890. *The Reactions of Alkyl Radicals. Part XI.* The Absolute Rate of Isopropyl Combination.*

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The absolute combination rate of isopropyl between 81° and 169°, under intermittent illumination, has been determined. The radicals were generated by the photo-initiated chain decomposition of isobutyraldehyde. Addition of isopropyl to ethylene was used to measure the relative radical concentration. The activation energy is zero within experimental error, and the *A* factor is $10^{13\cdot8}$ mole^{-1} cm.^{3} sec.$^{-1}$. A first-order termination correction was applied.

An earlier paper in this series [1] described the reactions of isopropyl produced by photo-initiated chain decomposition of isobutyraldehyde. The experimental rate constants were expressed relative to an assumed combination rate constant, $k_1 = 10^{14}$ mole^{-1} cm.^{3} sec.$^{-1}$. This paper describes the first absolute determination of the latter constant. There is a lack of absolute rate constants for higher alkyl radicals. Isopropyl was chosen because it is a secondary radical and because the primary photolytic act in which it is formed is relatively clean.

The theory of intermittent illumination can be applied to any system in which radicals are mutually destroyed in pairs, *e.g.*,

$$\begin{array}{rll} \mathrm{M} + h\nu & \longrightarrow \mathrm{R} & \text{Initiation} \\ \mathrm{R} + \mathrm{M'} & \longrightarrow \mathrm{R} & \text{Chain} \\ 2\mathrm{R} & \longrightarrow \text{Inactive products} & \text{Termination} \end{array}$$

The radical concentration then depends upon the square root of the light intensity.

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* Part X, Garcia Dominguez and Trotman-Dickenson, *J.*, 1962, 3357.

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

A full treatment of the theory including necessary data is given by Melville and Burnett.[2] They deduce the variation of $[\mathrm{rad}]_i/[\mathrm{rad}]_s$ with log m, where [rad] is radical concentration, the subscripts i and s refer to intermittent and steady illumination, and m is a dimensionless parameter defined by:

$$m = (Ink_t)^{\frac{1}{2}}\lambda, \qquad (1)$$

where In = rate of initiation, k_t = termination rate constant, and λ = length of light flash. It is also shown that

$$m = \lambda/\tau_s, \qquad (2)$$

where τ_s is the mean radical lifetime under steady conditions. The variation of $[\mathrm{rad}]_i/[\mathrm{rad}]_s$ with log λ is found experimentally. Now

$$\log \lambda - \log m = \log \tau_s. \qquad (3)$$

Therefore the displacement between the two curves is a measure of τ_s.

To measure relative radical concentration a " pilot " reaction is necessary, whose rate is of first power with respect to radical concentration. In the aldehyde system, hydrogen abstraction to give propane is unsuitable, because propane is also produced by the primary photolytic act. This defect does not apply to the ketone source of isopropyl. However, the high disproportionation rate means that the amount of propane from abstraction is much less than that from disproportionation, if second-order termination predominates. Thus the experimental error in measuring the abstraction rate is large. The problem was solved by photolysing the aldehyde in the presence of ethylene. The rate of addition of isopropyl to the double bond was followed by measuring the rate of formation of isopentane. Corrections to this measurement are discussed below.

In the low-temperature photolysis of isobutyraldehyde there are two reactions which destroy radicals, *viz.*, the combination of isopropyl to give 2,3-dimethylbutane:

$$2\mathrm{C_3H_7} \xrightarrow{k_1} \mathrm{C_6H_{14}} \quad \ldots\ldots\ldots\ldots \quad (i)$$

and the disproportionation:

$$2\mathrm{C_3H_7} \xrightarrow{k_2} \mathrm{C_3H_8}+\mathrm{C_3H_6} \quad \ldots\ldots\ldots\ldots \quad (ii)$$

From reaction (1)

$$R(\mathrm{C_6H_{14}}) = k_1[\mathrm{C_3H_7}]^2, \qquad (4)$$

where $R(\mathrm{C_6H_{14}})$ is the rate of formation of hexane. Now

$$[\mathrm{C_3H_7}]_s = \tau_s\, R(\mathrm{C_3H_7})_s. \qquad (5)$$

Under steady conditions the rates of production and destruction of the radical are equal. Therefore,

$$\begin{aligned} R(\mathrm{C_3H_7})_s &= 2\{R(\mathrm{C_6H_{14}})_s + R(\mathrm{C_3H_6})_s\} \\ &= 2 \times 1{\cdot}65R(\mathrm{C_6H_{14}})_s. \qquad (6) \end{aligned}$$

$$\text{Since } k_2/k_1 = 0{\cdot}65,^1$$

$$k_1 = 1/\{4\tau_s^2 1{\cdot}65^2 R(\mathrm{C_6H_{14}})_s\}. \qquad (7)$$

Corrections made to the theoretical curve to allow for first-order termination are discussed below.

