980. *The Reactions of Alkyl Radicals. Part VIII.* Isobutyl Radicals from the Photolysis of Isovaleraldehyde.*

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The photo-initiated chain decomposition of isovaleraldehyde has been studied, and a mechanism accounting for the rates of formation of the principal products constructed. On the assumption that the rate constant for the combination of isobutyl radicals is given by log k (mole^{-1} cm.^{3} sec.$^{-1}$) = 14, the following Arrhenius parameters of the principal rate-determining reactions have been found (A in mole^{-1} cm.^{3} sec.$^{-1}$ or sec.$^{-1}$; E in kcal. mole^{-1}):

	log A	E
$2C_4H_9 = C_4H_8 + C_4H_{10}$	13·21	0
$C_4H_9 + C_4H_9{\cdot}CHO = C_4H_{10} + C_4H_9{\cdot}CO$	11·7	6·5
$C_4H_9 + C_4H_9{\cdot}CHO = C_4H_{10} + C_4H_8{\cdot}CHO$	12·7	12·6
$C_4H_9 = CH_3 + C_3H_6$	12·8	26·2
$C_4H_9 = H + C_4H_8$	13·0	30·7

The behaviour of isobutyl is compared with that of other alkyl radicals.

Earlier papers in this series recorded the reactions of ethyl,[4] n-propyl,[1] isopropyl,[2] n-butyl,[3] and t-butyl[5] radicals produced in the photo-initiated chain decomposition of the appropriate aldehydes. This paper records a parallel study of isobutyl radicals from isovaleraldehyde. The photolysis of this aldehyde has not previously been fully studied over a range of temperatures, although the rates of the combination, disproportionation,

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* Part VII, Birrell and Trotman-Dickenson, *J.*, 1960, 4218.

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

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

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

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

[5] Birrell and Trotman-Dickenson, *J.*, 1960, 4218.

and abstraction reactions of isobutyl radicals produced by the photolysis of di-isobutyl ketone have been measured.[6]

Experimental.—The apparatus and procedure were substantially the same as those previously employed,[1] except that a quartz lens was used to focus the light, and in some runs the intensity of illumination was increased by the introduction of a concave cylindrical aluminium reflector behind the lamp. The condensable fraction of the products was analysed on a column (135 × 0·5 cm.) packed with 3% dinonyl phthalate/60—90 mesh activated alumina, which was heated during the analysis and rose from 20° to 140° in 70 min. From run 42 onwards the carbon monoxide was oxidised with iodine pentoxide (145°) in place of copper oxide (260°). Isovaleraldehyde (L. Light and Co.) was shown to be pure by gas chromatography.

RESULTS AND DISCUSSION

Table 1 records the conditions, products, and rate constants derived from the runs, These results show that all the reactions listed below occur during the photolysis. Deductions can be made about the rate constants of the reactions designated by a simple number.

The Photolytic Act, (a), (b), (c), *and* (d).—The primary process in the photolysis of isovaleraldehyde has not been fully investigated though Bamford and Norrish [6] showed that

$$(CH_3)_2CH{\cdot}CH_2{\cdot}CHO + h\nu \begin{cases} \longrightarrow (CH_3)_2CH{\cdot}CH_2 + CHO & (a) \\ \longrightarrow (CH_3)_3CH + CO & (b) \\ \longrightarrow C_3H_6 + CH_3{\cdot}CHO & (c) \\ \longrightarrow C_3H_6 + CH_3 + CHO & (d) \end{cases}$$

$$2C_4H_9 \xrightarrow{k_1} C_8H_{18} \qquad (1)$$

$$2C_4H_9 \xrightarrow{k_2} C_4H_{10} + C_4H_8 \qquad (2)$$

$$C_4H_9 + C_4H_9{\cdot}CHO \xrightarrow{k_3} C_4H_{10} + C_4H_9{\cdot}CO \qquad (3)$$

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

$$C_4H_9 + C_4H_9{\cdot}CHO \xrightarrow{k_4} C_4H_{10} + C_4H_8{\cdot}CHO \qquad (4)$$

