824. *The Reactions of Alkyl Radicals. Part VII.* t-Butyl Radicals from the Photolysis of Pivalaldehyde.*

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The photo-initiated chain decomposition of pivalaldehyde, alone and when mixed with ethylene, has been studied. A mechanism that accounts for the rates of formation of the principal products has been constructed. On the assumption that the rate constant for the combination of t-butyl radicals is given by log k (mole^{-1} cm.^{3} sec.$^{-1}$) = 14·0, the following Arrhenius parameters of the principal rate-determining reactions have been found:

	log A	E
$2C_4H_9 \longrightarrow C_4H_8 + C_4H_{10}$	14·64	0
$C_4H_9 + C_4H_9{\cdot}CHO \longrightarrow C_4H_{10} + C_4H_9CO$	10·5	4·3
$C_4H_9 + C_4H_9{\cdot}CHO \longrightarrow C_4H_{10} + C_4H_8{\cdot}CHO$	11·9	10·0
$C_4H_9 \longrightarrow C_4H_8 + H$	16·3	43·6
$C_4H_9 \longrightarrow C_3H_6 + CH_3$	16·0	46·3
$C_4H_9 + C_2H_4 \longrightarrow C_6H_{13}$	11·2	7·1

where k and A are in units of mole^{-1} cm.^{3} sec.$^{-1}$, or sec.$^{-1}$, and E is in kcal. mole^{-1}. The behaviour of t-butyl is compared with that of other radicals.

Earlier papers in this series described the reactions of ethyl,[1] n-propyl,[2] isopropyl,[3] and n-butyl[4] radicals produced in the photo-initiated chain decompositions of the appropriate aldehydes. This paper describes a parallel study of t-butyl radicals from pivalaldehyde. The photolysis of this aldehyde has not previously been studied in detail nor is much known about t-butyl radicals.

Experimental

The apparatus and procedure were substantially the same as those previously employed[4] except that the cell was illuminated by a 250-watt lamp focused by a quartz lens. The pivalaldehyde was prepared by a modification of the Bouveault method[5] and purified by passage through a wide-bore gas-chromatographic column. Its purity was proved by gas chromatography and by the nature of the photolytic products, which were analysed by low-temperature distillation followed by gas chromatography.

Results and Discussion

Table 1 gives the conditions, products, and rate constants derived from the runs. The results show that all the reactions listed below occur during the photolysis.

$$(CH_3)_3C{\cdot}CHO + h\nu \begin{cases} \longrightarrow (CH_3)_3C + CHO & (a) \\ \longrightarrow (CH_3)_3CH + CO & (b) \\ \longrightarrow CH_3 + C_3H_6 + CHO & (c) \end{cases}$$

$$2C_4H_9 \longrightarrow C_8H_{18} \qquad (1)$$

$$2C_4H_9 \longrightarrow C_4H_{10} + C_4H_8 \qquad (2)$$

$$C_4H_9 + C_4H_9{\cdot}CHO \longrightarrow C_4H_{10} + C_4H_9{\cdot}CO \qquad (3)$$

$$C_4H_9{\cdot}CO \longrightarrow C_4H_9 + CO \qquad (3a)$$

$$C_4H_9 + C_4H_9{\cdot}CHO \longrightarrow C_4H_{10} + C_4H_8{\cdot}CHO \qquad (4)$$

$$C_4H_8{\cdot}CHO \longrightarrow C_4H_8 + HCO \qquad (4a)$$

$$HCO + C_4H_9{\cdot}CHO \longrightarrow H_2CO + C_4H_9{\cdot}CO \qquad (4b)$$

$$HCO \longrightarrow H + CO \qquad (4c)$$

$$H + C_4H_9{\cdot}CHO \longrightarrow H_2 + C_4H_9{\cdot}CO \qquad (4d)$$

$$C_4H_9 \longrightarrow H + C_4H_8 \qquad (5)$$

$$C_4H_9 \longrightarrow CH_3 + C_3H_6 \qquad (6)$$

$$CH_3 + C_4H_9{\cdot}CHO \longrightarrow CH_4 + C_4H_9{\cdot}CO \qquad (6a)$$

$$2CH_3 \longrightarrow C_2H_6 \qquad (6b)$$

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* Part VI, Birrell and Trotman-Dickenson, *J.*, 1960, 2059.