EXPERIMENTAL

Isobutyraldehyde (B.D.H.) and " AnalaR " acetone were shown to be pure by gas chromatography, and by the nature of their photolytic products. Ethylene (B.O.C.) contained less than 1% of propene.

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[2] Melville and Burnett, " Technique of Organic Chemistry," Interscience Publ., Inc., New York, 1953, Vol. VIII, p. 138.

Intermittent illumination was produced by chopping the light beam with a rotating disc from which two slots had been cut to give a dark : light ratio of 3 : 1. The disc was driven by an Evershed and Vignoles D.C. servo motor, the speed being variable by adjustment of a rheostat in series with the motor which was fitted with a tacho generator. The voltage generated measured the speed of rotation of the disc. This was calibrated by using a Dawe Instrument Co. Strobflash. In two runs the sector was rotated manually with a light exposure of 10 sec.

The light source was an 80w Osram MB/U medium-pressure mercury arc. At full intensity the arc width was about 2 mm. This was mounted behind a narrow slit, immediately behind the rotating sector, so that a very narrow beam was chopped. The lamp was protected from draughts by a quartz window and a metal shield. The beam was rendered parallel by a quartz lens of focal length 10 cm., placed at the focal distance from the sector.

A stabilised D.C. voltage was supplied to the lamp. 230-v A.C. current was fed into an Advance 125-w constant-voltage transformer to stabilise mains fluctuations. The output voltage was then transformed by a Variac and rectified by a Powerpak, incorporating four selenium rectifiers. The amperage supplied to the lamp could be adjusted by means of the Variac and a rheostat in series with the lamp. The lamp tended to stabilise the voltage. The current, about 0·7 amp., and the potential difference across the lamp, about 100 v, were monitored.

The furnace was maintained at a constant temperature by a Sunvic R.T.2 thermoregulator. This did not vary by more than ±0·7°, but small fluctuations were corrected by adjusting the reaction rates to the required temperature.

The other apparatus and procedure were similar to those previously employed,[3,4] but the analysis of the condensable fraction of the products was made on a column (300 × 0·5 cm.) packed with 40—60 mesh activated alumina with 5% of squalane; the column was heated during the analysis, the temperature rising from 20° to 120° in 30 minutes.

RESULTS AND DISCUSSION

The reaction scheme has been already investigated [1] and the principal reactions below 170° are:

$$(\mathrm{CH_3})_2\mathrm{CH{\cdot}CHO} + h\nu \longrightarrow \left\{\begin{array}{ll} \mathrm{C_3H_7{\cdot}} + \mathrm{{\cdot}CHO} & \text{(a)} \\ \mathrm{C_3H_8} + \mathrm{CO} & \text{(b)} \\ \mathrm{CH_3{\cdot}} + \mathrm{{\cdot}C_2H_4{\cdot}CHO} & \text{(c)} \end{array}\right.$$

