325. The Reactions of Alkyl Radicals. Part V.* Ethyl Radicals from Propionaldehyde.

By J. A. KERR and A. F. TROTMAN-DICKENSON.

The photo-initiated chain decomposition of propionaldehyde, alone and when mixed with ethylene, has been studied. The amounts of hydrogen, carbon monoxide, methane, ethylene, ethane, and n-butane produced were determined, and a mechanism was devised which accounted for the bulk of the products. On the assumption that the rate constant for the combination of ethyl radicals is given by $\log k = 14$, the Arrhenius parameters for the following reactions have been found:

$2C_2H_5 \longrightarrow C_2H_4 + C_2H_6$	$\log A$	13.18	E	0
$C_2H_5 + C_2H_5 \cdot CHO \longrightarrow C_2H_6 + C_2H_5 \cdot CO$		11.1		5.9
$C_2H_5 + C_2H_4 \longrightarrow C_4H_9$		12.05		8.6

where k and A are in mole⁻¹ cm.³ sec.⁻¹ and E is in kcal. mole⁻¹. The rate constant for the reaction $C_2H_5 = H + C_2H_4$ is 10^2 sec.⁻¹ at 464° and 0.65 µmole cm.⁻³ concentration of the aldehyde.

EARLIER papers have described the reactions of n-propyl,^{1a} isopropyl,^{1b} and n-butyl^{1c} radicals produced by the photo-initiated chain decomposition of n-butyraldehyde, isobutyraldehyde, and n-valeraldehyde, respectively. This investigation is a natural

* Part IV, preceding paper.

¹ (a) Kerr and Trotman-Dickenson, Trans. Faraday Soc., 1959, **55**, 572; (b) p. 921; (c) J., preceding paper. extension of that series. Steacie² has reviewed the many previous investigations of the photolysis and thermal decomposition of propionaldehyde. In these, reaction was generally followed by measurement of the change of overall pressure with time. An exception is the work of Blacet and Pitts,³ who analysed the products of the photolysis of the pure aldehyde and of its mixtures with iodine. They were mainly concerned with the quantum yields of the various processes in the initial photolytic act and did not seek to derive information on the rates of the reactions of ethyl radicals.

EXPERIMENTAL

The apparatus and procedure were exactly as those previously employed.¹⁶ The propionaldehyde, a commercial sample, was shown to be pure by gas chromatography.

RESULTS AND DISCUSSION

Twenty-three runs were carried out in which the photo-initiated chain decomposition of propionaldehyde was studied between 50° and 505° c. The products were analysed for hydrogen, carbon monoxide, methane, ethylene, ethane, and n-butane. No other hydrocarbons were formed. The analytical results are given in Table 1. The following reaction mechanism serves as a useful framework for the discussion of the findings

- C_2H_5 ·CHO + $h_{\nu} \longrightarrow C_2H_5$ + CHO (a)
 - $\longrightarrow C_2H_6 + CO \dots (b)$
 - \longrightarrow C₂H₄ + H₂CO (c)
 - \longrightarrow CH₃ + CH₂·CHO (d)

$$2C_2H_5 \xrightarrow{k_1} C_4H_{10} \qquad (1)$$

$$2C_2H_5 \xrightarrow{\mathbf{r_1}} C_2H_4 + C_2H_6 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$C_{2}H_{5} + C_{2}H_{5} \cdot CHO \xrightarrow{\kappa_{1}} C_{2}H_{6} + C_{2}H_{5} \cdot CO \qquad (3)$$

$$C_{0}H_{\epsilon} \cdot CO \longrightarrow C_{0}H_{\epsilon} + CO \qquad (3a)$$

$$H + C_2 H_5 \cdot CHO \longrightarrow H_2 + C_2 H_5 \cdot CO \quad \dots \quad \dots \quad \dots \quad (4a)$$

The Primary Process (Reactions a-d).-Blacet and Pitts³ estimated the relative importance of the four primary photolytic processes at 30° for light of different wavelengths. Similar estimates cannot be accurately made from the present results. At 50° the rates of formation of methane (presumably from the reaction of methyl radicals with the aldehyde) and hydrogen (from the decomposition of formyl radicals and subsequent reaction of the atom with the aldehyde) were nearly equal. Each was equal to about $2\frac{1}{2}$ % of the rate of formation of carbon monoxide. Extrapolation from the rates of formation of ethane at higher temperatures indicates that about equal numbers of propionaldehyde molecules decomposed to ethyl radicals (a) and directly to ethane (b). This product distribution is roughly what would be expected for photolysis by light of 2700 Å. Consideration of the absorption curve for the aldehyde, the output of the lamp, and the transmission of quartz shows that this is reasonable. The same mean effective wavelength of the photolytic light was deduced for n-butyraldehyde.^{1a} None of the secondary photolytic processes is sufficiently important to necessitate corrections at higher temperatures.

The Combination of Ethyl Radicals (Reaction 1).-This is the source of the n-butane which is formed according to the equation $R_{C_4H_{10}} = k_1 [C_2H_5]^2$. By

² Steacie, "Atomic and Free Radical Reactions," Reinhold Publ. Corp., New York, 1954, p. 306.
³ Blacet and Pitts, J. Amer. Chem. Soc., 1952, 74, 3382.

study of the photolysis of diethyl ketone by the sector technique, Shepp and Kutschke⁴ found that log k_1 (mole⁻¹ cm.³ sec.⁻¹) = 14.5 - (2000/2.303 RT). The sector technique can be satisfactorily applied only to the cleanest reaction systems. It therefore seems possible that the temperature coefficient reported may not be real, in

TABLE 1.	The	photolysis	of	propionaldehyde.

