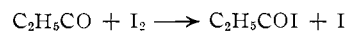
as C₂H₅COC₂H₅. Such reactions would reduce the ratio R_{CO}/R_{CO_2} as observed.

A third primary step, occurring in the photolysis of esters, has been suggested by Ausloos⁵



Previous³ and present attempts to confirm step 1c by identifying C₂H₅COOH as a reaction product have failed. This may be due, however, to the fact that C₂H₅COOH is absorbed easily on the walls of the vacuum system. Confirmation of ethylene formation *via* a molecular rearrangement reaction is given by run No. 28 (at 29°), where ethyl propionate was photolysed in the presence of iodine. In this experiment a considerable amount of ethylene was produced while methane, ethane, propane and butane were not

observed. Analysis of the liquid products showed that ethyl and methyl radicals had formed iodides, the ratio C₂H₅I/CH₃I being in the order of 13/1. It is also interesting to point out that the ratio $R_{CO}/R_{CO_2} \ll 3.4$ in this experiment. Reduction of the rate of CO formation may be caused by the reaction



The formation of ethanoyl iodide has been suggested previously⁶ to explain the decreased rate in CO formation when acetone is photolyzed in the presence of iodine.

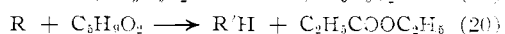
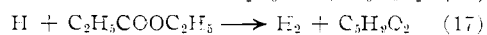
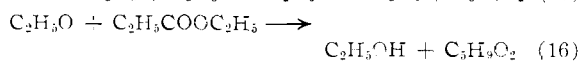
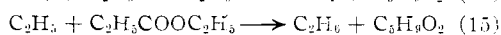
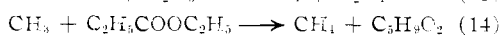
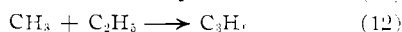
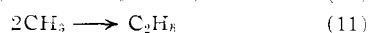
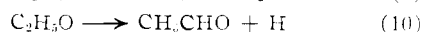
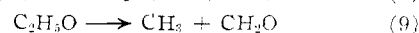
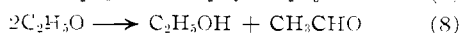
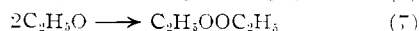
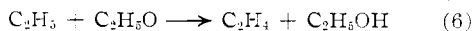
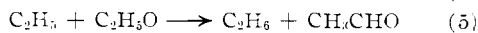
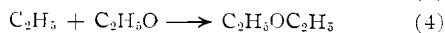
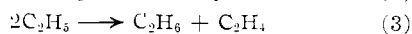
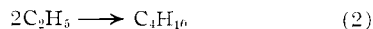
Accepting that the rate of CO₂ formation is not changed by the presence of iodine the relative importance of steps 1a, 1b and 1c at 29° has been calculated. These calculations indicate that steps

(5) P. Ausloos, *Can. J. Chem.*, **36**, 383 (1958).

(6) E. Gorin, *Acta Physicochim. U.R.S.S.*, **8**, 513 (1938); *J. Chem. Phys.*, **7**, 256 (1939).

1a, 1b and 1c account for, respectively, 67.5, 19.3 and 13.2% of the total primary process. It is, however, extremely likely that the relative importance of steps 1a, 1b and 1c will vary with wave length as observed by Ausloos⁵ and possibly even with temperature.

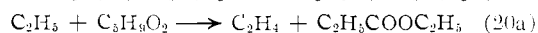
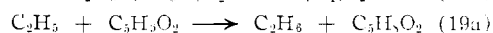
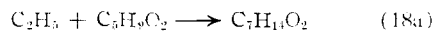
Reaction Mechanism.—The reaction mechanism shown has been suggested previously³ to explain the results obtained



Previous experiments³ indicated that no hydrogen is produced when ethyl propionate is photolyzed below 150°. Since we were interested mainly in the low temperature region we have not carried out any analysis for this compound. It is quite likely, however, that small amounts of hydrogen were produced at 195°. Present analysis by gas chromatography confirmed earlier results by mass spectrometer analysis regarding the absence of diethyl peroxide as a reaction product. Not included in the reaction mechanism are the possible recombination and disproportionation reactions of methyl and ethoxy radicals. Since methyl radicals are produced only by thermal decomposition of the ethoxy radical (reaction 9), their concentration is extremely low at low temperatures where recombination and disproportionation reactions are favored. A rough estimate of the amount of methyl ethyl ether formed may be obtained from $R_{CH_3OC_2H_5} \approx R_{C_2H_5OC_2H_5} \times R_{C_2H_5} / R_{C_4H_{10}}$. Such calculations indicate that the amount of methyl ethyl ether formed is in the order of 10% of the amount of ethyl ether formed. Only in experiments with large conversions (not reported here) was it possible to show the presence of methyl ethyl ether as a reaction product.