$$\begin{array}{rcll}
2\mathrm{C_3H_7{\cdot}} & \longrightarrow & \mathrm{C_6H_{14}} & (1) \\
2\mathrm{C_3H_7{\cdot}} & \longrightarrow & \mathrm{C_3H_6} + \mathrm{C_3H_8} & (2) \\
\mathrm{C_3H_7} + \mathrm{C_3H_7{\cdot}CHO} & \longrightarrow & \mathrm{C_3H_8} + \mathrm{C_3H_7{\cdot}CO{\cdot}} & (3) \\
\mathrm{C_3H_7{\cdot}CO{\cdot}} & \longrightarrow & \mathrm{C_3H_7{\cdot}} + \mathrm{CO} & (3a) \\
\mathrm{C_3H_7{\cdot}} + \mathrm{C_2H_4} & \longrightarrow & \mathrm{C_5H_{11}{\cdot}} & (4) \\
\mathrm{C_5H_{11}{\cdot}} + \mathrm{C_3H_7{\cdot}CHO} & \longrightarrow & \mathrm{C_5H_{12}} + \mathrm{C_3H_7{\cdot}CO{\cdot}} & (5) \\
\mathrm{C_5H_{11}{\cdot}} + \mathrm{C_2H_4} & \longrightarrow & \mathrm{C_7H_{15}{\cdot}} & (6) \\
\mathrm{C_3H_7{\cdot}} + \mathrm{C_5H_{11}{\cdot}} & \longrightarrow & \mathrm{C_8H_{18}} & (7) \\
\mathrm{C_3H_7{\cdot}} + \mathrm{C_5H_{11}{\cdot}} & \longrightarrow & \mathrm{C_3H_6} + \mathrm{C_5H_{12}} & (8) \\
\mathrm{C_3H_7{\cdot}} + \mathrm{C_5H_{11}{\cdot}} & \longrightarrow & \mathrm{C_5H_{10}} + \mathrm{C_3H_8} & (9) \\
2\mathrm{C_5H_{11}{\cdot}} & \longrightarrow & \mathrm{C_{10}H_{22}} & (10) \\
2\mathrm{C_5H_{11}{\cdot}} & \longrightarrow & \mathrm{C_5H_{12}} + \mathrm{C_5H_{10}} & (11)
\end{array}$$

The photolytic process (c) is unimportant, the methane produced being negligible. Reaction (4) was used as a measure of isopropyl concentration. Reactions (5)—(11) show the ways in which isopentyl may further react. Reaction (5) predominates, and in practice the rate of isopentane formation was used to measure isopropyl concentration. $R(\mathrm{C_5H_{12}}) = k_4[\mathrm{C_3H_7}][\mathrm{C_2H_4}]$, from (4), (5). Hence

$$\frac{[\mathrm{C_3H_7}]_{\mathrm{i}}}{[\mathrm{C_3H_7}]_{\mathrm{s}}} = \frac{R(\mathrm{C_5H_{12}})_{\mathrm{i}}[\mathrm{C_2H_4}]_{\mathrm{s}}}{R(\mathrm{C_5H_{12}})_{\mathrm{s}}[\mathrm{C_2H_4}]_{\mathrm{i}}}$$

Reaction (5) regenerates isopropyl, so the addition is not a termination reaction.

[3] Kerr and Trotman-Dickenson, *J.*, 1960, 1602; Metcalfe and Trotman-Dickenson, *J.*, 1960, 5072.
[4] Kerr and Trotman-Dickenson, *J.*, 1960, 1611.

Runs with alternate steady and intermittent illumination were made, and each intermittent run was compared with at least two steady runs, usually those preceding and following, to obtain mean $[C_3H_7]_i/[C_3H_7]_s$. The steady runs used for comparison are shown in the Tables. Intermittent runs were three times the length of steady runs. Aldehyde consumption did not exceed 10%, or ethylene consumption 2%.

To correct for small light-intensity fluctuations the experimental values of $[C_3H_7]_i/[C_3H_7]_s$ were plotted against $\log \lambda + \frac{1}{2} \log R(C_6H_{14})_s$.

From (7), we derive:

$$\log k_1 = 12 - \log (4 \times 1{\cdot}65^2) - 2 \log \tau_s - \log R(C_6H_{14})_s.$$

Since $R(C_6H_{14})$ has the units 10^{-12} moles cm.$^{-3}$ sec.$^{-1}$

$$\log k_1 = 10{\cdot}96 - \{2 \log \tau_s + \log R(C_6H_{14})_s\}.$$

If $$d = \{\log \lambda + \tfrac{1}{2} \log R(C_6H_{14})_s\} - \log m = \log \tau_s - \tfrac{1}{2} \log R(C_6H_{14})_s.$$

Then $$\log k_1 = 10{\cdot}96 - 2d.$$

With aldehyde concentrations of 1·2—1·4 × 10^{-6} moles cm.$^{-3}$ and suitable ethylene concentrations, determinations of k_1 were made at 81°, 115°, and 169°. Tables 1—3 record the conditions, products, and values of $[C_3H_7]_i/[C_3H_7]_s$ derived from the runs. There were changes in light intensity after runs 25, 30, and 54 owing to a change of lamp and cleaning of the cell. The Figure shows the experimental plots and the best fit with the theoretical curves. The values for $\log k_1$ from the plots are given in Table 4 as the uncorrected rate constants. Thus within experimental error there is no temperature coefficient and $k_1 = 10^{14\cdot5}$ mole^{-1} cm.^{3} sec.$^{-1}$.