[1] Kerr and Trotman-Dickenson, *J.*, 1960, 1611.

[2] Kerr and Trotman-Dickenson, *Trans. Faraday Soc.*, 1959, **55**, 572.

[3] Kerr and Trotman-Dickenson, *Trans. Faraday Soc.*, 1959, **55**, 921.

[4] Kerr and Trotman-Dickenson, *J.*, 1960, 1602.

[5] Kraus and Calvert, *J. Amer. Chem. Soc.*, 1957, **79**, 5921

TABLE 1. *Photolysis of pivalaldehyde.*

Run no.	Temp. (°K)	Time (sec.)	[R·CHO]	CO	H_2	CH_4	C_4H_8 Total	C_4H_{10}	C_8H_{18}	$\frac{k_2}{k_1}$	$\frac{k_3}{k_1^{\frac{1}{2}}}$
18	300	3000	3·04	59·6	0·47	0·70	22·0	51·8	3·47	6·34	5·3
17	330	3600	2·37	53·3	1·24	0·77	14·8	49·8	3·28	4·53	8·2
10	366	3600	2·55	52·7	1·06	0·83	10·8	47·1	2·58	4·27	8·9
20	402	8700	0·47	14·3	0·37	0·22	2·02	10·6	0·50	4·06	25·8
24	402	4200	1·56	59·4	1·83	1·14	9·6	48·7	2·50	3·84	15·8
16	405	4200	1·57	53·8	2·02	1·09	8·91	43·5	2·16	4·13	15·0
9	408	3060	2·18	67·0	2·10	1·83	10·5	53·9	2·26	4·64	16·4
19	413	3600	0·41	14·8	0·39	0·63	2·42	11·2	0·61	4·06	27·4
13	439	2400	2·11	88·3	3·37	1·22	14·6	72·4	3·23	4·53	15·3
8	448	3000	1·50	45·2	1·50	1·04	6·40	51·6	1·44	4·43	25·6
23	456	2460	1·43	79·2	2·39	1·61	12·9	68·8	2·99	4·31	22·6
11	481	1860	1·33	105·7	6·56	1·61	14·9	60·7	3·45	4·32	18·5
28	485	1800	1·48	121	5·18	2·67	16·4	100	3·78	4·35	29·1
30	503	1800	1·30	159	4·80	2·10	16·4	104	3·84	4·30	34·4
12	515	1200	1·54	173·2	3·67	1·32	24·5	105·4	2·92		30·8
22	523	1200	1·31	78·4	2·26	0·66	14·6	60·8	1·63		32·1
15	546	720	1·36	172·6	8·0	1·20	29·7	126·1	2·23		47·5
25	562	900	1·15	179·0	5·35	2·95	21·7	146·5	3·83		52·8
29	585	900	1·15	186	5·73	4·04	21·6	181	3·52		74·0
26	659	420	1·04	341	13·2	5·4	70·0	258	2·13		123·9
38	666	360	0·91	440	34·6	7·9	110	307	~	~	110(X)
27	696	300	0·99	547	48·3	10·7	173	362	~	~	126(X)
33	698	300	1·01	523	58·6	9·8	201	332	~	~	126(X)
36	708	240	0·88	828	29·2	17·3	272	332	~	—	132(X)
37	732	150	0·93	1510	233	45·2	640	414	~	—	148(X)
35	735	90	0·89	1990	372	61	968	552	~	~	148(X)
31	742	180	0·88	1615	269	65·8	819	424	—	—	155(X)
39	781	60	0·86	7440	1325	663	4030	813	—	—	178(X)
34	797	60	0·77	8080	1543	772	3910	567	~	~	191(X)