	Temp.	Time						
No.	(Å)	(sec.)	[Ald]	co	H ₂	CH	C₂H₄	C ₂ H ₆
1	323	2400	2.31	55-8	1.30	1.19	1.77	35.3
$\tilde{2}$	345	1440	2.14	58.9	$1 \cdot 22$	1.55	1.97	33.8
3	364	2160	3.46	87.1	1.49	1.69	2.54	57.4
4	382	1800	2.86	89.5	1.63	1.89	2.52	59.4
5	403	840	1.88	66.5	2.04	2.29	1.68	47.8
ĕ	426	1320	2.45	133	2.54	$\overline{2}\cdot\overline{21}$	a.f.	99.5
7	426	2160	0.66 8	25.0	1.17	$\tilde{1}\cdot\tilde{1}\tilde{0}$	0.525	15.2
8	427	1060	2.67	135	3.80	3.60	2.22	98·1
9	455	1560	1.12	62.6	2.12	2.40	1.09	48.1
10	482	960	0.955	80.8	3.63	3 .11	1.06	59.5
ĩĩ	482	1680	1.29	99.2	3.50	2.25	a.f.	76.7
$\tilde{12}$	522	600	1.80	266	9.90	3.72	1.08	200
13	561	600	0.707	143	5.20	2.78	0.565	102
14	588	600	0.796	177	5.03	3.93	0.436	153
15	588	900	0.774	141	4.53	2.56	a.f.	133
16	602	840	0.665	194	4.80	2.00 3.01	2.69	174
17	631	540	0.000	233	5.70	3.48	1.68	205
18	638	540	0.659	238	6.47	3.22	1.88	231
19	655	480	0.680	300	4.44	3.60	4.71	256
20	679	420	0.626	333	8.08	5.87	6.06	230
$\tilde{21}$	714	270	0.687	488	9.42	6.50	22.8	441
22	751	165	0.636	840	20.8	8.03	58.3	709
23	778	130	0.641	1094	51.4	12.8	116	956
20		100	0.011		01 1	120	110	200
	0.17		A TT A TT (A)	0.77.1		0.77 (0)	a	
No.	C4H10	k_{2}/k_{1}	$C_2H_6-C_2H_4(2)$	$C_4H_{10}^{\frac{1}{2}}$	k_{3}/k_{1}	$\mathbf{C_2H_4}(2)$	$C_2H_4(4)$	k_4/k_1
1	13 ·0	0.136	C ₂ H ₆ -C ₂ H ₄ (2)	C ₄ H ₁₀ ‡	k ₃ /k ₁ ‡	C ₂ H ₄ (2)	C ₂ H ₄ (4)	k ₄ /k ₁
$1 \\ 2$	13·0 13·7	0·136 0·144		_		C ₂ H ₄ (2)	C ₂ H ₄ (4) 	$\frac{k_4/k_1!}{-}$
1 2 3	13·0 13·7 16·0	$0.136 \\ 0.144 \\ 0.159$	<u> </u>	<u> </u>	 3.97	C ₂ H ₄ (2)	C ₂ H ₄ (4) 	k ₄ /k ₁ ‡
1 2 3 4	13·0 13·7 16·0 16·6	0·136 0·144 0·159 0·152	 54·9 56·9	4·00 4·07	 3.97 4.89	C ₂ H ₄ (2)	C ₂ H ₄ (4) 	k ₄ /k ₁ ¹
1 2 3 4 5	13.0 13.7 16.0 16.6 10.8	$0.136 \\ 0.144 \\ 0.159$		4·00 4·07 3·29	 3·97 4·89 7·45	C ₂ H ₄ (2) 	C ₂ H ₄ (4) — — — —	
1 2 3 4 5 6	13.0 13.7 16.0 16.6 10.8 12.85	0·136 0·144 0·159 0·152 0·156	54·9 56·9 46·1 97·6	4·00 4·07 3·29 3·58		C ₂ H ₄ (2) — — — — —	C ₂ H ₄ (4) — — — — —	k ₄ /k ₁ 1
1 2 3 4 5 6 7	13.0 13.7 16.0 16.6 10.8 12.85 3.56	0.136 0.144 0.159 0.152 0.156 0.148	$ \begin{array}{c}$	4.00 4.07 3.29 3.58 1.89	$ \begin{array}{c}$	C ₂ H ₄ (2) — — — — — — — —	C ₂ H ₄ (4) — — — — — — — —	
1 2 3 4 5 6 7 8	13.0 13.7 16.0 16.6 10.8 12.85 3.56 14.9	$\begin{array}{c} 0.136\\ 0.144\\ 0.159\\ 0.152\\ 0.152\\ 0.156\\\\ 0.148\\ 0.149\\ \end{array}$	$ \begin{array}{c}$	4·00 4·07 3·29 3·58 1·89 3·86			C ₂ H ₄ (4) — — — — — — — —	
1 2 3 4 5 6 7 8 9	$13.0 \\ 13.7 \\ 16.0 \\ 16.6 \\ 10.8 \\ 12.85 \\ 3.56 \\ 14.9 \\ 7.10$	$\begin{array}{c} 0.136\\ 0.144\\ 0.159\\ 0.152\\ 0.152\\ 0.156\\ \hline \\ 0.148\\ 0.149\\ 0.154\\ \end{array}$	$\begin{array}{c}$	4.00 4.07 3.29 3.58 1.89 3.86 2.66		C ₂ H ₄ (2) — — — — — — — — — — —	C ₂ H ₄ (4) — — — — — — — — —	