TABLE 1.

The combination of isopropyl radicals at 81°.

Run	$[C_2H_4]$	C_3H_8	C_3H_6	CO	C_5H_{12}	C_6H_{14}	Mean $[C_3H_7]_i/[C_3H_7]_s$	Check runs	f (λ)
80	4·17	47·0	14·5	74·2	6·97	10·1	—	—	—
81	3·91	12·3	2·48	19·3	2·42	1·95	0·377	80, 82	$\bar{2}$·750
82	4·07	47·0	8·80	73·5	6·60	10·7	—	—	—
83	3·75	12·6	2·10	19·9	2·78	2·11	0·451	82, 84	$\bar{2}$·125
84	4·17	49·0	10·5	73·6	6·94	10·1	—	—	—
85	3·91	12·4	2·81	18·9	2·30	1·98	0·337	84, 86	$\bar{1}$·419
86	3·88	48·1	10·8	74·1	7·15	10·1	—	—	—
87	4·01	12·0	a.f.	19·8	2·54	2·20	0·346	86, 88	$\bar{1}$·092
88	3·84	50·0	11·4	75·6	6·97	9·40	—	—	—
89	3·88	12·0	2·74	19·3	2·58	2·24	0·362	88, 90	$\bar{2}$·882
90	3·96	50·3	9·08	73·3	7·36	10·5	—	—	—
91	3·94	a.f.	a.f.	20·4	3·12	2·37	0·430	90, 92	$\bar{2}$·448
92	3·96	52·0	9·23	75·7	7·25	10·1	—	—	—
93	3·80	12·6	3·05	19·9	3·09	2·45	0·446	92, 96	$\bar{2}$·395
94	3·97	12·7	2·47	19·5	3·29	2·23	0·454	92, 96	$\bar{2}$·134
96	4·32	48·3	8·53	75·7	7·87	10·5	—	—	—
97	3·88	12·6	2·74	17·7	2·25	2·48	0·309	96, 98	$\bar{1}$·550
98	3·99	50·7	9·29	75·0	7·77	10·0	—	—	—
106	1·75	55·4	9·78	71·6	3·75	11·1	—	—	—
107	1·76	13·5	2·28	18·5	1·64	2·46	0·440	106, 108	$\bar{2}$·362
108	1·79	47·3	6·40	67·9	3·80	10·7	—	—	—
109	1·77	11·9	1·76	19·4	1·60	2·48	0·439	108, 110	$\bar{2}$·622
110	1·80	48·5	8·22	71·2	3·62	10·4	—	—	—
111	1·81	11·2	1·64	17·2	1·48	2·19	0·428	110, 112	$\bar{2}$·720
112	1·79	47·5	9·60	67·6	3·27	9·25	—	—	—

Rates of formation of products are given as 10^{-12} mole cm.$^{-3}$ sec.$^{-1}$. $[C_2H_4]$ is mean ethylene concentration in 10^{-6} mole cm.$^{-3}$. a.f. = analytical failure. Check runs are steady runs used for comparison. $f(\lambda)$ is $\log \lambda + \frac{1}{2} \log R(C_6H_{14})_s$.

Corrections.—If the only reactions removing isopropyl are (1) and (2), then the radical

TABLE 2.

The combination of isopropyl radicals at 115°.