Run no.	C_4H_8 (2)	C_4H_8 (tot.) $- C_4H_8$ (2)	$C_8H_{18}^{\frac{1}{2}}$	$\frac{k_4}{k_1^{\frac{1}{2}}}$	$\frac{k_3}{k_1^{\frac{1}{2}}} + \frac{k_4}{k_1^{\frac{1}{2}}}$	C_4H_8 (4*a*)	C_4H_8 (tot.) $- C_4H_8$ (4*a*) $- C_4H_8$ (2)	$\frac{k_5}{k_1^{\frac{1}{2}}}$	C_3H_6	$\frac{k_6}{k_1^{\frac{1}{2}}}$
18	—	—	—	—	—	—	—	—	—	—
17	—	—	—	—	—	—	—	—	—	—
10	—	—	—	—	—	—	—	—	—	—
20	—	—	—	—	—	—	—	—	—	—
24	—	—	—	—	—	—	—	—	—	—
16	—	—	—	—	—	—	—	—	—	—
9	—	—	—	—	—	—	—	—	—	—
19	—	—	—	—	—	—	—	—	—	—
13	—	—	—	—	—	—	—	—	—	—
8	—	—	—	—	—	—	—	—	—	—
23	—	—	—	—	—	—	—	—	—	—
11	—	—	—	—	—	—	—	—	—	—
28	—	—	—	—	—	—	—	—	—	—
30	—	—	—	—	—	—	—	—	—	—
12	12·9	11·6	1·71	4·43	—	—	—	—	—	—
22	7·17	7·43	1·28	4·42	—	—	—	—	—	—
15	9·80	19·9	1·49	9·81	—	—	—	—	—	—
25	—	—	—	—	—	—	—	—	—	—
29	—	—	—	—	—	—	—	—	—	—
26	9·40	60·6	1·46	39·8	—	—	—	—	—	—
38	—	—	2·24(X)	40·7(X)	151	83	18	8·1	—	—
27	—	—	2·02(X)	56·2(X)	182	112	60	29·7	—	—
33	—	—	1·81(X)	57·5(X)	183	105	88	48·7	—	—
36	—	—	1·92(X)	64·6(X)	197	109	155	80·6	—	—
37	—	—	1·94(X)	81·3(X)	229	147	484	249	—	—
35	—	—	2·74(X)	83·2(X)	231	203	755	276	—	—
31	—	—	1·96(X)	91·2(X)	246	158	660	337	434	22·1
39	—	—	3·08(X)	129 (X)	307	342	3675	1192	330	106·9
34	—	—	2·18(X)	148 (X)	339	249	3652	1676	434	198·2

Footnote to Table 1

Rates of formation of all products are given in units of 10^{12} mole cm.$^{-3}$ sec.$^{-1}$.

R·CHO is the mean concentration of the pivalaldehyde in units of 10^6 mole cm.$^{-6}$.

$k_3/k_1^{\frac{1}{2}}$ and $k_4/k_1^{\frac{1}{2}}$ are in units of mole$^{-\frac{1}{2}}$ cm.$^{\frac{3}{2}}$ sec.$^{-\frac{1}{2}}$; $k_5/k_1^{\frac{1}{2}}$ and $k_6/k_1^{\frac{1}{2}}$ are in units of mole$^{-\frac{1}{2}}$ cm.$^{-\frac{3}{2}}$ sec.$^{-\frac{1}{2}}$.

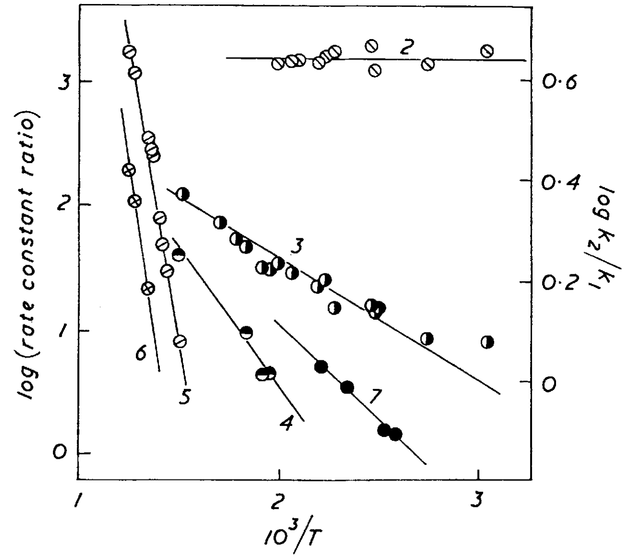
(X) indicates a calculated value.