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

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

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

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

$$C_4H_9 \xrightarrow{k_5} CH_3 + C_3H_6 \qquad (5)$$

$$CH_3 + C_4H_9{\cdot}CHO \longrightarrow CH_4 + C_4H_9{\cdot}CO \qquad (5a)$$

$$2CH_3 \longrightarrow C_2H_6 \qquad (5b)$$

$$C_4H_9 \xrightarrow{k_6} H + C_4H_8 \qquad (6)$$

both (*a*) and (*b*) occurred. The present work does not give quantitative data about the processes, but the results show that they all occur. At low temperatures the rate of production of isobutane is roughly constant; it is presumably produced by (*b*). The rate of production of propene, when corrected to unit aldehyde concentration and unit light intensity, is roughly constant from 26° to 206°; it is produced by (*c*), or possibly by (*d*). The runs below 70° show that (*c*) or (*d*) accounts for about 60% of the decomposition of the aldehyde. Kraus and Calvert [7] state that this type of primary process will occur in any

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[6] Bamford and Norrish, *J.*, 1935, 1504.

[7] Kraus and Calvert, *J. Amer. Chem. Soc.*, 1957, **79**, 5921; see also ref. 6 and earlier papers in the series by Norrish and his co-workers.

aldehyde or ketone with a straight side-chain of three or more carbon atoms, and also that it will increase in importance as the number of γ-hydrogen atoms increases, because a γ-hydrogen atom is transferred to the α-carbon atom as the bond between the α- and the β-carbon atom breaks. Process (*c*) occurs in the photolyses of n-butyraldehyde,[1] n-valeraldehyde,[3] and 1-methylbutyraldehyde [8] and is most important for isovaleraldehyde which has six γ-hydrogen atoms. Process (*d*) is postulated as well as (*c*) because there is a small constant rate of methane production at low temperatures. It is unlikely that all the methane is a secondary product from, say, the photolysis of acetaldehyde.

Combination of Isobutyl Radicals (1).—This reaction is the source of 2,5-dimethylhexane in the products, which is formed according to the equation $R_{C_8H_{18}} = k_1[C_4H_9]^2$. This rate constant has never been measured; for the purpose of the description of the experimental results, it has been assumed that $k_1 = 10^{14}$ mole^{-1} cm.^{3} sec.$^{-1}$.

Disproportionation of Isobutyl Radicals (2).—Twelve runs that provide direct information on k_2 were carried out between 26° and 124° with concentrations of aldehyde between 1 and 2 $\times$ 10^{-6} mole cm.$^{-3}$. Direct comparison of the rates of formation of isobutene and the octane gave the disproportionation-combination ratio: $k_2/k_1 = R_{C_4H_8}/R_{C_8H_{18}}$. The logarithms of this ratio are plotted against the reciprocal of the absolute temperature in the Figure. The results, calculated by the least-squares method, give $E_2 - E_1 = 0$ and $A_2 = 0{\cdot}165A_1$. Therefore $\log k_2$ (mole^{-1} cm.^{3} sec.$^{-1}$) $= 13{\cdot}21 \pm 0{\cdot}03$.

The value of 0·165 does not agree with that of 0·42 found by Kraus and Calvert [7] from the photolysis of di-isobutyl ketone. Their value is probably too high because isobutene can be produced both by disproportionation and by the decomposition of the radical formed when isobutyl abstracts hydrogen from its parent ketone.

If $k_2/k_1 = 0{\cdot}42$, then their results yield by least squares

$$\log k_7 \text{ (mole}^{-1}\text{ cm.}^3\text{ sec.}^{-1}) = (11{\cdot}40 \pm 0{\cdot}20) - (7560 \pm 360)/2{\cdot}3\boldsymbol{R}T$$

for the abstraction reaction (7). If the value of $k_2/k_1 = 0{\cdot}165$ found in this work is used in

$$C_4H_9 + C_4H_9{\cdot}CO{\cdot}C_4H_9 \xrightarrow{k_7} C_4H_{10} + C_4H_9{\cdot}CO{\cdot}C_4H_8 \quad . \ . \ . \ . \ . \ . \ . \quad (7)$$

the recalculation of Kraus and Calvert's results, then

$$\log k_7 \text{ (mole}^{-1}\text{ cm.}^3\text{ sec.}^{-1}) = (11{\cdot}06 \pm 0{\cdot}09) - (6830 \pm 160)/2{\cdot}3\boldsymbol{R}T$$