Run	$[C_2H_4]$	C_3H_8	C_3H_6	CO	C_5H_{12}	C_6H_{14}	Mean $[C_3H_7]_i/[C_3H_7]_b$	Check runs	f(λ)
15	2·00	68·1	11·8	112	10·4	12·7	—	—	—
17	2·19	75·9	14·8	118	11·5	11·9	—	—	—
18	2·10	21·2	6·9	33·5	5·25	3·12	0·471	15, 17, 20	$\bar{2}$·219
19	2·10	18·6	2·9	33·8	5·17	2·04	0·462	15, 17, 20	$\bar{2}$·221
20	2·10	73·6	12·3	113	11·6	12·1	—	—	—
21	2·13	20·3	2·49	30·7	3·32	2·42	0·294	15, 17, 20	$\bar{1}$·435
22	2·10	74·6	15·5	108	10·9	12·5	—	—	—
23	2·24	18·4	4·06	32·1	4·08	2·08	0·355	20, 22, 24	$\bar{1}$·019
24	2·03	72·5	11·0	117	9·57	a.f.	—	—	—
25	2·15	16·7	4·2	28·1	4·21	2·21	0·383	20, 22, 24	$\bar{2}$·794
27	2·14	80·8	12·3	130	11·0	10·9	—	—	—
28	2·08	15·9	4·51	31·0	4·74	2·13	0·446	27, 29	$\bar{2}$·336
29	2·10	54·8	11·9	110	10·6	8·60	—	—	—
30	2·12	15·2	2·32	29·5	3·46	1·91	0·319	27, 29	$\bar{1}$·077
33	2·01	53·2	11·8	100	8·66	8·70	—	—	—
34	2·03	13·8	2·60	27·7	3·49	1·48	0·424	33, 35, 37	$\bar{2}$·485
35	2·13	52·0	8·25	99·8	8·07	8·01	—	—	—
36	2·06	12·5	1·93	24·6	1·94	1·80	0·232	33, 35, 37	$\bar{1}$·450
37	2·11	53·9	8·58	99·9	8·66	8·23	—	—	—

See notes under Table 1.

TABLE 3.

The combination of isopropyl radicals at 169°.

Run	$[C_2H_4]$	C_3H_8	C_3H_6	CO	C_5H_{12}	C_6H_{14}	Mean $[C_3H_7]_i/[C_3H_7]_s$	Check runs	f(λ)
40	2·19	80·5	10·6	145	31·5	8·95	—	—	—
41	1·09	83·2	8·85	133	17·4	9·66	—	—	—
42	1·10	23·0	2·06	40·2	7·63	1·78	0·442	40, 41, 43	$\bar{2}$·127
43	1·10	92·2	9·66	136	18·6	7·74	—	—	—
44	1·17	21·1	1·91	35·0	5·95	1·90	0·305	43, 45	$\bar{1}$·269
45	1·13	85·3	1·06	135	18·8	8·92	—	—	—
46	1·11	22·5	2·23	38·7	6·98	1·84	0·369	45, 47	$\bar{2}$·985
47	1·11	95·9	8·98	131	18·9	8·55	—	—	—
48	1·11	21·5	1·79	37·9	7·30	1·71	0·396	47, 49	$\bar{2}$·757
49	1·20	81·0	9·49	132	19·1	7·63	—	—	—
50	1·14	25·5	2·19	39·4	7·99	1·75	0·434	49, 52	$\bar{2}$·569
51	1·09	23·2	2·11	39·7	8·01	1·51	0·456	49, 52	$\bar{2}$·087
52	1·19	88·2	9·97	130	19·5	8·62	—	—	—
53	1·13	21·0	3·96	36·3	6·43	1·66	0·350	52, 54	$\bar{1}$·091
54	1·11	86·7	9·39	132	18·1	8·11	—	—	—
56	1·08	93·2	10·7	143	17·9	9·67	—	—	—
57	1·09	26·0	2·10	42·0	8·77	1·78	0·459	56, 58	$\bar{2}$·139
58	1·08	90·1	11·2	144	20·5	9·11	—	—	—
59	1·13	27·7	2·58	41·3	7·15	2·29	0·357	58, 60	$\bar{1}$·251
60	1·08	89·8	10·6	139	17·3	8·70	—	—	—
61	1·19	27·1	2·36	42·6	9·22	2·04	0·499	60, 62	$\bar{2}$·093
62	1·15	102	10·0	143	21·5	10·1	—	—	—
63	1·11	22·0	2·58	37·1	4·90	2·49	0·257	60, 62	1·502