Deductions may be made about the rate constants of the reactions designated by a simple number.

Some other reactions, such as the attack of hydrogen atoms and methyl radicals on the alkyl group of the aldehyde, must occur but the postulated reactions account so well for the observed products that it can safely be said that the other reactions are of secondary importance.

The Photolytic Act (a), (b) *and* (c).—The primary process in the photolysis of pivalaldehyde has not previously been investigated. The present results indicate that about half the number of molecules that yield carbon monoxide yield isobutane directly (*b*). A small amount of methane is always formed, presumably by reaction (*c*). These findings are in keeping with observations on other aldehydes, for all of which reactions of type (*c*) are responsible for about 2—3% of the decomposition. It appears to be a general rule that the importance of the direct split into a hydrocarbon and carbon monoxide (*b*) increases with increasing substitution on the α-carbon atom. Such branching both in aldehydes and in ketones reduces the formation of small olefinic fragments. Branching produces ketones that split simply into radicals because reactions analogous to (*b*) cannot occur.

Arrhenius plots for the reaction of t-butyl.



(2) Disproportionation k_2/k_1 (the scale at the top right-hand corner refers to this plot); (3) abstraction of aldehydic hydrogen, $k_3/k_1^{\frac{1}{2}}$ (mole$^{-\frac{1}{2}}$ cm.$^{\frac{3}{2}}$, sec.$^{-\frac{1}{2}}$); (4) abstraction from alkyl group, $k_4/k_1^{\frac{1}{2}}$ (mole$^{-\frac{1}{2}}$ cm.$^{\frac{3}{2}}$ sec.$^{-\frac{1}{2}}$); (5) decomposition to isobutene and a hydrogen atom, $10^6k_5/k_1^{\frac{1}{2}}$ (mole$^{\frac{1}{2}}$ cm.$^{-\frac{3}{2}}$ sec.$^{-\frac{1}{2}}$); (6) decomposition to propene and a methyl radical, $10^6k_6/k_1^{\frac{1}{2}}$ (mole$^{\frac{1}{2}}$ cm.$^{-\frac{3}{2}}$ sec.$^{-\frac{1}{2}}$); (7) addition to ethylene, $k_7/k_1^{\frac{1}{2}}$ (mole$^{-\frac{1}{2}}$ cm.$^{\frac{3}{2}}$ sec.$^{-\frac{1}{2}}$).

Combination of t-Butyl Radicals (1).—This reaction is the source of 2,2,3,3-tetramethylbutane in the products, which is formed according to the equation $R_{C_8H_{18}} = k_1[C_4H_9]^2$. No attempt has been made to measure the rate constant by the rotating sector method although the photolysis of di-t-butyl ketone would appear suitable for the application of this technique. For purposes of the description of the experimental results, it has been assumed that log k_1 (mole^{-1} cm.^{3} sec.$^{-1}$) = 14·00.

Disproportionation of t-Butyl Radicals (2).—Ten runs that provide direct information on k_2 were carried out between 27° and 230° with concentrations of aldehyde between 1 and 2 μmole cm.$^{-3}$. Direct comparison of the rates of formation of isobutene and the octane gave the disproportionation : combination ratio $k_2/k_1 = R_{C_4H_8}/R_{C_8H_{18}}$, where

$R_{C_4H_8}$ is the rate of formation of isobutene. The logarithms of this ratio are plotted against the reciprocal temperature in the Figure, whence it can be seen that $E_2 - E_1 = 0$ and $A_2 = 4{\cdot}38A_1$. Therefore log k_2 (mole^{-1} cm.^{3} sec.$^{-1}$) $= 14{\cdot}64$.