1 2 3 4 5 6 7 8 9 10	$13.0 \\ 13.7 \\ 16.0 \\ 16.6 \\ 10.8 \\ 12.85 \\ 3.56 \\ 14.9 \\ 7.10 \\ 7.08$	$\begin{array}{c} 0.136\\ 0.144\\ 0.159\\ 0.152\\ 0.152\\ 0.156\\\\ 0.148\\ 0.149\\ \end{array}$	$\begin{array}{c} \\ \\ 54 \cdot 9 \\ 56 \cdot 9 \\ 46 \cdot 1 \\ 97 \cdot 6 \\ 14 \cdot 7 \\ 95 \cdot 9 \\ 47 \cdot 0 \\ 58 \cdot 4 \end{array}$	4.00 4.07 3.29 3.58 1.89 3.86 2.66 2.66	3.97 4.89 7.45 11.1 11.6 9.30 15.8 23.0		C ₂ H ₄ (4) — — — — — — — — — — —	
1 2 3 4 5 6 7 8 9 10 11	$13.0 \\ 13.7 \\ 16.0 \\ 16.6 \\ 10.8 \\ 12.85 \\ 3.56 \\ 14.9 \\ 7.10 \\ 7.08 \\ 5.05$	$\begin{array}{c} 0.136\\ 0.144\\ 0.159\\ 0.152\\ 0.156\\\\ 0.148\\ 0.149\\ 0.154\\ 0.150\\\\\\\\\\\\\\\\\\\\ -$	$\begin{array}{c}$	$ \begin{array}{c}$	$\begin{array}{c}$		C2H4(4)	
1 2 3 4 5 6 7 8 9 10 11 12	$13.0 \\ 13.7 \\ 16.0 \\ 10.8 \\ 12.85 \\ 3.56 \\ 14.9 \\ 7.10 \\ 7.08 \\ 5.05 \\ 7.15$	0.136 0.144 0.159 0.152 0.156 	$\begin{array}{c}$	$ \begin{array}{c}$	3.97 4.89 7.45 11.1 11.6 9.30 15.8 23.0 26.1 41.5		C2H4(4) 	
1 2 3 4 5 6 7 8 9 10 11 12 13	$13.0 \\ 13.7 \\ 16.0 \\ 16.6 \\ 10.8 \\ 12.85 \\ 3.56 \\ 14.9 \\ 7.10 \\ 7.08 \\ 5.05 \\ 7.15 \\ 3.77 \\ $	$\begin{array}{c} 0.136\\ 0.144\\ 0.159\\ 0.152\\ 0.156\\ \hline \\ 0.156\\ 0.148\\ 0.149\\ 0.154\\ 0.150\\ \hline \\ 0.151\\ 0.150\\ \end{array}$	$\begin{array}{c}$	4.00 4.07 3.29 3.58 1.89 3.86 2.66 2.66 2.66 2.25 2.67 1.94	3·97 4·89 7·45 11·1 11·6 9·30 15·8 23·0 26·1 41·5 74·0		C2H4(4) 	
1 2 3 4 5 6 7 8 9 10 11 12 13 14	$13.0 \\ 13.7 \\ 16.0 \\ 16.6 \\ 10.8 \\ 12.85 \\ 3.56 \\ 14.9 \\ 7.10 \\ 7.08 \\ 5.05 \\ 7.15 \\ 3.77 \\ 2.82$	0.136 0.144 0.159 0.152 0.156 	$\begin{array}{c}$	4.00 4.07 3.29 3.58 1.89 3.86 2.66 2.66 2.25 2.67 1.94 1.68			C ₂ H ₄ (4) 	
$ \begin{array}{r} 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \\ 7 \\ 8 \\ 9 \\ 10 \\ 11 \\ 12 \\ 13 \\ 14 \\ 15 \\ \end{array} $	$13.0 \\ 13.7 \\ 16.0 \\ 16.6 \\ 10.8 \\ 12.85 \\ 3.56 \\ 14.9 \\ 7.10 \\ 7.08 \\ 5.05 \\ 7.15 \\ 3.77 \\ 2.82 \\ 3.14$	$\begin{array}{c} 0.136\\ 0.144\\ 0.159\\ 0.152\\ 0.156\\ \hline \\ 0.156\\ 0.148\\ 0.149\\ 0.154\\ 0.150\\ \hline \\ 0.151\\ 0.150\\ \end{array}$	$\begin{array}{c}$	4.00 4.07 3.29 3.58 1.89 3.86 2.66 2.25 2.66 2.25 2.67 1.94 1.68 1.77	$\begin{array}{c}\\\\\\ 3\cdot97\\ 4\cdot89\\ 7\cdot45\\ 11\cdot1\\ 11\cdot6\\ 9\cdot30\\ 15\cdot8\\ 23\cdot0\\ 26\cdot1\\ 41\cdot5\\ 74\cdot0\\ 114\\ 96\cdot9 \end{array}$			
$ \begin{array}{r} 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \\ 7 \\ 8 \\ 9 \\ 10 \\ 11 \\ 12 \\ 13 \\ 14 \\ 15 \\ 16 \\ \end{array} $	$13.0 \\ 13.7 \\ 16.0 \\ 16.6 \\ 10.8 \\ 12.85 \\ 3.56 \\ 14.9 \\ 7.10 \\ 7.08 \\ 5.05 \\ 7.15 \\ 3.77 \\ 2.82 \\ 3.14 \\ 5.72$	$\begin{array}{c} 0.136\\ 0.144\\ 0.159\\ 0.152\\ 0.156\\ \hline \\ 0.156\\ 0.148\\ 0.149\\ 0.154\\ 0.150\\ \hline \\ 0.151\\ 0.150\\ \end{array}$	$\begin{array}{c} \\ \\ 54 \cdot 9 \\ 56 \cdot 9 \\ 46 \cdot 1 \\ 97 \cdot 6 \\ 14 \cdot 7 \\ 95 \cdot 9 \\ 47 \cdot 0 \\ 58 \cdot 4 \\ 75 \cdot 9 \\ 199 \\ 101 \\ 153 \\ 133 \\ \end{array}$	4.00 4.07 3.29 3.58 1.89 3.86 2.66 2.25 2.66 2.25 2.67 1.94 1.68 1.77 2.68(X)				