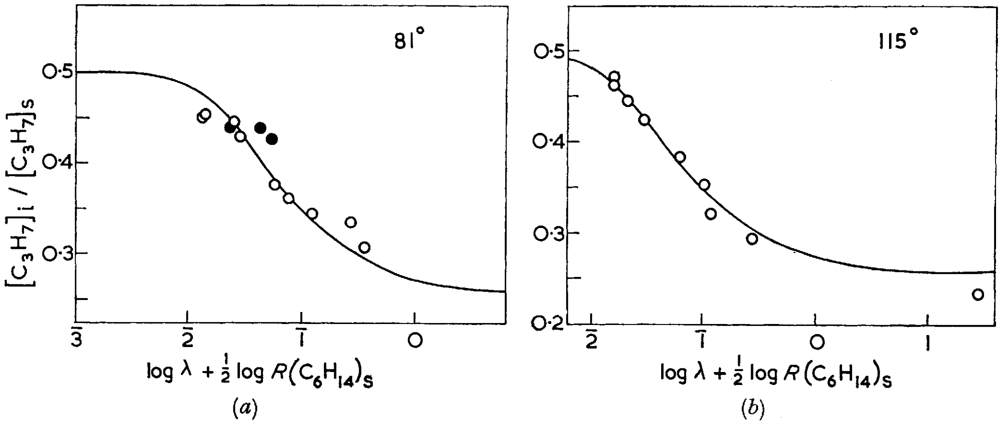
See notes under Table 1.

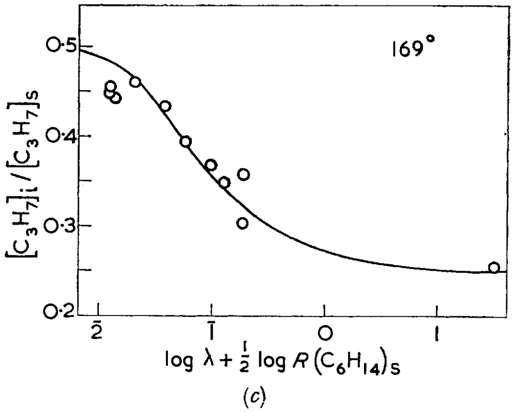
concentration depends on the square root of the light intensity, and this may be monitored by $R(C_6H_{14})^{\frac{1}{2}}$. Thus it should be possible to correct for any run-to-run intensity fluctuations, by multiplying $[C_3H_7]_i/[C_3H_7]_s$ by the factor $R(C_6H_{14})_s^{\frac{1}{2}}/2R(C_6H_{14})_i^{\frac{1}{2}}$. Ideally this ratio should be 1·0; in fact the average value was 1·08.

The well-established acetone system was used to check the experimental technique. The corresponding ethane ratio was exactly unity. Thus experimental effects, such as a light-intensity loss owing to cooling of the lamp by the sector, are precluded. The photolysis of the aldehyde alone also gave a ratio very close to unity, and a few runs made at 81°

with half the usual ethylene concentration, gave a ratio 1·04. Thus this effect must be due to a reaction involving ethylene or isopentyl.

In the above scheme, reactions (3) and (4) followed by (5) or (6) will regenerate isopropyl, and so do not affect its concentration. However, if (4) is followed by any of reactions (7)—(11), it constitutes a chain-terminating process which is of the first-order with respect to isopropyl concentration. The concentration of isopentyl is small compared with that of isopropyl, therefore (10) and (11) will be ignored. The predominating reaction between isopropyl and isopentyl will be (7), the cross-combination. Octane was not definitely identified, but the presence of a small amount, appearing as a wide peak at the same time as the aldehyde began to be eluted, cannot be excluded. Such a small amount could not have been accurately measured under these conditions, although an upper limit may be set on it. The following estimation of the first-order termination rate was made:





Curves obtained from rotating sector experiments at 81°, 115°, and 169°. The full circles indicate low ethylene concentrations.

From (3),
$$k_3/k_1^{\frac{1}{2}} = \frac{R(C_3H_8)(3)}{[\text{Ald}]R(C_6H_{14})^{\frac{1}{2}}}$$

and from (5),
$$k_5/k_{10}^{\frac{1}{2}} = \frac{R(C_5H_{12})}{[\text{Ald}]R(C_{10}H_{22})^{\frac{1}{2}}}$$

$k_3/k_1^{\frac{1}{2}}$ has been determined.[1] $k_5/k_{10}^{\frac{1}{2}}$ has not, but it is known that this rate constant ratio is similar for ethyl,[4] propyl,[1,5] and butyl[3,6,7] radicals, so will probably be about the same for isopentyl. For calculation purposes it is assumed that isopentyl behaves like isobutyl. The ratio $(k_5/k_{10}^{\frac{1}{2}})/(k_3/k_1^{\frac{1}{2}})$ was calculated at each temperature on this basis, and was about 1·8.