Reactions 14 to 17 represent the hydrogen abstraction reactions from ethyl propionate by the various radicals produced in the system. The radicals formed by these abstraction reactions are given as $C_5H_9O_2$ rather than expressing an opinion whether the abstraction occurs at the propionyl or ethoxy group of the ester molecule.

Reactions 18, 19 and 20 represent possible recombination and disproportionation reactions between the $C_5H_9O_2$ radical and various other radicals present in the system. In the case of ethyl radicals these reactions are



The formation of $C_7H_{14}O_2$ has been observed as discussed under Experimental. Evidence will be presented regarding reactions 19a and 20a. We have not observed the addition product of methyl radicals to $C_5H_9O_2$. We feel that the failure to observe $C_6H_{12}O_2$ is due first to its small quantities formed (the concentration of methyl radicals is considerably lower than the ethyl radical concentration) and secondly to possible masking of its peak by tailing effect of the excess of undecomposed ethyl propionate during the gas chromatography analysis. In the forthcoming discussion of the reaction mechanism we will neglect the reactions of ethoxy radicals with $C_5H_9O_2$ radicals, since alcohol and acetaldehyde productions by reactions such as 19 and 20 are negligible compared to alcohol and acetaldehyde formation by other reactions. As will be shown later, at 29° and higher, ethoxy radicals react extremely rapidly to form ethyl alcohol *via* reaction 16. The fraction of ethoxy radicals taking part in recombination and disproportionation reactions at these temperatures is therefore extremely small as may be seen from the small amount of ethyl ether. On the other hand, the results show that at 15° very little hydrogen abstraction from ethyl propionate occurred thus reducing the concentration of the $C_5H_9O_2$ radical to such an extent that even the addition product of C_2H_5 and $C_5H_9O_2$ radicals could hardly be observed.

Previous investigations have shown that no hydrogen is produced in the photolysis of ethyl propionate below 150° indicating that at these temperatures reaction 10 (thermal decomposition of the ethoxy radical into CH_3CHO and H atoms) does not occur to any appreciable extent. At 15 and 29°, acetaldehyde will thus be produced mainly by reactions 5 and 8 and equation (I) may be derived

$$\frac{R_{C_4H_{10}} R_{CH_3CHO}}{R_{C_2H_5OC_2H_5}^2} = \frac{k_5}{k_4} \frac{R_{C_4H_{10}}}{R_{C_2H_5OC_2H_5}} + \frac{k_3 k_2}{k_4^2} \quad (I)$$

Equation I is plotted in Fig. 1 for the temperatures 15 and 29° and establishes a value of $\frac{k_5}{k_4} = 1.3 \pm 0.2$, within experimental error, independent of temperature. Figure 1 also shows that the maximum value of $\frac{k_3 k_2}{k_4^2}$ is not likely to exceed 2.5.

According to the proposed reaction mechanism ethylene is produced by primary step 1c and reactions 3, 6, 13 and 20a. $R_{C_2H_4}$ (3) (rate of ethylene production by reaction 3 only) = $0.12 R_{C_4H_{10}}$ ^{7,8} $R_{C_2H_4}$ (13) = $0.06 R_{C_2H_5}$ ^{9,10} By subtracting from

(7) P. Ausloos and E. W. R. Steacie, *Can. J. Chem.*, **32**, 593 (1954).

(8) H. Cerfontaine and K. D. Kutschke, *ibid.*, **36**, 344 (1958).

(9) P. Ausloos and E. W. R. Steacie, *ibid.*, **33**, 1062 (1955).

(10) C. A. Heller, *J. Chem. Phys.*, **28**, 1255 (1958).

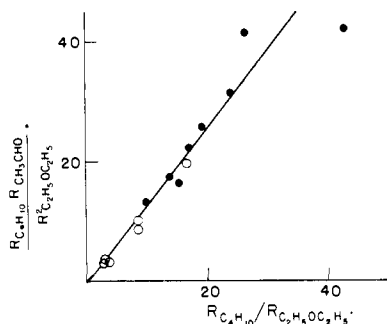


Fig. 1.—Plot of $R_{C_4H_{10}}R_{CH_3CHO}/R_{C_2H_5OC_2H_5}^2$ versus $R_{C_4H_{10}}/R_{C_2H_5OC_2H_5}$ at 15 and at 29°. Open circles represent data obtained at 15°, closed circles at 29°.