$ \begin{array}{r} 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \\ 7 \\ 8 \\ 9 \\ 10 \\ 11 \\ 12 \\ 13 \\ 14 \\ 15 \\ 16 \\ 17 \\ \end{array} $	$13.0 \\ 13.7 \\ 16.0 \\ 16.6 \\ 10.8 \\ 12.85 \\ 3.56 \\ 14.9 \\ 7.10 \\ 7.08 \\ 5.05 \\ 7.15 \\ 3.77 \\ 2.82 \\ 3.14 \\ 5.72 \\ a.f.$	$\begin{array}{c} 0.136\\ 0.144\\ 0.159\\ 0.152\\ 0.156\\ \hline \\ 0.156\\ 0.148\\ 0.149\\ 0.154\\ 0.150\\ \hline \\ 0.151\\ 0.150\\ \end{array}$	$\begin{array}{c}$	$\begin{array}{c} & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & $				
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18	$13.0 \\ 13.7 \\ 16.0 \\ 16.6 \\ 10.8 \\ 12.85 \\ 3.56 \\ 14.9 \\ 7.10 \\ 7.08 \\ 5.05 \\ 7.15 \\ 3.77 \\ 2.82 \\ 3.14 \\ 5.72 \\ a.f. \\ 2.82$	$\begin{array}{c} 0.136\\ 0.144\\ 0.159\\ 0.152\\ 0.156\\ \hline \\ 0.156\\ 0.148\\ 0.149\\ 0.154\\ 0.150\\ \hline \\ 0.151\\ 0.150\\ \end{array}$	$\begin{array}{c} \\ \\ 54 \cdot 9 \\ 56 \cdot 9 \\ 46 \cdot 1 \\ 97 \cdot 6 \\ 14 \cdot 7 \\ 95 \cdot 9 \\ 47 \cdot 0 \\ 58 \cdot 4 \\ 75 \cdot 9 \\ 199 \\ 101 \\ 153 \\ 133 \\ \end{array}$	$\begin{array}{c}$	$\begin{array}{c}\\\\\\ 3\cdot97\\ 4\cdot89\\ 7\cdot45\\ 11\cdot1\\ 11\cdot6\\ 9\cdot30\\ 15\cdot8\\ 23\cdot0\\ 26\cdot1\\ 41\cdot5\\ 74\cdot0\\ 114\\ 96\cdot9\\ 97\cdot7\\ 126\\ 135\end{array}$			
$ \begin{array}{r} 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \\ 7 \\ 8 \\ 9 \\ 10 \\ 11 \\ 12 \\ 13 \\ 14 \\ 15 \\ 16 \\ 17 \\ 18 \\ 19 \\ \end{array} $	$13.0 \\ 13.7 \\ 16.0 \\ 16.6 \\ 10.8 \\ 12.85 \\ 3.56 \\ 14.9 \\ 7.10 \\ 7.08 \\ 5.05 \\ 7.15 \\ 3.77 \\ 2.82 \\ 3.14 \\ 5.72 \\ a.f. \\ 2.82 \\ 1.77 \\ 1.77$	$\begin{array}{c} 0.136\\ 0.144\\ 0.159\\ 0.152\\ 0.156\\ \hline \\ 0.156\\ 0.148\\ 0.149\\ 0.154\\ 0.150\\ \hline \\ 0.151\\ 0.150\\ \end{array}$	$\begin{array}{c} \\ \\ 54 \cdot 9 \\ 56 \cdot 9 \\ 46 \cdot 1 \\ 97 \cdot 6 \\ 14 \cdot 7 \\ 95 \cdot 9 \\ 47 \cdot 0 \\ 58 \cdot 4 \\ 75 \cdot 9 \\ 199 \\ 101 \\ 153 \\ 133 \\ \end{array}$	4.00 4.07 3.29 3.58 1.89 3.86 2.66 2.25 2.66 2.25 2.67 1.94 1.68 1.77 2.68(X) 2.29(X) 2.60(X) 2.49(X)	$\begin{array}{c}\\\\\\ 3\cdot97\\ 4\cdot89\\ 7\cdot45\\ 11\cdot1\\ 11\cdot6\\ 9\cdot30\\ 15\cdot8\\ 23\cdot0\\ 26\cdot1\\ 41\cdot5\\ 74\cdot0\\ 114\\ 96\cdot9\\ 97\cdot7\\ 126\\ 135\\ 151\\ \end{array}$			
$ \begin{array}{r} 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \\ 7 \\ 8 \\ 9 \\ 10 \\ 11 \\ 12 \\ 13 \\ 14 \\ 15 \\ 16 \\ 17 \\ 18 \\ 19 \\ 20 \\ \end{array} $	$\begin{array}{c} 13 \cdot 0 \\ 13 \cdot 7 \\ 16 \cdot 0 \\ 16 \cdot 6 \\ 10 \cdot 8 \\ 12 \cdot 85 \\ 3 \cdot 56 \\ 14 \cdot 9 \\ 7 \cdot 10 \\ 7 \cdot 08 \\ 5 \cdot 05 \\ 7 \cdot 15 \\ 3 \cdot 71 \\ 5 \cdot 72 \\ 3 \cdot 14 \\ 5 \cdot 72 \\ a \cdot f. \\ 2 \cdot 82 \\ 1 \cdot 77 \\ t \end{array}$	$\begin{array}{c} 0.136\\ 0.144\\ 0.159\\ 0.152\\ 0.156\\ \hline \\ 0.156\\ 0.148\\ 0.149\\ 0.154\\ 0.150\\ \hline \\ 0.151\\ 0.150\\ \end{array}$	$\begin{array}{c} \\ \\ 54 \cdot 9 \\ 56 \cdot 9 \\ 46 \cdot 1 \\ 97 \cdot 6 \\ 14 \cdot 7 \\ 95 \cdot 9 \\ 47 \cdot 0 \\ 58 \cdot 4 \\ 75 \cdot 9 \\ 199 \\ 101 \\ 153 \\ 133 \\ \end{array}$	4.00 4.07 3.29 3.58 1.89 3.86 2.66 2.25 2.66 2.25 2.67 1.94 1.68 1.77 2.68(X) 2.29(X) 2.60(X) 2.49(X) 2.27(X)	$\begin{array}{c}\\\\\\ 3\cdot97\\ 4\cdot89\\ 7\cdot45\\ 11\cdot1\\ 11\cdot6\\ 9\cdot30\\ 15\cdot8\\ 23\cdot0\\ 26\cdot1\\ 41\cdot5\\ 74\cdot0\\ 114\\ 96\cdot9\\ 97\cdot7\\ 126\\ 135\\ 151\\ 186\end{array}$			
