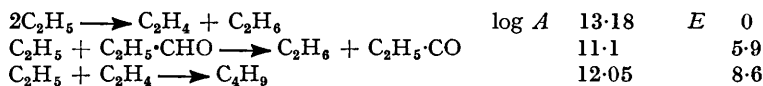


325. *The Reactions of Alkyl Radicals. Part V.\* Ethyl Radicals from Propionaldehyde.*

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:



where  $k$  and  $A$  are in  $\text{mole}^{-1} \text{cm}^3 \text{sec}^{-1}$  and  $E$  is in  $\text{kcal. mole}^{-1}$ . The rate constant for the reaction  $\text{C}_2\text{H}_5 = \text{H} + \text{C}_2\text{H}_4$  is  $10^2 \text{ sec}^{-1}$  at  $464^\circ$  and  $0.65 \mu\text{mole cm}^{-3}$  concentration of the aldehyde.

EARLIER papers have described the reactions of n-propyl,<sup>1a</sup> isopropyl,<sup>1b</sup> and n-butyl<sup>1c</sup> 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.

<sup>1</sup> (a) Kerr and Trotman-Dickenson, *Trans. Faraday Soc.*, 1959, **55**, 572; (b) p. 921; (c) *J.*, preceding paper.



study of the photolysis of diethyl ketone by the sector technique, Shepp and Kutschke<sup>4</sup> found that  $\log k_1$  (mole<sup>-1</sup> cm.<sup>3</sup> sec.<sup>-1</sup>) = 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 I. The photolysis of propionaldehyde.

No.	Temp. (Å)	Time (sec.)	[Ald]	CO	H <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>
1	323	2400	2.31	55.8	1.30	1.19	1.77	35.3
2	345	1440	2.14	58.9	1.22	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
6	426	1320	2.45	133	2.54	2.21	a.f.	99.5
7	426	2160	0.668	25.0	1.17	1.10	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
11	482	1680	1.29	99.2	3.50	2.25	a.f.	76.7
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	3.01	2.69	174
17	631	540	0.711	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	0.656	333	8.08	5.87	6.06	277
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

No.	C <sub>4</sub> H <sub>10</sub>	k <sub>2</sub> /k <sub>1</sub>	C <sub>2</sub> H <sub>6</sub> -C <sub>2</sub> H <sub>4</sub> (2)	C <sub>4</sub> H <sub>10</sub> <sup>‡</sup>	k <sub>3</sub> /k <sub>1</sub> <sup>‡</sup>	C <sub>2</sub> H <sub>4</sub> (2)	C <sub>2</sub> H <sub>4</sub> (4)	k <sub>4</sub> /k <sub>1</sub> <sup>‡</sup>
1	13.0	0.136	—	—	—	—	—	—
2	13.7	0.144	—	—	—	—	—	—
3	16.0	0.159	54.9	4.00	3.97	—	—	—
4	16.6	0.152	56.9	4.07	4.89	—	—	—
5	10.8	0.156	46.1	3.29	7.45	—	—	—
6	12.85	—	97.6	3.58	11.1	—	—	—
7	3.56	0.148	14.7	1.89	11.6	—	—	—
8	14.9	0.149	95.9	3.86	9.30	—	—	—
9	7.10	0.154	47.0	2.66	15.8	—	—	—
10	7.08	0.150	58.4	2.66	23.0	—	—	—
11	5.05	—	75.9	2.25	26.1	—	—	—
12	7.15	0.151	199	2.67	41.5	—	—	—
13	3.77	0.150	101	1.94	74.0	—	—	—
14	2.82	0.155	153	1.68	114	—	—	—
15	3.14	—	133	1.77	96.9	—	—	—
16	5.72	—	—	2.68(X)	97.7	1.08	1.61	0.600?
17	a.f.	—	—	2.29(X)	126	0.786	0.89	0.380
18	2.82	—	—	2.60(X)	135	1.02	0.86	0.331
19	1.77	—	—	2.49(X)	151	0.932	3.78	1.52
20	t	—	—	2.27(X)	186	0.773	5.29	2.33
21	u	—	—	2.80(X)	229	1.18	21.6	7.72
22	u	—	—	3.95(X)	282	2.34	56.0	14.2
23	u	—	—	4.30(X)	347	2.78	113	26.4

Rates of formation of all products are given as 10<sup>-12</sup> mole cm.<sup>-3</sup> sec.<sup>-1</sup>.