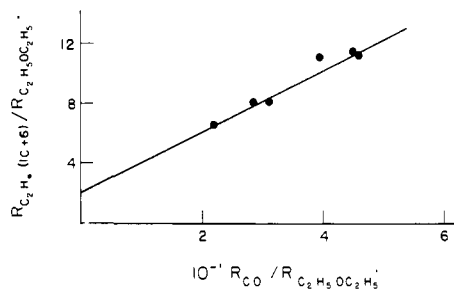


Fig. 2.—Plot of $R_{C_2H_4(1c+6)}/R_{C_2H_5OC_2H_5}$ versus $R_{CO}/R_{C_2H_5OC_2H_5}$ at 29°.

the total amount of ethylene produced the fractions originating from reactions 13 and 3, it is possible to calculate the fraction of ethylene produced by reactions 1c, 6 and 20a. Later results will show that the amount of ethylene produced by reaction 20a is only in the order of about 5% of the total amount of ethylene produced by reactions 1c, 6 and 20a. Neglecting temporarily reaction 20 equation (II) may be derived

$$\frac{R_{C_2H_4(1c+6)}}{R_{C_2H_5OC_2H_5}} = \frac{k_6}{k_4} + \alpha \frac{R_{CO}}{R_{C_2H_5OC_2H_5}} \quad (II)$$

In this equation α indicates the ratio of the rate of C_2H_4 formation by step 1c over the rate of CO produced by step 1a. According to our iodine experiment $\alpha = 0.2$. Equation II is plotted in Fig. 2 for the data obtained at 29° and confirms the value of $\alpha = 0.2$. From the intercept in Fig. 2 we obtain $k_6/k_4 = 2$. It may be mentioned here that, if corrections are made for reaction 20a, α is reduced to 0.18 and k_6/k_4 increases to 2.3. Accepting

therefore $k_6/k_4 = 2.3 \pm 0.3$ and accepting that this value is independent of temperature, as usually is observed for reactions of this type, it is possible to derive the equation

$$\frac{(R_{C_2H_5OH-2.3R_{C_2H_5OC_2H_5}})R_{C_4H_{10}}}{R_{C_2H_5OC_2H_5}^2} = \frac{k_8k_2}{k_4^2} + \frac{k_{16}k_2^{1/2}}{k_4} \frac{R_{C_4H_{10}}^{1/2}[EP]}{R_{C_2H_5OC_2H_5}} \quad (III)$$

The data are plotted in Fig. 3 according to equation III for the temperatures 15 and 29°. From Fig. 3 we obtain $k_{16}k_2^{1/2}/k_4 = 18 \times 10^{-12}$ at 15° and 32×10^{-12} at 20° in $\text{molec.}^{1/2}/(\text{sec.}^{1/2} \text{cc.}^{1/2})$. The intercepts,

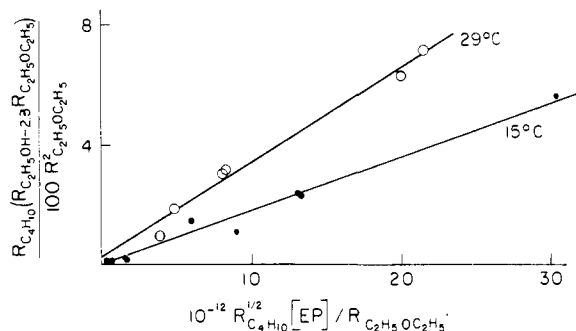


Fig. 3.—Plot of $(R_{C_2H_5OH-2.3R_{C_2H_5OC_2H_5}})R_{C_4H_{10}}/R_{C_2H_5OC_2H_5}^2$ versus $R_{C_4H_{10}}^{1/2}[EP]/R_{C_2H_5OC_2H_5}$ at 15 and 29°.

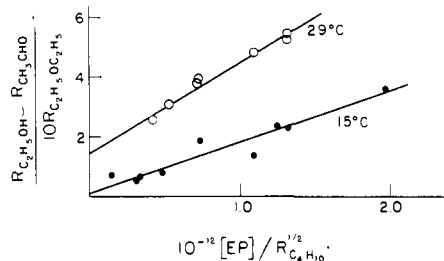


Fig. 4.—Plot of $(R_{C_2H_5OH} - R_{CH_3CHO})/R_{C_2H_5OC_2H_5}$ versus $[EP]/R_{C_4H_{10}}^{1/2}$ at 15 and 29°. The origin for the line at 29° has been displaced upward by one ordinate scale unit.

if present at all, are not large enough to allow us to draw any conclusions regarding k_8k_2/k_4^2 from Fig. 3.