$ \begin{array}{r} 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \\ 7 \\ 8 \\ 9 \\ 10 \\ 11 \\ 12 \\ 13 \\ 14 \\ 15 \\ 16 \\ 17 \\ 18 \\ 19 \\ 20 \\ 21 \\ \end{array} $	$13.0 \\ 13.7 \\ 16.0 \\ 16.6 \\ 10.8 \\ 12.85 \\ 3.56 \\ 14.9 \\ 7.10 \\ 7.08 \\ 5.05 \\ 7.15 \\ 3.77 \\ 2.82 \\ 3.14 \\ 5.72 \\ a.f. \\ 2.82 \\ 1.77 \\ t \\ u$	$\begin{array}{c} 0.136\\ 0.144\\ 0.159\\ 0.152\\ 0.156\\ \hline \\ 0.156\\ 0.148\\ 0.149\\ 0.154\\ 0.150\\ \hline \\ 0.151\\ 0.150\\ \end{array}$	$\begin{array}{c} \\ \\ 54 \cdot 9 \\ 56 \cdot 9 \\ 46 \cdot 1 \\ 97 \cdot 6 \\ 14 \cdot 7 \\ 95 \cdot 9 \\ 47 \cdot 0 \\ 58 \cdot 4 \\ 75 \cdot 9 \\ 199 \\ 101 \\ 153 \\ 133 \\ \end{array}$	$\begin{array}{c} \\$	$\begin{array}{c}$			
$ \begin{array}{r} 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \\ 7 \\ 8 \\ 9 \\ 10 \\ 11 \\ 12 \\ 13 \\ 14 \\ 15 \\ 16 \\ 17 \\ 18 \\ 19 \\ 20 \\ 21 \\ 22 \\ \end{array} $	$\begin{array}{c} 13 \cdot 0 \\ 13 \cdot 7 \\ 16 \cdot 0 \\ 16 \cdot 6 \\ 10 \cdot 8 \\ 12 \cdot 85 \\ 3 \cdot 56 \\ 14 \cdot 9 \\ 7 \cdot 10 \\ 7 \cdot 08 \\ 5 \cdot 05 \\ 7 \cdot 15 \\ 5 \cdot 05 \\ 7 \cdot 15 \\ 3 \cdot 77 \\ 2 \cdot 82 \\ 3 \cdot 14 \\ 5 \cdot 72 \\ a \cdot f \\ 2 \cdot 82 \\ 1 \cdot 77 \\ t \\ u \\ u \end{array}$	$\begin{array}{c} 0.136\\ 0.144\\ 0.159\\ 0.152\\ 0.156\\ \hline \\ 0.156\\ 0.148\\ 0.149\\ 0.154\\ 0.150\\ \hline \\ 0.151\\ 0.150\\ \end{array}$	$\begin{array}{c} \\ \\ 54 \cdot 9 \\ 56 \cdot 9 \\ 46 \cdot 1 \\ 97 \cdot 6 \\ 14 \cdot 7 \\ 95 \cdot 9 \\ 47 \cdot 0 \\ 58 \cdot 4 \\ 75 \cdot 9 \\ 199 \\ 101 \\ 153 \\ 133 \\ \end{array}$	$\begin{array}{c}$	$\begin{array}{c}\\\\\\ 3\cdot97\\ 4\cdot89\\ 7\cdot45\\ 11\cdot1\\ 11\cdot6\\ 9\cdot30\\ 15\cdot8\\ 23\cdot0\\ 26\cdot1\\ 41\cdot5\\ 74\cdot0\\ 114\\ 96\cdot9\\ 97\cdot7\\ 126\\ 135\\ 151\\ 186\\ 229\\ 282\\ \end{array}$			
$ \begin{array}{r} 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \\ 7 \\ 8 \\ 9 \\ 10 \\ 11 \\ 12 \\ 13 \\ 14 \\ 15 \\ 16 \\ 17 \\ 18 \\ 19 \\ 20 \\ 21 \\ \end{array} $	$13.0 \\ 13.7 \\ 16.0 \\ 16.6 \\ 10.8 \\ 12.85 \\ 3.56 \\ 14.9 \\ 7.10 \\ 7.08 \\ 5.05 \\ 7.15 \\ 3.77 \\ 2.82 \\ 3.14 \\ 5.72 \\ a.f. \\ 2.82 \\ 1.77 \\ t \\ u$	$\begin{array}{c} 0.136\\ 0.144\\ 0.159\\ 0.152\\ 0.156\\ \hline \\ 0.156\\ 0.148\\ 0.149\\ 0.154\\ 0.150\\ \hline \\ 0.151\\ 0.150\\ \end{array}$	$\begin{array}{c} \\ \\ 54 \cdot 9 \\ 56 \cdot 9 \\ 46 \cdot 1 \\ 97 \cdot 6 \\ 14 \cdot 7 \\ 95 \cdot 9 \\ 47 \cdot 0 \\ 58 \cdot 4 \\ 75 \cdot 9 \\ 199 \\ 101 \\ 153 \\ 133 \\ \end{array}$	$\begin{array}{c} \\$	$\begin{array}{c}$			