Thus the errors are halved by the adoption of the lower value of k_2/k_1. It is impossible to derive an accurate value of k_2/k_1 from Kraus and Calvert's work but their results are compatible with the value obtained here.

Abstraction of Hydrogen Atoms from Isovaleraldehyde (4).—Above 178° the rate of formation of isobutene rose sharply. The temperature is too low for decomposition of the isobutyl radical. The extra isobutene can be accounted for by reaction (4) followed by (4*a*). Hence,

$$\begin{aligned} C_4H_8 \text{ (reaction } 4a) &= C_4H_8 \text{ (total)} - C_4H_8 \text{ (reaction 2)} \\ &= C_4H_8 \text{ (total)} - 0{\cdot}165C_8H_{18} \end{aligned}$$

where the reactions noted 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 between 178° and 307°, plotted in the Figure, and calculated by the least-squares method, yield

$$\log k_4 \text{ (mole}^{-1}\text{ cm.}^3\text{ sec.}^{-1}) = (12{\cdot}62 \pm 0{\cdot}05) - (12{,}700 \pm 200)/2{\cdot}3\boldsymbol{R}T$$

[8] Gruver and Calvert, *J. Amer. Chem. Soc.*, 1956, **78**, 5208.

TABLE 1.

No.	Temp.	Time (sec.)	[Ald.]	CO	H_2	CH_4	C_3H_6	C_4H_{10}	C_4H_8	C_8H_{18}	k_2/k_1	$k_3/k_1^{\frac{1}{2}}$	$k_4/k_1^{\frac{1}{2}}$	$k_5/k_1^{\frac{1}{2}}$	$k_6/k_1^{\frac{1}{2}}$
21R	25·7°	12,000	1·14	18·4	2·69	3·80	12·6	5·18	0·129	0·920	0·140	—	—	—	—
19R	47·0	9600	1·46	21·4	3·30	3·99	29·7	17·1	0·382	2·26	0·169	—	—	—	—
20R	47·8	8400	1·74	30·4	2·39	2·33	37·7	21·9	0·504	2·84	0·178	—	—	—	—
18	66·8	10,800	2·02	21·1	2·30	4·64	27·3	22·8	0·319	2·15	0·149	—	—	—	—
16	86·9	10,800	0·972	10·6	0·829	2·15	11·8	9·89	0·136	0·709	0·192	—	—	—	—
17	90·6	8100	1·22	14·2	0·858	3·22	25·6	18·0	0·195	1·26	0·155	—	—	—	—
15	92·9	11,533	1·25	11·6	1·02	2·93	14·1	16·7	0·200	1·21	0·165	—	—	—	—
4	117·0	9600	1·57	14·8	0·788	4·96	18·5	26·7	0·227	1·77	0·128	12·7	—	—	—
5	117·9	7200	1·77	21·0	0·926	0·918	a.f.	a.f.	0·243	1·43	0·170	—	—	—	—
3	118·2	7041	1·47	20·8	0·963	2·63	22·9	33·7	0·233	1·46	0·159	18·8	—	—	—
1	121·1	10,218	1·48	21·4	1·16	10·7	13·9	20·4	0·227	1·08	0·210	13·1	—	—	—
2	123·9	11,455	1·23	12·6	1·11	17·3	13·2	20·4	0·261	1·57	0·166	13·0	—	—	—
14	141·3	7300	1·57	15·0	0·672	2·89	9·67	26·6	0·225	0·727	—	19·7	—	—	—
13	151·6	4800	1·87	22·8	0·985	2·50	15·6	39·9	0·188	0·777	—	24·1	—	—	—
34	158·5	1800	1·59	41·8	3·11	4·74	29·0	66·2	0·439	1·85	—	30·4	—	—	—
22R	161·2	1200	2·77	110	7·61	25·5	71·8	198	1·16	7·27	—	26·4	—	—	—
23R	165·7	4200	0·675	18·0	2·96	2·96	19·5	26·4	0·323	1·76	—	29·1	—	—	—
33	175·6	1800	1·74	69·6	4·08	4·08	27·0	82·2	0·690	2·07	—	32·7	—	—	—