From equation I we obtained $k_8k_2/k_4^2 \leq 2.5$. Considering the extremely small amounts of diethyl ether formed at 63.5°, it is obvious that the amount of alcohol produced *via* reaction 8 will be extremely minute at this temperature. Neglecting therefore reaction 8 as contributing to any appreciable extent in the alcohol production at 63.5° equation III may be simplified to

$$\frac{(R_{C_2H_5OH-2.3R_{C_2H_5OC_2H_5}})R_{C_4H_{10}}^{1/2}}{R_{C_2H_5OC_2H_5}[EP]} = \frac{k_{16}k_2^{1/2}}{k_4}$$

Thus we obtain $\frac{k_{16}k_2^{1/2}}{k_4} = 77 \pm 4 \times 10^{-12} \text{ molec.}^{1/2}/(\text{sec.}^{1/2} \text{cc.}^{1/2})$ at 63.5°. Information regarding $k_{16}k_2^{1/2}/k_4$ may be obtained from the equation

$$\frac{R_{C_2H_5OH} - R_{CH_3CHO}}{R_{C_2H_5OC_2H_5}} = \frac{k_6 - k_5}{k_4} + \frac{k_{16}k_2^{1/2}}{k_4} \frac{[EP]}{R_{C_4H_{10}}^{1/2}} \quad (IV)$$

Equation IV is plotted in Fig. 4 for the temperatures 15 and 29°. We obtain $k_{16}k_2^{1/2}/k_4 = 17 \times 10^{-12}$ at 15 and 31×10^{-12} at 29° in $\text{molec.}^{1/2}/(\text{sec.}^{1/2} \text{cc.}^{1/2})$. These data are in excellent agreement with those obtained from equation III. The intercepts in Fig. 4 are not pronounced enough to allow an accurate estimate of $k_6 - k_5/k_4$. They are, however, of the same order of magnitude as expected from data obtained for k_6/k_4 and k_5/k_4 *via* equations I and II.

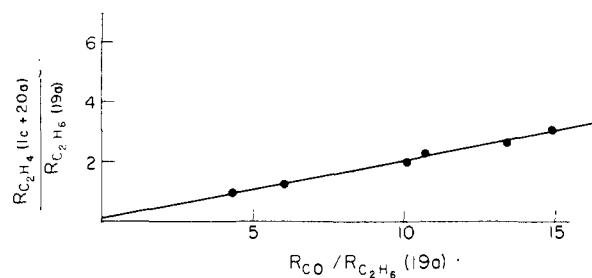


Fig. 5.—Plot of $R_{C_2H_4}(1c + 20a)/R_{C_2H_6}(19a)$ versus $R_{CO}/R_{C_2H_6}(19a)$ at 29° .

Little attention has been given so far to the amounts of ethane and ethylene produced. According to the reaction mechanism $R_{C_2H_6}$ (total) = $R_{C_2H_6}(3) + R_{C_2H_6}(5) + R_{C_2H_6}(11) + R_{C_2H_6}(15) + R_{C_2H_6}(19a)$, where $R_{C_2H_6}(x)$ is the rate of ethane production by reaction x only. $R_{C_2H_6}(3) = 0.12R_{C_2H_5}^{7,8}$, $R_{C_2H_6}(11) = 0.29R_{C_2H_5}^2/R_{C_2H_5O}^{9-11}$. By subtracting from the total amount of ethane produced the fractions originating from reactions 3 and 11, it is possible to calculate the fraction of ethane formed by reactions 5, 15 and 19a. Since $k_{15}/k_2^{1/2}$ previously has been determined over a wide range of temperature,³ it is also possible to calculate $R_{C_2H_6}(15)$. Such calculations indicate that at 29 and 15° , $R_{C_2H_6}(15)$ contributes less than 2% of the amount of ethane produced by reactions 5 and 19a. Reaction 15 may thus be neglected at these temperatures.

In Table II we compare the values calculated for $R_{C_2H_6}(5 + 19a)$ with those obtained for R_{CH_3CHO} . The results discussed earlier indicated that at low temperatures acetaldehyde is almost exclusively produced by reaction 5. It is thus obvious that if reaction 19a occurs $R_{C_2H_6}(5 + 19a) > R_{CH_3CHO}$. This is indeed observed as seen in Table I. It is also interesting to point out that $R_{C_2H_6}(5 + 19a)/R_{CH_3CHO}$ increases from 15 to 29° . This is expected since hydrogen abstraction reactions (producing the $C_5H_9O_2$ radical required for reaction 19a) increase with increasing temperature. Similarly the addition product of ethyl radicals to the $C_5H_9O_2$ radical was observed clearly at 29° , while at 15° this product was too small to be estimated. It also follows from the previous derivations that $R_{C_2H_6}(19a) = R_{C_2H_6}(19a + 5) - R_{CH_3CHO}$.