Rates of formation of all products are given as 10^{-12} mole cm.⁻³ sec.⁻¹. [Ald] is the mean concentration of the propionaldehyde in 10^{-6} mole cm.⁻³. $k_3/k_1^{\frac{1}{2}}$ is in units of mole⁻¹ cm.⁻³ sec.⁻¹; $k_4/k_1^{\frac{1}{2}}$ in units of 10^6 mole¹ cm.⁻³ sec.⁻¹. (X) indicates a calculated value. a.f. = analytical failure. u = not detectable. t = trace.

spite of the care taken by the investigators. This supposition is supported by the fact that no considerable temperature coefficient has been found for the rate-constant ratios for cross-combinations,¹ which are much easier to measure. Accordingly, in this paper the conventional value log k_1 (mole⁻¹ cm.³ sec.⁻¹) = 14 has been used throughout, in addition to the experimental value which is given in square brackets.

⁴ Shepp and Kutschke, J. Chem. Phys., 1957, 26, 1020.

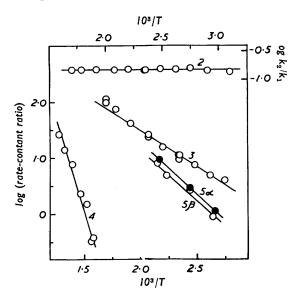
The Disproportionation of Ethyl Radicals (Reaction 2).-Twelve runs that provide direct information on k_2 were carried out between 50° and 215° with mean aldehyde concentrations between 0.67 and 3.5 mole cm.-3. The number of radicals disproportionating was taken as twice the quantity of ethylene found at the end of the run. Values of log (k_2/k_1) are plotted in the Figure.

As $E_2 - E_1 = 0$ and $A_2 = 0.150A_1$, therefore

 $\log k_2$ (mole⁻¹ cm.³ sec.⁻¹) = 13.18 [13.68 - 2000/2.303RT].

The values of k_2 found are independent of the pressure in the system.

No considerable value of $E_2 - E_1$ has ever been reliably reported. Two of the values of A_2/A_1 that appear most reliable have been obtained by the study of the photolysis of



Arrhenius plots for the reaction of ethyl: 2, disproportionation, k2/k1; 3, hydrogen abstraction, $(k_3/k_1^{\frac{1}{2}})$ (mole^{- $\frac{1}{2}} cm.^{<math>\frac{3}{2}}$ </sup> sec.^{- $\frac{1}{2}$});</sup> 4, decomposition to ethylene, $10^{6}(k_{4}/k_{1}^{\frac{1}{2}})$ (mole $\frac{1}{2}$ cm. $-\frac{3}{2}$ sec. $-\frac{1}{2}$); 5, addition to ethylene, $(k_5/k_1^{\frac{1}{2}})$ (mole^{- $\frac{1}{2}$} cm.^{$\frac{3}{2}}$ </sup> sec.^{- $\frac{1}{2}$}), 5 α , aldehyde : ethylene = 1 : 1, 5β , hyde : ethylene = 1 : 2. alde-

diethyl ketone (0.14) ⁵ and of the mercury-photosensitised addition of hydrogen atoms to ethylene (0.15).⁶ They are in excellent agreement with the present result. All three methods are likely to err in the overestimation of A_2/A_1 if at all. The value of 0.12 found by Brinton and Steacie ⁷ may be more accurate, but the difference is little greater than the probable experimental errors. Much higher values of A_2/A_1 have been reported for radicals that probably contained abnormal amounts of energy. The radicals studied here were, especially at higher temperatures, largely formed by the thermal decomposition of propionyl and will have been in thermal equilibrium with their surroundings.

The Abstraction of Hydrogen Atoms from Propionaldehyde (Reaction 3).—The increasing amounts of ethane found at higher temperatures can be ascribed to the abstraction of an aldehydic hydrogen by the ethyl radical. Allowance must be made for the formation of ethane by disproportionation in estimating the extent of this reaction. Hence

$$\begin{aligned} R_{\mathrm{C_{sH_{s}}}} & (\mathrm{reaction} \ 3) = R_{\mathrm{C_{sH_{s}}}} - R_{\mathrm{C_{sH_{s}}}} (\mathrm{reaction} \ 2) \\ k_{3}/k_{1}^{\frac{1}{2}} &= [R_{\mathrm{C_{sH_{s}}}} - R_{\mathrm{C_{rH_{s}}}}(\mathrm{reaction} \ 2)]/R_{\mathrm{C_{sH_{s}}}}^{\frac{1}{2}}[\mathrm{C_{2}H_{5}} \cdot \mathrm{CHO}]. \end{aligned}$$

and

Since R_{C,H_4} (reaction 2) = R_{C,H_4} (reaction 2), and below 315° ethylene is only formed by disproportionation, this ratio can readily be evaluated. It is independent of the mean

- ⁵ James and Steacie, Proc. Roy. Soc., 1958, A, 244, 289.
- ⁶ Smith, Beatty, Pinder, and Le Roy, Canad. J. Chem., 1955, **33**, 821. ⁷ Brinton and Steacie, Canad. J. Chem., 1955, **33**, 1840.