The value of $E_2 - E_1 = 0$ is in agreement with previous work on the larger alkyl radicals. The only exception reported is the disproportionation of n-butyl radicals that has a small activation energy.[4]

The value of $A_2/A_1 = 4{\cdot}38$ is in excellent agreement with that of 4·59 obtained by Kraus and Calvert[5] from the investigation of the photolysis of di-t-butyl ketone. Moreover, it is in keeping with the value of the cross combination : disproportionation ratio for methyl and t-butyl radicals found by Kerr and Trotman-Dickenson.[6] Boddy and Robb[7] gave 2·2 as the value of this ratio. Their radicals were produced by the mercury-photosensitised addition of hydrogen atoms to isobutene. This procedure has two disadvantages. The radicals when first formed are very excited vibrationally and may not behave like radicals in thermal equilibrium with their environment. Also, it is very inconvenient to have to follow disproportionations by determination of the saturated products, for these may come from abstraction reactions when a reactive compound such as isobutene is present in high concentration. Accordingly, the low value may be rejected in favour of the value obtained with aldehydes and ketones.

Abstraction of Hydrogen Atoms from Pivalaldehyde (4).—Above 240° the rate of formation of isobutene rose sharply. The temperature is too low for any decomposition of the t-butyl radical. The extra isobutene can be satisfactorily accounted for by reaction (4) followed by (4*a*). Hence,

$$\begin{aligned} C_4H_8 \text{ (reaction } 4a) &= C_4H_8 \text{ (total)} - C_4H_8 \text{ (reaction 2)} \\ &\simeq C_4H_8 \text{ (total)} - 4{\cdot}38C_8H_{18} \end{aligned}$$

where the reactions in parentheses are those by which the products are formed. Therefore,

$$R_{C_4H_{10}} \text{ (reaction 4)} = R_{C_4H_8} \text{ (reaction } 4a) = k_4[C_4H_9][C_4H_9{\cdot}CHO]$$

and

$$k_4/k_1^{\frac{1}{2}} = R_{C_4H_8} \text{ (reaction } 4a)/R_{C_8H_{18}}^{\frac{1}{2}}[C_4H_9{\cdot}CHO]$$

The values of this ratio plotted in the Figure yield log k_4 (mole^{-1} cm.^{3} sec.$^{-1}$) $= 11{\cdot}9 - 10{,}000/2{\cdot}3\boldsymbol{R}T$. Both the A factor and the activation energy are reasonable and are close to the values for the attack of methyl radicals on acetone. A knowledge of k_4 is chiefly important in order that the necessary small corrections may be applied when other rate constants are calculated. The rather large probable error in the determination is not too serious. Reaction (4*b*) must be postulated as a means of removal of formyl radicals in addition to reaction (4*c*) because less hydrogen than isobutene is always formed. Reaction (4*b*) may be exothermic, but too little is known of the strengths of bonds in aldehydes to estimate the amount. Reasonable values of the Arrhenius parameters would correspond to the consumption of more formyl radicals by reaction (4*b*) than by (4*c*).

Abstraction of Hydrogen Atoms from Pivalaldehyde (*Reaction* 3).—According to the mechanism the rate of attack of t-butyl on the carbonyl hydrogen atom in pivalaldehyde can be taken as

$$R_{C_4H_{10}} - R_{C_4H_8} \text{ (reaction } 4a) - R_{C_4H_8} \text{ (reaction 2)}$$

Hence, $k_3/k_1^{\frac{1}{2}} = R\{_{C_4H_{10}} - R_{C_4H_8} \text{ (reaction } 4a) - R_{C_4H_8} \text{ (reaction 2)}\}/R_{C_8H_{18}}^{\frac{1}{2}}[C_4H_9{\cdot}CHO]$. $k_3/k_1^{\frac{1}{2}}$ was determined in nineteen runs between 27° and 386°. Below 240° the production of isobutene by reaction (4*a*) was negligible. The Arrhenius plot is shown in the Figure. The results between 60° and 386° with aldehyde concentrations between 1 and 2 μmole cm.$^{-3}$ yield

$$\log k_3 \text{ (mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}) = 10{\cdot}5 - 4300/2{\cdot}3\boldsymbol{R}T$$

[6] Kerr and Trotman-Dickenson, *J.*, 1960, 1609.

[7] Boddy and Robb, *Proc. Roy. Soc.*, 1959, *A*, **249**, 518.