The amount of ethylene produced during the reaction is given by $R_{C_2H_4}$ (total) = $R_{C_2H_4}(1c) + R_{C_2H_4}(3) + R_{C_2H_4}(6) + R_{C_2H_4}(13) + R_{C_2H_4}(20a)$. $R_{C_2H_4}(3) = 0.12R_{C_2H_5}^{7,8}$; $R_{C_2H_4}(13) = 0.06R_{C_2H_5}^9$. The foregoing discussion has shown that $R_{C_2H_4}(6)$ is in the order of about 2.5 the amount of diethyl ether formed at 29° and is thus very small. Neglecting therefore ethylene production by reaction 6 we may derive the equation

$$\frac{R_{C_2H_4}(1c + 20a)}{R_{C_2H_6}(19a)} = \frac{\alpha R_{CO}}{R_{C_2H_6}(19a)} + \frac{k_{20a}}{k_{19a}} \quad (V)$$

Equation V is plotted in Fig. 5 for the data at 29° . In spite of the rather complex way by which we had to calculate $R_{C_2H_4}(1c + 20a)$ and $R_{C_2H_6}(19a)$ the data agree well with equation V. The value obtained from Fig. 5 for $\alpha = 0.19$ is in good agree-

TABLE II
COMPARISON OF ETHANE PRODUCTION BY REACTIONS 5 AND 19a WITH PRODUCTION OF ACETALDEHYDE

Run no.	$10^{10}R_{C_2H_6}(5 + 19a)$	$10^{10}R_{CH_3CHO}$
Temp. 15°		
31-32	8.6	4.6
38-39	17.4	16.1
Temp. 29°		
1-2	19.9	2.5
3-4	17.7	4.7
5-6	59.7	16.0
8-9	57.8	18.1
10-11	63.2	20.1
13	14.6	4.3

ment with the value obtained from the iodine experiment ($\alpha = 0.2$) and from equation II ($\alpha = 0.2$). The small intercept observed in Fig. 5 indicates that reaction 19a is considerably more important than reaction 20a.

Data obtained for ratios of rate constants are summarized in Table III.

Material Balance.—Since CO and C_2H_5O are both produced by 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 $R_{C_2H_5O} = R_{C_2H_5OH} + R_{CH_3CHO} + R_{C_2H_5OC_2H_5} + R_{CH_3}$, where R_{CH_3} is a measure for the amount of ethoxy radicals decomposed *via* reaction 9. The rate of methyl radical production is given by $R_{CH_3} = R_{CH_3} + R_{C_2H_5} + 2R_{C_2H_6}(11) + R_{C_6H_{12}O_2}$. The rates of methane and propane production are measured directly. As pointed out earlier $R_{C_2H_6}(11)$ may be calculated from the amounts of propane and butane formed. We have not observed the addition product of methyl radicals to the radical R_1 (reaction 18). The fact that the addition product of an ethyl radical to R_1 has been observed leaves however no doubt that such a reaction occurs. For the present material balance calculations, we have neglected the amount of methyl radicals disappearing to form $C_6H_{12}O_2$. $R_{C_6H_{12}O_2}$ is only a fraction of R_{CH_3} , which in its turn is only a small fraction of the total amount of ethoxy radicals produced. Neglecting to account for $R_{C_6H_{12}O_2}$ should therefore not upset the material balance calculations for $R_{CO}/R_{C_2H_5O}$ to any appreciable extent. Calculations carried out for the runs at 29° indicate $R_{CO}/R_{C_2H_5O} = 1.0 \pm 0.1$ as expected from primary step 1a. As an over-all result of the three primary steps the ratio $\frac{R_{CO} + 2R_{CO_2}}{R_{C_2H_6} - \alpha R_{CO}}$ should be equal to unity. $R_{C_2H_6}$ is the rate of ethyl radicals production and is given by $R_{C_2H_6} = R_{C_2H_6}(11) + R_{C_2H_4} + R_{C_2H_6} + 2R_{C_2H_6} + R_{C_2H_5OC_2H_5} + R_{C_3H_7O_2}$. The total amount of ethyl radicals produced should be reduced by αR_{CO} ($= 0.2 R_{CO}$ at 29°) to compensate for the ethylene produced by step 1c. At 29° we obtained $\frac{R_{CO} + 2R_{CO_2}}{R_{C_2H_6} - 0.2R_{CO}} = 0.98 \pm 0.04$ in good agreement with the expected value of unity.