8	178·4	3664	1·35	31·2	3·22	3·38	12·3	51·6	0·632	0·910	—	39·5	0·374	—	—
7	182·6	3600	1·47	45·6	2·83	1·82	18·8	70·3	0·816	1·412	—	39·8	0·334	—	—
6	184·4	3707	1·27	38·2	2·20	1·92	12·2	57·9	0·731	1·37	—	38·5	0·340	—	—
35	190·1	1500	1·34	58·5	4·04	6·57	20·7	70·0	0·753	1·62	—	40·6	0·285	—	—
37R	191·7	1800	1·06	59·7	5·19	3·64	26·2	83·1	1·16	2·55	—	49·0	0·435	—	—
31	200·1	2400	1·43	93·3	10·3	7·58	30·6	116	1·34	2·12	—	55·2	0·479	—	—
32	205·7	1800	1·73	95·5	9·54	13·9	31·4	150	1·66	1·79	—	64·1	0·647	—	—
12	226·2	2700	1·12	29·6	4·23	8·26	9·10	52·1	0·858	0·377	—	74·8	1·16	—	—
11	230·3	2444	0·938	25·0	2·47	9·47	8·67	49·9	0·855	0·485	—	75·1	1·19	—	—
10	253·9	1201	1·12	93·2	5·13	8·60	24·7	106	2·68	1·22	—	83·1	2·00	—	—
9	258·4	1200	1·21	86·2	5·32	18·7	33·0	135	3·06	0·753	—	126	2·81	—	—
40	278·9	900	1·19	187	11·6	38·5	68·4	261	6·91	2·34 *	—	—	3·61	27·6	—
38	306·1	720	0·957	123	12·4	154	112	224	10·2	1·42 *	—	—	8·74	83·0	—
39	307·5	900	1·17	182	35·7	182	132	291	12·4	1·59 *	—	—	8·24	90·4	—
43	329·0	420	0·954	297	27·2	270	262	291	21·7	1·60 *	—	—	—	196	8·08
42	344·7	480	0·659	294	29·5	292	324	198	21·8	1·18 *	—	—	—	292	11·9
44	373·3	360	0·983	379	62·7	699	681	257	44·6	0·547 *	—	—	—	914	40·8
45	401·4	240	1·03	895	218	920	1153	250	70·4	0·304 *	—	—	—	2085	97·5
46	417·6	120	1·14	858	135	2328	2057	341	138	0·361 *	—	—	—	3418	187

Rates of formation of products are given as 10^{-12} mole cm.$^{-3}$ sec.$^{-1}$. [Ald.] is the mean concentration of aldehyde, in 10^{-6} mole cm.$^{-3}$. $k_3/k_1^{\frac{1}{2}}$ and $k_4/k_1^{\frac{1}{2}}$ are in 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 10^6 mole$^{-\frac{1}{2}}$ cm.$^{-\frac{3}{2}}$ sec.$^{-\frac{1}{2}}$.

* Calculated value. a.f. = analytical failure. R = reflector present.

The runs at 307° were neglected in this calculation because some isobutene may be produced by reaction (6) at this temperature.

Reactions (4*c*) and (4*d*) are postulated because the rate of hydrogen production increased with that of isobutene. Reaction (4*b*) is suggested because it is known to follow the reaction analgous to (4) in the photolyses of n-butyraldehyde,[1] isobutyraldehyde,[2] and pivalaldehyde,[5] but it is less certain in the case of isovaleraldehyde because the rate of hydrogen production was always greater than that of isobutene. It is probable that the hydrogen atom abstracted in reaction (4) is the tertiary atom, because the radical thereby produced can form isobutene directly.