Runs 19 and 20 at aldehyde concentrations of about 0·4 μmole cm.$^{-3}$ yielded rate constants that were almost a factor of 2 too large. Furthermore, the Arrhenius-plot curves at low temperatures give unduly large rate constants. These findings could be accounted for if considerable amounts of isobutane were formed in the primary process (reaction *b*). The Arrhenius plot could be improved by the introduction of a correction based on this supposition, but the procedure was not adopted because it is too arbitrary until more has been learned of the primary process. Even without a correction the rate constants at the higher temperatures and concentrations should be fairly reliable. E_3 is probably underestimated.

Decomposition of t-Butyl to Isobutene (*Reaction* 5).—Above 390° the rate of formation of isobutene rose sharply. This was attributed to reaction (5) and hence,

$$k_5/k_1^{\frac{1}{2}} = \{R_{\mathrm{C_4H_8}} - R_{\mathrm{C_4H_8}}\ (\text{Reaction } 4a) - R_{\mathrm{C_4H_8}}\ (\text{reaction } 2)\}/R_{\mathrm{C_8H_{18}}}{}^{\frac{1}{2}}$$

The results are plotted in the Figure. The amount of the tetramethylbutane formed at the highest temperatures comprised a very small proportion of the products and had to be calculated from the yield of isobutane and k_1, k_3, and k_4. It was found that

$$\log k_5\ (\text{sec.}^{-1}) = 16{\cdot}3 - 43{,}600/2{\cdot}3\boldsymbol{R}T$$

The activation energy is of the expected size, but the A factor is unusually high. The result is generally in good agreement with that derived [8] from Bywater and Steacie's study [9] of the decomposition of butyl radicals formed by the mercury-photosensitised decomposition of isobutane, which yielded: $\log k_5\ (\text{sec.}^{-1}) = 15{\cdot}7 - 40{,}000/2{\cdot}3\boldsymbol{R}T$. Their method suffered from uncertainty as to the nature of the butyl radicals formed.

Decomposition of t-Butyl to Propene (*Reaction* 6).—Above 470° considerable propene was formed, accompanied by a corresponding increase in methane. This could be explained by the occurrence of reaction (6) whose rate constant could be derived from:

$$k_6/k_1^{\frac{1}{2}} = R_{\mathrm{C_3H_6}}/R_{\mathrm{C_8H_{18}}}{}^{\frac{1}{2}} = R_{\mathrm{CH_4}}/R_{\mathrm{C_8H_{18}}}{}^{\frac{1}{2}}$$

The amount of the tetramethylbutane again had to be estimated. The points plotted in the Figure are derived from $R_{\mathrm{C_3H_6}}$ as it was more reproducible than $R_{\mathrm{CH_4}}$. The expression for k_6 (sec.$^{-1}$), $\log k_6 = 16{\cdot}0 - 46{,}300/2{\cdot}3\boldsymbol{R}T$, is based on only three runs; consequently the values of the parameters are doubtful. Bywater and Steacie's expression [8,9] $\log k_6 = 8{\cdot}5 - 18{,}500/2{\cdot}3\boldsymbol{R}T$ is not to be relied upon as their propene was probably formed by the decomposition of the isobutyl radical.

Addition of t-Butyl to Ethylene (*Reaction* 7).—When ethylene is admitted to the reaction vessel, reaction (7) takes place. This is largely followed by (7*a*) if the concentration of

$$\mathrm{C_4H_9 + C_2H_4 = C_6H_{13}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$\mathrm{C_6H_{13} + C_4H_9{\cdot}CHO = C_6H_{14} + C_4H_9{\cdot}CO} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7a)$$

ethylene is double that of pivalaldehyde, but about 10% of the hexyl radicals add a further molecule of ethylene and subsequently form octane. A correction of 1% must be made to allow for the hexyl radicals that finally form decane. Some hexyl radicals dimerise, combine with t-butyl, and disproportionate. The amounts of the corresponding products were small and were not determined. Hence:

$$k_7/k_1^{\frac{1}{2}} = R_{\text{Hexyl products}}/R_{\mathrm{C_8H_{18}}}{}^{\frac{1}{2}}\,[\mathrm{C_2H_4}]$$

where $R_{\text{Hexyl products}} = 1{\cdot}15R_{\mathrm{C_6H_{14}}}$. The points plotted in the Figure correspond to:

$$\log k_7\ (\text{mole}^{-1}\ \text{cm.}^3\ \text{sec.}^{-1}) = 11{\cdot}2 - 7100/2{\cdot}3\boldsymbol{R}T$$