Discussion

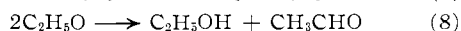
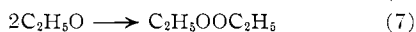
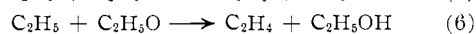
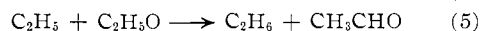
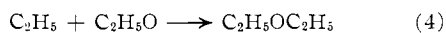
A. Recombination and Disproportionation Reactions.—The recombination and disproportiona-

(11) M. H. J. Wijnen, *J. Chem. Phys.*, **32**, 1631 (1954).

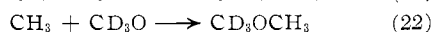
TABLE III

Temp. °C.	RATIO OF RATE CONSTANTS						
	k_5/k_4	k_6/k_4	k_8k_2/k_4^2	$10^{12}k_1k_2^{1/2}/k_4$	k_{20a}/k_{19a}	$10^{19}k_{16}/k_9$	$10^{-5}k_9k_2^{1/2}/k_4$
15	1.3 ± 0.2		<2.5	17.5 ± 1.0			
19	1.3 ± 0.2	2.3 ± 0.3	<2.5	31.0 ± 1.0	~ 0.1	130 ± 20.0	25 ± 4.0
63.5				77 ± 4.0		59 ± 6.0	
114						11.0 ± 3.0	
195						2.1 ± 0.2	

tion reactions involving ethoxy radicals proposed in our reaction mechanism were



From the data discussed in the previous section we obtained $k_5/k_4 = 1.3 \pm 0.2$ and $k_6/k_4 = 2.3 \pm 0.3$. The results thus indicate that disproportionation reactions between ethoxy and ethyl radicals are more important than their recombination reaction. No other data are available in the literature for a direct comparison. These data are however similar to those reported regarding reactions 21 and 22.

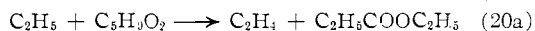
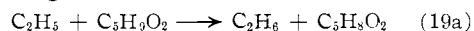


Here a value of $k_{21}/k_{22} = 1.4$ has been reported,¹² also indicating that the disproportionation reaction is more important than the recombination reaction. Data obtained for k_5/k_4 at 15 and 29° are within experimental error identical, indicating an activation energy of zero kcal. for reaction 5. Similarly a zero activation energy for reaction 21 has been reported.¹²

The value obtained for k_6/k_4 is somewhat more doubtful since it was obtained from intercept measurements. There seems to be little doubt however that ethyl alcohol and ethylene are the main products resulting from the reaction of ethyl and ethoxy radicals.

A maximum value of 2.5 was obtained for the ratio k_8k_2/k_4^2 . This value allows us to calculate the maximum amount of ethyl alcohol produced by disproportionation of two ethoxy radicals. Such calculations indicate that under the present conditions alcohol and acetaldehyde formation *via* reaction 8 is very small indeed at temperatures of 29° and higher.

Concerning reactions 19a and 20a



the results indicate that reaction 19a is considerably more important than reaction 20a and as an approximate figure $k_{19}/k_{20} = 10$ may be accepted. Unfortunately we were not able to obtain accurate figures for the amount of $C_7H_{14}O_2$ produced so that it is not possible to relate the disproportionation of ethyl and $C_5H_9O_2$ radicals to their recombination reaction.

B. Abstraction and Thermal Decomposition Reactions.—The hydrogen abstraction reaction from ethyl propionate by ethoxy radicals has been

(12) M. H. J. Wijnen, *J. Chem. Soc.*, **28**, 271 (1958).

related to recombination reactions of ethyl and ethoxy radicals to form diethyl ether and butane by the obtained ratio of rate constants $\frac{k_{16}k_2^{1/2}}{k_4}$.

Data for $\frac{k_{16}k_2^{1/2}}{k_4}$ obtained at 15, 29 and 63.5° are given in Table III. In Fig. 6 we plotted $\log \frac{k_{16}k_2^{1/2}}{k_4}$ against $1/T$. From Fig. 6 we obtain $E_{16} + \frac{1}{2}E_2 - E_4 \simeq 5.5$ kcal. Accepting $E_2 = E_4 = 0$ kcal., the results indicate that the abstraction of a hydrogen atom from ethyl propionate requires an activation energy of about 5.5 kcal. No other direct determinations are available for this activation energy. This value is comparable however to the activation energy of about 5 kcal. for the abstraction of a hydrogen atom from methyl acetate¹² by methoxy radicals and adds further proof that alkoxy radicals are considerably more reactive than the corresponding alkyl radicals.