Abstraction of Hydrogen Atoms from Isovaleraldehyde (3).—According to the mechanism, the rate of attack of isobutyl on the carbonyl hydrogen atom in isovaleraldehyde can be taken as

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

Hence $k_3/k_1^{\frac{1}{2}} = R_{C_4H_{10}} - R_{C_4H_8}/R_{C_8H_{18}}^{\frac{1}{2}}[C_4H_9{\cdot}CHO]$.

At the temperatures considered no isobutene was produced by decomposition of isobutyl, so

$$R_{C_4H_8}\ (\text{total}) = R_{C_4H_8}\ (2) + R_{C_4H_8}\ (4a)$$

$k_3/k_1^{\frac{1}{2}}$ was determined in 19 runs between 117° and 230° at aldehyde concentrations between 0·7 and 3·1 × 10^{-6} mole cm.$^{-3}$. The results, plotted in the Figure and calculated by the least squares method, yield

$$\log k_3\ (\text{mole}^{-1}\ \text{cm.}^3\ \text{sec.}^{-1}) = (11{\cdot}71 \pm 0{\cdot}07) - (6500 \pm 100)/2{\cdot}3\boldsymbol{R}T$$

The changes in aldehyde concentration and a change in light intensity produced by the use of the reflector in some runs did not affect the rate constants. A series of five consecutive runs in which log $k_3/k_1^{\frac{1}{2}}$ was uniformly slightly high has been rejected: an impurity was probably present in the aldehyde, because a fresh sample yielded normal rate constants.

Decomposition of Isobutyl to Propene (5).—Above 279° the rate of formation of propene rose sharply. This was attributed to reaction (5) and hence,

$$k_5/k_1^{\frac{1}{2}} = \{R_{C_3H_6}\ (\text{total}) - R_{C_3H_6}\ (\text{initial act})\}/R_{C_8H_{18}}^{\frac{1}{2}}$$

For 25 runs below 206° the rate of propene production, corrected to unit aldehyde concentration and unit light intensity, varied between 11·4 and 34·4 × 10^{12} moles cm.$^{-3}$ sec.$^{-1}$. On average $R_{C_3H_6}$ (initial act)/$[C_4H_9{\cdot}CHO]R_{C_8H_{18}} = 9{\cdot}5$.

This correction was applied in the calculation of k_5. At the lowest temperature at which k_5 was determined the propene from the initial act was 40% of the total, but at the highest temperature it contributed less than 1% to the total propylene.

At these temperatures the runs were short and the amount of octane produced was too small to be measured; it was therefore calculated from $R_{C_4H_{10}}$, k_1, k_3, and k_4. Eight runs between 279° and 417° are plotted in the Figure, and the results, calculated by the least-squares method, give

$$\log k_5\ (\text{sec.}^{-1}) = (12{\cdot}82 \pm 0{\cdot}08) - (26{,}200 \pm 300)/2{\cdot}3\boldsymbol{R}T$$

Similarly, from the mechanism,

$$k_5/k_1^{\frac{1}{2}} = (R_{CH_4} + 2R_{C_2H_6})/R_{C_8H_{18}}^{\frac{1}{2}}$$

Even at the highest temperatures the amount of ethane produced was very small, and was neglected. The results, calculated by least squares from the rate of methane production, give

$$\log k_5\ (\text{sec.}^{-1}) = (12{\cdot}36 \pm 0{\cdot}31) - (24{,}700 \pm 1100)/2{\cdot}3\boldsymbol{R}T$$