Thus $$R(C_5H_{10})/R(C_{10}H_{22})^{\frac{1}{2}} = 1{\cdot}8R(C_3H_8)(3)/R(C_6H_{14})^{\frac{1}{2}}.$$

Now $$R(C_8H_{18}) = 2R(C_6H_{14})^{\frac{1}{2}}R(C_{10}H_{22})^{\frac{1}{2}}.$$

Therefore, $$R(C_8H_{18}) = 2R(C_6H_{14})R(C_5H_{12})/1{\cdot}8R(C_3H_8)(3),$$

where $R(C_3H_8)(3) = R(C_3H_8)(\text{total}) - R(C_3H_6) - R(C_3H_8)(\text{b})$. Reasonable estimates may be made for propane from the photolytic act. Propene was calculated as $0{\cdot}65R(C_6H_{14})$, because the ethylene contained a small amount of propene as impurity.

At each temperature mean values of the rate of octane formation, under steady and intermittent illumination, were estimated. By analogy with isobutyl we may estimate $(k_8 + k_9)/k_7 = 0{\cdot}3$. This estimation is uncertain, but has little effect on the calculation. Hence

$$\text{First-order termination} = 2 \times 1{\cdot}3 \times R(C_8H_{18}),$$

since each of the reactions (7)—(9) effectively destroys two isopropyl radicals. Therefore,

$$\alpha_c = \frac{\text{1st order termination}}{\text{2nd order termination}} = \frac{1{\cdot}3R(C_8H_{18})}{1{\cdot}65R(C_6H_{14})}.$$

This value was used to derive a new theoretical curve at each temperature, Shepp's modified theory being used which includes a first-order termination. If the total termination rate is substituted for that of hexane, in the expression $R(C_6H_{14})_s^{\frac{1}{2}}/2R(C_6H_{14})_i^{\frac{1}{2}}$, then the discrepancy between theoretical and experimental values is reduced to less than half. The remaining small discrepancy is within experimental error.

The rate of reaction (4) was followed by measuring isopentane formation; this estimates isopentyl disappearing by reactions (5), (8), and (11). Reaction (10) may be ignored. Reaction (6) will produce isoheptane; this was not detected but will be proportional to the amount of isopentane and so cancels. However, isopentyl radicals disappearing by reactions (7) and (9) should be included.

Strictly $$\frac{[C_3H_7]_i}{[C_3H_7]_s} = \frac{\{R(C_5H_{12}) + R(C_7H_{16}) + R(C_8H_{18}) + R(C_5H_{10})\}_i}{\{R(C_5H_{12}) + R(C_7H_{16}) + R(C_8H_{18}) + R(C_5H_{10})\}_s}$$

which closely approximates to $$\frac{\{R(C_5H_{12})}{\{R(C_5H_{12})} + \frac{R(C_8H_{18})\}_i}{R(C_8H_{18})\}_s}$$

At each temperature a ratio was calculated from mean rates of octane and isopentane formation, which corresponded to a value of 0·375 for isopentane formation only. Thus the comparison was made on the most sensitive part of the curve. The fit between the two curves was altered, and a correction applied to the rate constant.

A final correction concerns the equating of the rate of radical production with termination:

$$R_{\text{termination}} = (1 + \alpha_c)\ \text{2nd order termination}.$$

Therefore the expression (7) for k_1 should be divided by $(1 + \alpha_c)^2$.

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[5] Kerr and Trotman-Dickenson, *Trans. Faraday Soc.*, 1959, **55**, 572.
[6] Birrell and Trotman-Dickenson, *J.*, 1960, 4218.
[7] Gruver and Calvert, *J. Amer. Chem. Soc.*, 1956, **78**, 5208.

The rate constants and the corrections applied are summarised in Table 4.

TABLE 4.

Temperature	80·8°	114·8°	169·3°
Uncorrected log k_1	14·52	14·50	14·42
α_c	0·23	0·20	0·21
First-order termin. corrn.	−0·72	−0·64	−0·66
Corrn. to $[C_3H_7]_i/[C_3H_7]_s$	+0·26	+0·18	+0·14
Corrn. to $R(C_3H_7)$	−0·18	−0·16	−0·16
Corr. log k_1	13·88	13·88	13·74

This yields a negative activation energy of 1·3 kcal. mole^{-1}. However, this is due to the determination at 169° alone, where the points are more scattered than at lower temperatures. It is approximately equal to the 95% confidence error, so little importance is attached to it. If the activation energy is zero, then log A_1 = 13·8 mole^{-1} cm.^{3} sec.$^{-1}$.