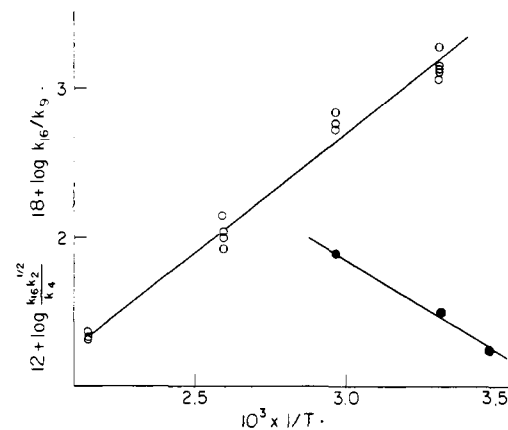


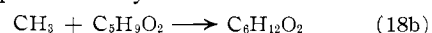
Fig. 6.—Plot of $18 + \log k_{16}/k_9$ and of $12 + \log k_{16}k_2^{1/2}/k_4$ versus $10^3 \times 1/T$.

So far we have not discussed the thermal decomposition reaction of the ethoxy radical into CH_3 and CH_2O . Since we have not analyzed for formaldehyde, information regarding this reaction has to be obtained from the rate of methyl radicals production by reaction 9. Equations (VI) and (VII) may be derived from the reaction mechanism.

$$\frac{R_{CH_3}R_{C_4H_{10}}^{1/2}}{R_{C_2H_5OC_2H_5}} = \frac{k_9k_2^{1/2}}{k_4} \quad (VI)$$

$$\frac{R_{C_2H_5OH(18)}}{R_{CH_3[EP]}} = \frac{k_{16}}{k_5} \quad (VII)$$

In equations VI and VII $R_{CH_3} = R_{CH_4} + 2R_{C_2H_5} + R_{C_3H_8} + R_{C_6H_{12}O_2}$. In analogy to reaction 18a, $C_6H_{12}O_2$ is produced by



Since we did not determine $C_6H_{12}O_2$, we have cal-

culated $R_{C_6H_{12}O_2}$ from the equation

$$R_{C_6H_{12}O_2} = \frac{k_2^{1/2}k_{18b}}{k_{11}^{1/2}k_{18a}} \frac{R_{C_2H_5^{1/2}}(11)}{R_{C_4H_{10}^{1/2}}} R_{C_7H_{14}O_2}$$

assuming $k_2^{1/2}k_{18b}/k_{11}^{1/2}k_{18a} = 1$. Data obtained for $R_{C_6H_{12}O_2}$ by this calculation are admittedly extremely rough. The final result for R_{CH_3} will, however, be considerably more accurate since $R_{C_6H_{12}O_2}$ does not contribute more than 20% of the total value of R_{CH_3} .

Data obtained *via* equation VI indicate $k_9k_2^{1/2}/k_4 = 25 \pm 4 \times 10^5$ molec.^{1/2}/(sec.^{1/2} cc.^{1/2}) at 29°. Data calculated for k_{16}/k_9 are given in Table III. In Fig. 6 $\log k_{16}/k_9$ is plotted against $1/T$. Although the data in this plot show considerable scatter, they leave little doubt that $E_9 - E_{16} = 7.5 \pm 1$ kcal. Accepting, as determined earlier, $E_{16} = 5.5$ kcal., an activation energy of about 13 kcal. is obtained for the thermal decomposition reaction of the ethoxy radical into methyl radicals and formaldehyde.

It is interesting to compare the activation energy of reaction 9 with the value obtained for reaction 23.



Recent data for the activation energy of reaction 23 are $E_{23} = 11 \pm 2$ kcal.,^{13,14} $E_{23} = 9 \pm 2$ kcal.¹⁵ and $E_{23} = 13.2 \pm 2.4$ kcal.¹⁶

Values for the dissociation energy of the C_2H_5O radical into CH_3 and CH_2O and of the *t*-butoxy radical into CH_3 and CH_3COCH_3 have been calculated by Luft¹⁷ as 7.5 and 6.6 kcal., respectively. From these values it might be expected that E_9 and E_{16} would not differ to any appreciable extent. Our value of about 13 kcal. for E_9 is thus in good agreement with data obtained for the activation energy of reaction 23.