Effect of Structure on the Reactivity of Alkyl Radicals.—The results that have been reported in this series of papers together with a few obtained by other workers are

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[8] Trotman-Dickenson, " Gas Kinetics," Butterworths, London, 1955, p. 303.

[9] Bywater and Steacie, *J. Chem. Phys.*, 1951, **19**, 172.

summarised in Table 2. The rate constants determined near the centre of the experimental temperature ranges are the most reliable quantities. When two reactions of the same kind have similar rate constants but different Arrhenius parameters it is likely that the parameters are in error.

Disproportionation Reactions.—Several workers have pointed out the regularity of the variations between the rate constants for the disproportionation and combination of propyl and butyl radicals.[4,5] The simple proportionality can be best understood if the assumption is made, as it is here, that all the combination reactions occur at the same rate.

TABLE 2. *Reactions of alkyl radicals.*

Radical, R Reaction	Et [1]	Pr^{n} [2]	Pr^{i} [3]	Bu^{n} [4]	Bu^{s} [a]	Bu^{t}
2R = R$_2$ ...... 100°	14·0, *0* **14·0**	14·0, *0* **14·0**	14·0, *0* **14·0**	14·0, *0* **14·0**	14·0, *0* **14·0**	14·0, *0* **14·0**
2R = Alkane + Alkene ...... 100°	13·2, *0* **13·2**	13·2, *0* **13·2**	13·8, *0* **13·8**	14·6, *1·3* **13·9**	14·3, *0* **14·3**	14·6, *0* **14·6**
R + R·CHO = RH + RCO ...... 182°	11·1, *5·9* **8·3**	11·3, *6·7* **8·1**	11·3, *6·3* **8·3**	10·9, *5·4* **8·3**	10·7, *4·9* **8·3**	10·5, *4·3* **8·4**
CH$_3$ + R·CHO = CH$_4$ + RCO [b]... 182°	12·0, *7·5* **8·2**	11·8, *7·3* **8·3**	12·6, *8·7* **8·4**	12·1, *8·0* **8·2**	13·1, *10·4* **8·2**	13·0, *10·2* **8·2**
R = H + Alkene ...... 400°	14·0, *40* **1·1**	13·6, *35* **2·2**	13·8, *37* **1·8**	— —	— —	16·3, *44* **2·2**
R = CH$_3$ + Alkene ...... 400°	— —	11·7, *25* **3·5**	12·0, *33* **1·0**	12·1, *27* **3·3**	11·7, *24* **3·9**	16·0, *46* **1·0**
R = C$_2$H$_5$ + Alkene...... 400°	— —	— —	— —	11·2, *22* **4·1**	— —	— —
R + C$_2$H$_4$ = Radical ...... 142°	12·1, *8·6* **7·6**	10·9, *6·5* **7·5**	11·4, *6·9* **7·8**	11·1, *7·3* **7·3**	— —	11·2, *7·1* **7·5**

The *A* factors (log, in ordinary type) and the rate constants (log, in bold type) are in sec.$^{-1}$ or mole^{-1} cm.^{3} sec.$^{-1}$. The activation energies (italics) are in kcal. mole^{-1}.

[a] Gruver and Calvert, *J. Amer. Chem. Soc.*, 1956, **78**, 5208. Birrell and Trotman-Dickenson, *J.*, 1960, 2059.