The corrections applied introduce uncertainty into the rate constant. However, the estimation of octane is unlikely to be far in error. The assumption that isopentyl resembles isobutyl, and therefore $(k_5/k_{10}^{\frac{1}{2}})/(k_3/k_1^{\frac{1}{2}})$ is 1·8 probably underestimates octane. However, had the amount of octane been much larger it could have been definitely measured. Also, if α_c were much greater than 0·2 the upper limiting value of $[C_3H_7]_i/[C_3H_7]_s$ would be lower than the limiting values found experimentally. This experimental upper limiting value also shows that no other first-order termination, such as

$$C_3H_7\cdot + \cdot CHO \longrightarrow C_3H_7\cdot CHO \qquad (12)$$

takes place to a significant extent.

The few determinations made at 81° and low ethylene concentration do not fit the simple curve well, or the corrected curve with $\alpha_c = 0·23$. However, they would correspond better to a curve for which α_c is about 0·1, a reasonable value at low ethylene concentration.

It is also observed that if the anomaly in the ratio $R(C_6H_{14})_s^{\frac{1}{2}}/2R(C_6H_{14})_i^{\frac{1}{2}}$ were attributed to a real variation in light intensity, and the experimental values were corrected accordingly, then, within experimental error, the temperature coefficient is zero, and log A_1 = 13·9 mole^{-1} cm.^{3} sec.$^{-1}$.

Thus the uncertainty lies only in the *A* factor; the activation energy is zero no matter what correction is applied.

If a collision diameter of 4·75 Å is assumed for isopropyl, equating it with that calculated by Rowlinson [8] for propane, and the activation energy is zero, then the collision rate at 115° is $10^{14\cdot12}$ mole^{-1} cm.^{3} sec.$^{-1}$. The experimental rate of bimolecular termination at 115°, including combination and disproportionation, is $10^{14\cdot10}$ mole^{-1} cm.^{3} sec.$^{-1}$, giving the reaction a steric factor of unity. For methyl radicals, and a collision diameter of 3·5 Å, the collision rate at 125° is $10^{14\cdot09}$ mole^{-1} cm.^{3} sec.$^{-1}$. The experimental value of Kistiakowsky and Roberts,[10] corrected by Shepp,[9] $10^{13\cdot34}$ mole^{-1} cm.^{3} sec.$^{-1}$ at 125°, gives a steric factor of 0·2. It appears that alkyl radicals react on nearly every collision in the gas phase.

The rate constants of radical combinations are thermodynamically related to those of the symmetrical decompositions of alkanes. The relation can be considered in terms of the *A* factors of the reactions. The relative values of these factors for combination and decomposition can be found from the overall entropy change.[11] Because it is difficult to measure temperature coefficients, the *A* factors for combination are best equated with the rate constants at some convenient temperature, which can be taken here as 100°. If it is assumed that the radicals have the same entropy as the hydrocarbons with one more

[8] Rowlinson, *Quart. Rev.*, 1954, **8**, 168.
[9] Shepp, *J. Chem. Phys.*, 1956, **24**, 939.
[10] Kistiakowsky and Roberts, *J. Chem. Phys.*, 1953, **21**, 1637.
[11] Trotman-Dickenson, *J. Chem. Phys.*, 1953, **21**, 211.

hydrogen atom (almost certainly an underestimate by 2—4 cal. mole^{-1} deg.$^{-1}$), then it is found that log A (sec.$^{-1}$) for the symmetrical decompositions of ethane, butane, and 2,3-dimethylbutane are 16·3, 16·6, and 18·5, respectively. The rate constants for the combination are those of Kistiakowsky and Roberts [10] corrected by Shepp [9] for methyl, of Shepp and Kutschke [12] for ethyl, and of the present work for isopropyl. More realistic estimates of the entropies of the radicals would raise these values by as much as one unit.

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[12] Shepp and Kutschke, *J. Chem. Phys.*, 1957, **26**, 1020.