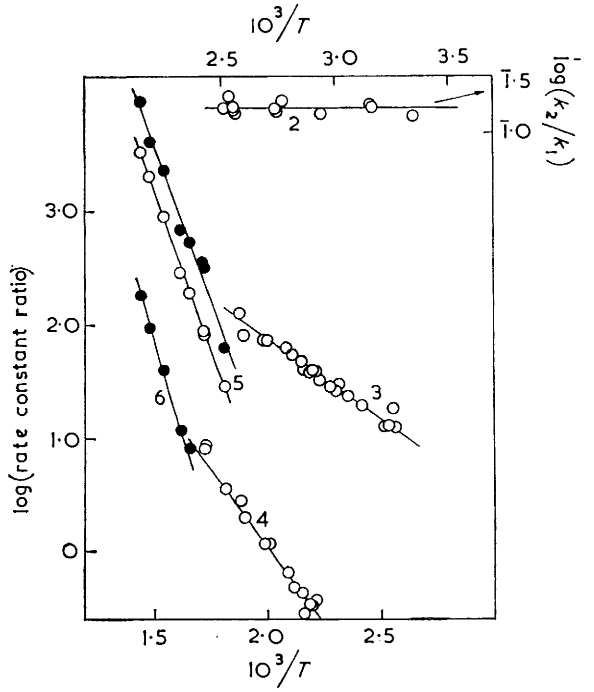
The results calculated on methane show less precision than those calculated on propene, but they almost agree within experimental error.

Decomposition of Isobutyl to Isobutene (6).—Above 329° the rate of formation of isobutene rose sharply and could no longer be accounted for by reactions (4) and (4*a*). This was attributed to reaction (6), and hence

$$k_6/k_1^{\frac{1}{2}} = \{R_{C_4H_8} - R_{C_4H_8}\ (\text{reaction } 4a) - R_{C_4H_8}\ (\text{reaction } 2)\}/R_{C_8H_{18}}{}^{\frac{1}{2}}$$

or $k_6/k_1^{\frac{1}{2}} = R_{H_2}/R_{C_8H_{18}}{}^{\frac{1}{2}}$.

The rate of octane formation was again calculated from $R_{C_4H_{10}}$, k_1, k_3, and k_4. The isobutene from reaction (4*a*) was calculated; that from reaction (2) was negligible. Five runs between 329° and 417° at aldehyde concentrations of about $0{\cdot}9 \times 10^{-6}$ mole cm.$^{-3}$ are shown in the Figure, and yield



Arrhenius plots for the reactions of isobutyl: (2) *disproportionation*, k_2/k_1; (3) *hydrogen abstraction*, $k_3/k_1^{\frac{1}{2}}$ (*mole*$^{-\frac{1}{2}}$ *cm.*$^{-\frac{3}{2}}$ *sec.*$^{-\frac{1}{2}}$); (4) *hydrogen 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 methyl and propylene*, $10^6k_5/k_1^{\frac{1}{2}}$ (*mole*$^{-\frac{1}{2}}$ *cm.*$^{-\frac{3}{2}}$ *sec.*$^{-\frac{1}{2}}$)—*open circles, results based on propene*; *filled circles and line, results based on methane* (*which are displaced upwards by* 0·4 *log unit*); (6) *decomposition to hydrogen and isobutene*, $10^6k_6/k_1^{\frac{1}{2}}$ (*mole*$^{-\frac{1}{2}}$ *cm.*$^{-\frac{3}{2}}$ *sec.*$^{-\frac{1}{2}}$).

$$\log k_6\ (\text{sec.}^{-1}) = 13{\cdot}0 - (30{,}700/2{\cdot}3\boldsymbol{R}T)$$

The rate constants calculated on the rate of production of hydrogen were very scattered but in each case gave higher values than those calculated on the isobutene production. It is believed that the hydrogen analyses were unreliable, because it is difficult to determine small amounts of hydrogen in the presence of large amounts of carbon monoxide and methane.

Comparison of Isobutyl with Other Alkyl Radicals.—The value of $E_2 - E_1 = 0$ for the disproportionation reaction is in agreement with previous work on the alkyl radicals, with the exception of n-butyl,[3] which shows a small activation energy for disproportionation (see Table 2).

The Arrhenius parameters for the abstraction reaction (3) agree fairly well with those of other alkyl radicals; also log k_3 at 182° is similar to the other abstraction-rate constants.