The scales in the top right-hand corner refer to curve 2.

concentration of aldehyde between 0.67 and 2.7 μ mole cm.⁻³ at 150°; over the whole temperature range the mean concentration was varied between 0.67 and $3.5 \ \mu$ mole cm.⁻³. The Arrhenius plot for $k_3/k_1^{\frac{1}{2}}$ between 91° and 315° is shown in the Figure. Hence, we have

log k_3 (mole⁻¹ cm.³ sec.⁻¹) = 11·1 - (5900/2·303RT) or [11·35 - 6900/2·303RT]

 $k_3/k_1^{\frac{1}{2}}$ has not been reliably determined previously. Blacet and Pitts³ suggested that the temperature coefficient for the rate of formation of carbon monoxide in the hightemperature photolysis of propional dehyde was equal to $E_3 - \frac{1}{2}E_1$. Hence they found $E_3 - \frac{1}{2}E_1 = 8.1$ kcal. mole⁻¹. If it is assumed that the light intensity they used was constant in the runs at 3130 Å (their Table III) and that the pressure of aldehyde was also constant, a value of $E_3 - \frac{1}{2}E_1 = 6.3$ kcal. mole⁻¹ can be deduced by the treatment outlined here. Dodd ⁸ concluded that the effect of temperature on the overall rate of photodecomposition of propionaldehyde could not be represented by the Arrhenius equation. On the other hand, Niclause⁹ suggested that the correct interpretation of Dodd's work indicated that $E_3 - \frac{1}{2}E_1 = 10$ kcal. mole⁻¹.

The Decomposition of Ethyl Radicals to Ethylene (Reaction 4).—Above 350° the rate of formation of ethylene began to rise sharply. This increase can be attributed to the decomposition of ethyl radicals, so we can write

$$k_4/k_1^{\frac{1}{2}} = [R_{C_2H_4} - R_{C_2H_4} \text{ (reaction 2)}]/R_{C_4H_{10}}^{\frac{1}{2}}$$

At these temperatures the runs were very short and the amounts of *n*-butane formed were usually too small to measure. Its rate of formation was therefore calculated from the rate of formation of ethane and the known values of $k_3/k_1^{\frac{1}{2}}$. $R_{C_4H_4}$ (reaction 2) could then be obtained from $R_{C_{iH_{10}}}$; in practice it could be neglected. It seemed probable that k_4 would depend upon the pressure in the system; therefore the mean concentration of aldehyde was held constant at 0.67 μ mole cm.⁻³. The Arrhenius plot of k_4/k_1^4 for the runs between 360° and 505° is shown in the Figure. Hence

log
$$k_4$$
 (sec.⁻¹) - 11·2 - 31,000/2·303RT or [11·45 - 32,000/2·303RT].

In principle $k_4/k_1^{\frac{1}{2}}$ could be derived from the rate of formation of hydrogen by reaction (4a). However, the determination of small quantities of hydrogen in 20 to 50 times the amount of carbon monoxide is not easy and it is doubtful if the analyses were reliable.

The activation energy found for the decomposition is certainly too low; it should be greater than the endothermicity of the reaction, which is 39 kcal. mole⁻¹ if $D(C_{2}H_{5}-H)$ is 98 kcal. mole⁻¹. The error is probably at least partially caused by the overestimation of the amounts of n-butane formed at high temperature and hence of the concentation of ethyl radicals. Such an overestimation would occur if an additional source of ethane were important at high temperatures. The attack of ethyl radicals on the alkyl group in propionaldehyde would produce ethane. At low temperatures this reaction is unlikely to be important compared with reaction (3), because of its presumably greater activation energy which is probably at least as great as that for attack of ethyl radicals on diethyl ketone; 10 furthermore, the A factor will be comparatively low. The higher energy of activation would decrease in significance as the temperature is raised. This complication should have little effect on the value obtained for the rate constant at, say, 400° . The present work yields log k_4 (sec.⁻¹) = 1.2. Bywater and Steacie,¹¹ who produced ethyl by the mercury-photosensitised decomposition of ethane, found that $\log \hat{k}_4$ (sec.⁻¹) = $1\cdot 1$

⁸ Dodd, J., 1952, 878.

<sup>Niclause, Thesis, Nancy, 1953.
¹⁰ Kutschke, Wijnen, and Steacie, J. Amer. Chem. Soc., 1952, 74, 714.
¹¹ Bywater and Steacie, J. Chem. Phys., 1951, 19, 326.</sup>

at 400°.¹² This agreement is far better than could reasonably have been expected and depends largely on the temperature chosen for the comparison. Nevertheless, it encourages the belief that the assumptions underlying both determinations are correct.

The Addition of Ethyl Radicals to Ethylene (Reaction 5).-When ethylene is added to the propional dehyde, reaction (5) takes place

This is followed by

$$C_4H_9 + C_2H_5 \cdot CHO \longrightarrow C_4H_{10} + C_2H_5 \cdot CO \qquad (5a)$$

and also by

$$C_2H_5 + C_4H_9 \longrightarrow C_6H_{14} \qquad (5b)$$

and

$$C_4H_9 + C_2H_4 \longrightarrow C_6H_{13} \qquad (5c)$$

The hexyl radicals may form hexane by hydrogen abstraction or add a further ethylene to give an octyl radical. This system is not as simple as that for the addition of propyl radicals to ethylene because the critical products can be formed by different routes. Hence the interpretation of the analytical determinations of ethane, n-butane, and n-hexane is not as certain as is desirable. The results were treated as follows: from $R_{C_{2}H_{4}}$ the concentration of ethyl radicals and $R_{C_{4}H_{10}}$ (reaction 1) are found from the known values of $k_3/k_1^{\frac{1}{2}}$. Then

$$R_{C_{4}H_{10}}$$
 (reaction 5a) = $R_{C_{4}H_{10}} - R_{C_{4}H_{10}}$ (reaction 3).

Each hexane molecule, whether it is formed by reaction (5b) or reaction (5c), corresponds to the addition of an ethyl radical to ethylene. Hence,

the rate of addition of ethyl radicals to ethylene = $R_{C_{eH_{10}}}$ (reaction 5a) + $R_{C_{eH_{10}}}$.