[Ald] is the mean concentration of the propionaldehyde in 10<sup>-6</sup> mole cm.<sup>-3</sup>.

k<sub>3</sub>/k<sub>1</sub><sup>‡</sup> is in units of mole<sup>-1</sup> cm.<sup>3</sup> sec.<sup>-1</sup>; k<sub>4</sub>/k<sub>1</sub><sup>‡</sup> in units of 10<sup>6</sup> mole<sup>1</sup> cm.<sup>-3</sup> sec.<sup>-1</sup>.

(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,<sup>1</sup> which are much easier to measure. Accordingly, in this paper the conventional value  $\log k_1$  (mole<sup>-1</sup> cm.<sup>3</sup> sec.<sup>-1</sup>) = 14 has been used throughout, in addition to the experimental value which is given in square brackets.

<sup>4</sup> Shepp and Kutschke, *J. Chem. Phys.*, 1957, **26**, 1020.

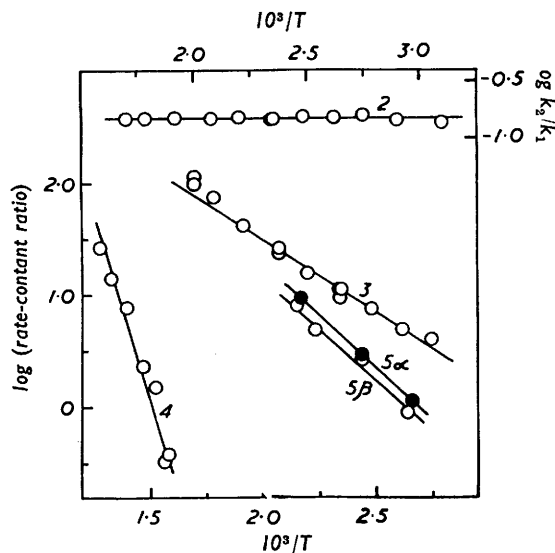
*The Disproportionation of Ethyl Radicals (Reaction 2).*—Twelve runs that provide direct information on  $k_2$  were carried out between 50° and 215° with mean aldehyde concentrations between 0.67 and 3.5 mole cm.<sup>-3</sup>. The number of radicals disproportionating was taken as twice the quantity 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

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

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,  $k_2/k_1$ ; 3, hydrogen abstraction,  $(k_3/k_1)^{1/2}$  (mole<sup>-1/2</sup> cm.<sup>3/2</sup> sec.<sup>-1/2</sup>); 4, decomposition to ethylene,  $10^6(k_4/k_1)^{1/2}$  (mole<sup>1/2</sup> cm.<sup>-3/2</sup> sec.<sup>-1/2</sup>); 5, addition to ethylene,  $(k_5/k_1)^{1/2}$  (mole<sup>-1/2</sup> cm.<sup>3/2</sup> sec.<sup>-1/2</sup>), 5 $\alpha$ , aldehyde : ethylene = 1 : 1, 5 $\beta$ , aldehyde : ethylene = 1 : 2.

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

diethyl ketone (0.14)<sup>5</sup> and of the mercury-photosensitised addition of hydrogen atoms to ethylene (0.15).<sup>6</sup> 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<sup>7</sup> 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

$$R_{C_2H_6} \text{ (reaction 3)} = R_{C_2H_6} - R_{C_2H_6} \text{ (reaction 2)}$$

and

$$k_3/k_1^{1/2} = [R_{C_2H_6} - R_{C_2H_6} \text{ (reaction 2)}] / R_{C_2H_5}^{1/2} [C_2H_5 \cdot CHO].$$

Since  $R_{C_2H_5} \text{ (reaction 2)} = R_{C_2H_4} \text{ (reaction 2)}$ , and below 315° ethylene is only formed by disproportionation, this ratio can readily be evaluated. It is independent of the mean

<sup>5</sup> James and Steacie, *Proc. Roy. Soc.*, 1958, **A**, 244, 289.

<sup>6</sup> Smith, Beatty, Pinder, and Le Roy, *Canad. J. Chem.*, 1955, **33**, 821.

<sup>7</sup> Brinton and Steacie, *Canad. J. Chem.*, 1955, **33**, 1840.