The activation energy for the decomposition to methyl and propene is close to the value for the heat of reaction (25 kcal. mole^{-1}) (see Table 3). This is true for all alkyl radicals that decompose to give methyl and an alkene without rearrangement. However,

TABLE 2. *The reactions of alkyl radicals.*

Radical R Reaction	Et [4]	Pr^{n} [1]	Pr^{i} [2]	Bu^{n} [3]	Bu^{s} [8]	Bu^{i}	Bu^{t} [5]
2R = R_2	14·0, *0*	14·0, *0*	14·0, *0*	14·0, *0*	14·0, *0*	14·0, *0*	14·0, *0*
100°	**14·0**	**14·0**	**14·0**	**14·0**	**14·0**	**14·0**	**14·0**
2R = Alkane + Alkene	13·2, *0*	13·2, *0*	13·8, *0*	14·6, *1·3*	14·3, *0*	13·2, *0*	14·6, *0*
100°	**13·2**	**13·2**	**13·8**	**13·9**	**14·3**	**13·2**	**14·6**
R + R·CHO = RH + R·CO	11·1, *5·9*	11·3, *6·7*	11·3, *6·3*	10·9, *5·4*	10·7, *4·9*	11·7, *6·5*	10·5, *4·3*
182°	**8·3**	**8·3**	**8·3**	**8·3**	**8·3**	**8·6**	**8·4**
CH_3 + R·CHO = CH_4 + R·CO	12·0, *7·5*	11·8, *7·3*	12·6, *8·7*	12·1, *8·0*	13·1, *10·4*	12·3, *8·4*	13·0, *10·2*
182°	**8·2**	**8·3**	**8·4**	**8·2**	**8·2**	**8·2**	**8·2**
R = H + Alkene	14·0, *40* [10]	13·6, *35*	13·8, *37*	—	—	13·0, *31*	16·3, *44*
400°	**1·1**	**2·2**	**1·8**	—	—	**3·0**	**2·2**
R = CH_3 + Alkene	—	11·7, *25*	12·0, *33*	12·1, *27*	11·7, *24*	12·8, *26*	16·0, *46*
400°	—	**3·5**	**1·0**	**3·3**	**3·9**	**4·3**	**1·0**
R = C_2H_5 + Alkene	—	—	—	11·2, *22*	—	—	—
400°	—	—	—	**4·1**	—	—	—
R + C_2H_4 = Radical	12·1, *8·6*	10·9, *6·5*	11·4, *6·9*	11·1, *7·3*	—	—	11·2, *7·1*
142°	**7·6**	**7·5**	**7·8**	**7·3**	—	—	**7·5**

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

TABLE 3. *The decomposition of alkyl radicals.*

	Et [4]	Pr^{n} [1]	Pr^{i} [2]	Bu^{n} [3]	Bu^{s} [8]	Bu^{i}	Bu^{t} [5]
Loss of hydrogen							
ΔH	39	37	41	—	—	35	42
E	40 [9]	35	37	—	—	31	44
Loss of methyl							
ΔH	—	25	(29)	(22)	26	25	(32)
E	—	25	33	27	24	26	46
Loss of ethyl							
ΔH	—	—	—	23	—	—	—
E	—	—	—	22	—	—	—

ΔH and E are in kcal. mole^{-1}.
ΔH based on D(Me–H) = 102·5, D(primary–H) = 97, D(secondary–H) = 93, D(tertiary–H) = 90. The values of ΔH in parentheses indicate that the reaction involves a rearrangement.

E_5 is certainly low because the activation energy for the addition of methyl to propene has been estimated to be 6 kcal. mole^{-1},[9] in line with activation energies found for other addition reactions.

The activation energy for the decomposition to hydrogen and isobutene is again probably low, because in common with those of the other alkyl radicals that decompose to give hydrogen without rearrangement, it is a few kcal. mole^{-1} less than the heat of reaction (see Table 3).

The *A* factors for both decompositions should be 10^{13} sec.$^{-1}$, if the entropies of the radicals and the *A* factors for the addition reactions are assumed to be normal. In both cases the experimental *A* factors are close to this value.

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