This expression may not be complete because some of the original butyl radicals may finish up as octanes or higher hydrocarbons. An indication of the importance of such additional reactions can be obtained by apportioning the hexane between reactions (5b) and (5c). This can be done if it is assumed that n-butyl radicals react with propionaldehyde at the same rate as they react with n-valeraldehyde.^{1e} This assumption is supported by the observation that methyl radicals react with the two aldehydes at identical rates.¹³ Hence from the rate of formation of n-butane by reaction (5a), the steady-state concentration of n-butyl and the rate of formation of n-octane can be found. $R_{C_{4}\Pi_{14}}$ (reaction 5b) is then the geometric mean of the rates of formation by combination of n-butane and n-octane.¹⁴ In all cases $R_{C_{n}H_{1}}$ (comb.) is small and can hereinafter be neglected. Two series of runs were carried out. In the first series, α , the ratio of aldehyde concentration to ethylene concentration was 1 : 1 and $R_{C_{t}H_{14}}$ (reaction 5b) was within experimental error equal to $R_{C_{t}H_{14}}$. When the ratio was 1 : 2, series β , $R_{C_{6}H_{14}}$ (reaction 5b) was considerably lower than $R_{C_{6}H_{14}}$. Under these conditions it is probable that considerable amounts of octane were formed from n-hexyl. In the first instance the expression

$$k_5/k_1^{\frac{1}{2}} = \{R_{C_4H_{10}} \text{ (reaction } 5a) + R_{C_4H_{14}}\}/R_{C_4H_{10}}^{\frac{1}{2}} \text{ (reaction 1)} \cdot [C_2H_4]$$

will be adequate; in the second the expression will lead to a low value of k_5 . Values of $k_5/k_1^{\frac{1}{2}}$ obtained in both series of experiments are plotted in the Figure. The ratio of aldehyde to ethylene radicals has little effect on the activation energy but clearly affects

¹² Trotman-Dickenson, "Gas Kinetics," Butterworths, London, 1955, p. 303.
¹³ Birrell and Trotman-Dickenson, unpublished results.

¹⁴ Kerr and Trotman-Dickenson, Chem. and Ind., 1959, 125.

the apparent rate constant. Two additional runs with higher concentrations of ethylene yielded still lower values of $k_5/k_1^{\frac{1}{2}}$. The line 5α (Figure) corresponds to

log k_5 (mole⁻¹cm.³ sec.⁻¹) = $12 \cdot 1 - (8600/2 \cdot 303RT)$ or $[12 \cdot 35 - (9600/2 \cdot 303RT)]$.

The rate of reaction (5) has previously been measured by Pinder and Le Roy.¹⁵ The activation energy and A factor they record seem very low. On the other hand, their value (0.11) of log $(k_5/k_1^{\frac{1}{2}})$ (mole^{$-\frac{1}{2}$} cm.³ sec.^{$-\frac{1}{2}$}) at 111° is in excellent agreement with the value of 0.17 found in this work. The Arrhenius parameters found for the unsubstituted double bond are close to those that might have been predicted from the work of James and Steacie,¹⁶ as is shown by the following Table:

Ethylene	Unsubstituted	Monosubstituted	Disubstituted
$E - E_1$	8.6	6.9	5.7
$\log (A/A_1^{\frac{1}{2}}) (\text{mole}^{-\frac{1}{2}} \text{ cm}^{\frac{3}{2}} \text{ sec}^{-\frac{1}{2}}) \dots$	5.0	4.1	3 .6

It seems likely that E_5 and A_5 have been slightly overestimated in the present work.

The Relative Rates of Abstraction and Addition of Alkyl Radicals.-In Part I,^{1a} the relation between the relative rates of abstraction of hydrogen atoms and addition for methyl and n-propyl radicals was considered. This discussion can now be extended. The rates of addition (k_a) of ethyl, n-propyl, isopropyl, and n-butyl radicals to ethylene have now been measured by us, and the rate of addition of methyl to ethylene has been measured by Brinton.¹⁷ Since the rate of reaction of methyl radicals with the sources of the different radicals does not vary with the structure of the alkyl group,¹³ the rate constant for the reaction of an alkyl radical with its parent aldehyde (k_b) can be regarded as a measure of its activity in transfer reactions. A series of ratios, $k_{\rm a}/k_{\rm b}$, can then be compiled which correspond to the relative activities of the radicals in addition and transfer. This has been done in the Table below for the rate constants at 143°, which is a convenient temperature near the centre of the experimental ranges. These ratios can be compared with those obtained by Smid and Szwarc¹⁸ for the relative rates at which the radicals abstract hydrogen atoms from iso-octane $(k_{\rm b}')$ and add to benzene $(k_{\rm a}')$ at 65° (35° for isopropyl).

Radical	Me	Et	\Pr^n	$\mathbf{Pr^{i}}$	Bun
k _a /k _b	0.45	0.33	0.20	0.63	0.16
k_{a}'/k_{b}'	0.29	$2 \cdot 9$	$2 \cdot 0$	6.0	

The absence of any correlation between the two sets of results is marked. It is unlikely that it can be ascribed solely to the change from the gas phase to solution. The work in solution did not yield absolute rate constants so it cannot be determined whether the ratios vary because of changes in k_a' , k_b' , or both. Probably k_a'/k_b' increases from methyl to isopropyl partly because k_b' decreases. k_b does not vary greatly either because the reactions with the aldehydes are more exothermic than those with iso-octane or because the polar nature of the aldehydes is important. Further measurements of the rate constants of the higher radicals would be very interesting.

The research described in Parts III-V was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society which is gratefully acknowledged.

EDINBURGH UNIVERSITY.

[Received, April 8th, 1959.]

¹⁵ Pinder and Le Roy, Canad. J. Chem., 1957, 35, 588.

¹⁶ James and Steacie, Proc. Roy. Soc., 1958, A, 244, 297.
 ¹⁷ Brinton, J. Chem. Phys., 1958, 29, 781.

¹⁸ Smid and Szwarc, J. Amer. Chem. Soc., 1956, 78, 3322; 1957, 79, 1534; J. Chem. Phys., 1958, 29, 432.