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

$$\log k_3 \text{ (mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}\text{)} = 11.1 - (5900/2.303RT) \text{ or } [11.35 - 6900/2.303RT]$$

$k_3/k_1^{\frac{1}{2}}$  has not been reliably determined previously. Blacet and Pitts<sup>3</sup> suggested that the temperature coefficient for the rate of formation of carbon monoxide in the high-temperature photolysis of propionaldehyde was equal to  $E_3 - \frac{1}{2}E_1$ . Hence they found  $E_3 - \frac{1}{2}E_1 = 8.1 \text{ kcal. mole}^{-1}$ . 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  $E_3 - \frac{1}{2}E_1 = 6.3 \text{ kcal. mole}^{-1}$  can be deduced by the treatment outlined here. Dodd<sup>8</sup> concluded that the effect of temperature on the overall rate of photo-decomposition of propionaldehyde could not be represented by the Arrhenius equation. On the other hand, Niclaue<sup>9</sup> suggested that the correct interpretation of Dodd's work indicated that  $E_3 - \frac{1}{2}E_1 = 10 \text{ kcal. mole}^{-1}$ .

*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

$$k_4/k_1^{\frac{1}{2}} = [R_{C_2H_5} - R_{C_2H_5} \text{ (reaction 2)}]/R_{C_2H_5}^{\frac{1}{2}}$$

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  $k_3/k_1^{\frac{1}{2}}$ .  $R_{C_2H_5}$  (reaction 2) could then be obtained from  $R_{C_2H_6}$ ; 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  $\mu\text{mole cm.}^{-3}$ . The Arrhenius plot of  $k_4/k_1^{\frac{1}{2}}$  for the runs between 360° and 505° is shown in the Figure. Hence

$$\log k_4 \text{ (sec.}^{-1}\text{)} = 11.2 - 31,000/2.303RT \text{ or } [11.45 - 32,000/2.303RT].$$

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<sup>-1</sup> if  $D(C_2H_5-H)$  is 98 kcal. mole<sup>-1</sup>. 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 concentration 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;<sup>10</sup> 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  $\log k_4 \text{ (sec.}^{-1}\text{)} = 1.2$ . Bywater and Steacie,<sup>11</sup> who produced ethyl by the mercury-photosensitised decomposition of ethane, found that  $\log k_4 \text{ (sec.}^{-1}\text{)} = 1.1$

<sup>8</sup> Dodd, *J.*, 1952, 878.

<sup>9</sup> Niclaue, Thesis, Nancy, 1953.

<sup>10</sup> Kutschke, Wijnen, and Steacie, *J. Amer. Chem. Soc.*, 1952, **74**, 714.

<sup>11</sup> Bywater and Steacie, *J. Chem. Phys.*, 1951, **19**, 326.



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 5 $\alpha$  (Figure) corresponds to

$$\log k_5 \text{ (mole}^{-1}\text{cm.}^3 \text{ sec.}^{-1}\text{)} = 12.1 - (8600/2.303RT) \text{ or } [12.35 - (9600/2.303RT)].$$

The rate of reaction (5) has previously been measured by Pinder and Le Roy.<sup>15</sup> The activation energy and  $A$  factor they record seem very low. On the other hand, their value (0.11) of  $\log (k_5/k_1^{\frac{1}{2}})(\text{mole}^{-\frac{1}{2}} \text{ cm.}^3 \text{ sec.}^{-\frac{1}{2}})$  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,<sup>16</sup> as is shown by the following Table:

Ethylene	Unsubstituted	Monosubstituted	Disubstituted
$E - E_1$ .....	8.6	6.9	5.7
$\log (A/A_1^{\frac{1}{2}})(\text{mole}^{-\frac{1}{2}} \text{ cm.}^3 \text{ sec.}^{-\frac{1}{2}})$ .....	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,<sup>1a</sup> 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.<sup>17</sup> 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,<sup>13</sup> 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,  $k_a/k_b$ , 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 Szwarc<sup>18</sup> for the relative rates at which the radicals abstract hydrogen atoms from iso-octane ( $k_b'$ ) and add to benzene ( $k_a'$ ) at 65° (35° for isopropyl).

Radical	Me	Et	Pr <sup>n</sup>	Pr <sup>i</sup>	Bu <sup>n</sup>
$k_a/k_b$ .....	0.45	0.33	0.50	0.63	0.16
$k_a'/k_b'$ .....	0.29	2.9	2.0	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.

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EDINBURGH UNIVERSITY.

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<sup>15</sup> Pinder and Le Roy, *Canad. J. Chem.*, 1957, **35**, 588.

<sup>16</sup> James and Steacie, *Proc. Roy. Soc.*, 1958, *A*, **244**, 297.

<sup>17</sup> Brinton, *J. Chem. Phys.*, 1958, **29**, 781.

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