Abstraction Reactions.—If the assumption made about the combinations is correct, then the reactions by which alkyl radicals abstract carbonyl hydrogens from their parent aldehydes all proceed at the same rate. This is unexpected because the C–H bond formed by an ethyl radical is almost 10 kcal. mole^{-1} stronger than that formed by the t-butyl radical and it is generally thought to be more reactive. The decreased reactivity of t-butyl might have been compensated by the greater lability of the hydrogen in pivalaldehyde. The evidence is against this, for methyl radicals have been found to react with all the saturated aliphatic aldehydes at the same rate. Apparently, therefore, there is little difference in the reactivites of the lower alkyl radicals. This finding will only apply when the abstractions are exothermic. It may be that aldehydes are unique and that differences in reactivity would have been found with other classes of compound.

Decomposition of Alkyl Radicals.—The correlation between the observed activation energies for the decompositions and their heats is good as is shown in Table 3 except for those reactions (ΔH values in parentheses) in which the decomposition involves a rearrangement of the radical or activated complex. The agreement is, however, illusory because E should exceed ΔH by the activation energy of the back reaction, which is the addition of an atom or radical to an olefin. The activation energies for such reactions that have been studied quantitatively, as for the addition to ethylene in the present work, lie between 6 and 9 kcal. mole^{-1}. Therefore the measured activation energies must be judged in error by about this amount. The probable error in this estimate is a few kcal. mole^{-1} because it depends upon several quantities such as bond strengths that are not precisely known.

The activation energies of those decompositions that require a rearrangement of the hydrogen atoms are all greater than the values of ΔH for the overall reactions. It is reasonable that some energy should be associated with the rearrangement, so the activation energies of these reactions are also probably too low. The rearrangement may occur during the process of decomposition or before it. If the rearrangement is an earlier and separate process it should be possible to detect the other products of the rearranged radicals.

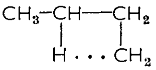
TABLE 3. *Decompositions of alkyl radicals.*

Radical	Et	Pr^n	Pr^i	Bu^n	Bu^s	Bu
Loss of hydrogen						
ΔH	39	37	41	—	—	42
E	40	35	37	—	—	44
Loss of methyl						
ΔH	—	25	(29)	(22)	26	(32)
E	—	25	33	27	24	46
Loss of ethyl						
ΔH	—	—	—	23	—	—
E	—	—	—	22	—	—

ΔH and E are in kcal. mole^{-1}.
ΔH based on $D(\text{Me–H}) = 102{\cdot}5$, D (primary-H) $= 97$, D(secondary-H) $= 93$, D(tertiary-H) $= 90$.[a]
[a] Fettis and Trotman-Dickenson, *J. Amer. Chem. Soc.*, 1959, **81**, 5260, and unpublished results.

This has not yet been done, perhaps because at the low concentrations generally used the radical contains such an excess of energy from the exothermic rearrangement that it decomposes before it is deactivated by collision and before it can react in other ways. On the other hand, no system which is really suitable for testing the mode of decomposition has yet been studied. If rearrangement occurred during decomposition, then the addition of radicals to olefins would be likely to yield rearranged products. n-Butane is not found in decisive quantities when methyl radicals at high concentration are added to ethylene.[10] At the moment the scanty evidence slightly favours rearrangement as a reaction separate from and previous to decomposition.

The rate constants for the decompositions of the radicals show marked regularities. Three of the reactions in which a hydrogen atom splits off have almost identical rate constants. The fourth, the decomposition of ethyl, is almost certainly low because the rate is controlled largely by the rate of transfer of energy to the small molecule. The rates of those decompositions yielding radicals that do not involve rearrangement, *viz.*, n-propyl, s-butyl, and n-butyl to ethylene, are also very similar. On the other hand, the decompositions of s-propyl and t-butyl radicals that involve rearrangement are slow. The decomposition of n-butyl radicals to propene is much faster. It probably involves a different mechanism. s-Propyl and t-butyl radicals can only rearrange by the three-centre transfer of a hydrogen atom between adjacent carbon atoms. n-Butyl can rearrange by a four-centre process, which probably involves much less strain by way of the activated complex shown:



This is the second piece of evidence for the existence of such a complex; it was invoked to explain the nature of the products of the decomposition of $CH_3{\cdot}CD_2{\cdot}CD_2{\cdot}CH_2$.[4]

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[10] Brinton, *J. Chem. Phys.*, 1958, **29**, 781; Garcia Dominguez and Trotman-Dickenson, unpublished results.