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

(13) D. H. Volman and W. M. Glaven, *This Journal*, **75**, 311 (1953).

(14) G. R. McMillan, Am. Chem. Soc. Meeting, Sept. 1959, Atlantic City.

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

(16) F. W. Birss, C. J. Danby and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **238A**, 154 (1957).

(17) N. W. Luft, *Z. Elektrochem.*, **60**, 94 (1956).

[CONTRIBUTION FROM THE CENTRAL RESEARCH LABORATORIES, TOYO RAYON CO., LTD., OTSU, SHIGA-KEN, JAPAN]

CH₂ Rocking Frequencies of Ethylene Glycol and Its Derivatives in Relation to the Configuration of Polyethylene Glycol

By AKIHISA MIYAKE

RECEIVED OCTOBER 29, 1959

Ethylene glycol, its esters and its ethers always show two absorption bands about 20 cm.⁻¹ apart in the range 950–850 cm.⁻¹. These two bands are assigned to the CH₂ rocking vibrations of a *gauche* OCH₂CH₂O group. The CH₂ rocking vibration of a *trans* OCH₂CH₂O group appears in the range 850–800 cm.⁻¹. From these assignments, it has been concluded that the OCH₂CH₂O groups in polyethylene glycol exist in two forms, *trans* and *gauche*.

A complete X-ray analysis of the structure of polyethylene glycol has not yet been reported. The dimensions of the unit cell^{1,2} show that the chain has a crooked configuration. From infrared absorption studies, Davison³ has proposed a helical structure in which OCH₂CH₂O groups exist only in the *gauche* configuration. His conclusion is primarily based on the analogies between the spectra of the polymer and *gauche* 1,2-dichloroethane. The positions of two CH₂ rocking vibrations of polyethylene glycol, 960 (doublet) and 844 cm.⁻¹, were in better agreement with those of the *gauche* dichloroethane than those of the *trans*.

In several esters of ethylene glycol, however, CH₂ rocking frequencies are different from those of dichloroethane. Table I lists the frequencies in some of the esters previously investigated.^{4,5} In these esters, the CH₂ rocking frequency of a *trans* OCH₂CH₂O group has been assigned to bands at about 850 cm.⁻¹. This is supported by the fact that a similar band in polyethylene terephthalate (848 cm.⁻¹) intensifies as the polymer crystallizes. It has been shown by X-ray diffraction studies⁶

that the OCH₂CH₂O group in the crystalline part of this polyester exists in a *trans* configuration. Two bands at about 900 cm.⁻¹ assigned to the *gauche* CH₂ rocking frequencies (A and B), weaken as the band mentioned above intensifies, indicating that these two arise from a different isomeric configuration.⁴

TABLE I^a
CH₂ ROCKING FREQUENCIES IN CM.⁻¹ OF ETHYLENE
GLYCOL ESTERS

Compound	GLYCOL ESTERS				Ref.
	B _g	A	B	A ₁₁	
C ₆ H ₅ COOCH ₂ CH ₂ - OOCCH ₃ (soln.)		900	884	847	4
CH ₃ C ₆ H ₄ COOCH ₂ CH ₂ - OOCCH ₃ H ₄ CH ₃ (cryst.)		899	884	853	4
[OCC ₆ H ₄ COOCH ₂ - CH ₂ O] ₃ (cryst.)		904	891		4
HOCH ₂ CH ₂ OOCCH ₃ H ₄ - COOCH ₂ CH ₂ OH (α -form)	909	897	870	861	5

^a Symmetry species are those for point groups C_{2h} (B_g and A_o; *trans*) and C₂ (A and B; *gauche*).

Thus the assignments given in Table I are believed to be well established. In comparing these frequencies with the known CH₂ rocking frequencies of other 1,2-disubstituted ethanes (Table II), at least two important differences are apparent. The first is that the A₁₁ type vibration occurs near

(6) R. Danbney, C. Bunn and C. Brown, *Proc. Roy. Soc. (London)*, **A226**, 531 (1954).

- (1) E. Sauter, *Z. physik. Chem.*, **B21**, 161 (1933).
- (2) E. R. Walter and F. P. Reding, Abstracts of the 133rd Meeting of the American Chemical Society, San Francisco, April, 1958.
- (3) W. H. T. Davison, *J. Chem. Soc.*, 3270 (1955).
- (4) A. Miyake, *J. Polymer Sci.*, **38**, 479 (1959).
- (5) A. Miyake, *Bull. Chem. Soc. Japan*, **30**, 361 (1957).