

**671.** *The Absolute Rate of Combination of the t-Butyl Radical.*

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The absolute combination rate of t-butyl has been determined at 81° and 115°. The radicals were generated by the photo-initiated chain decomposition of pivalaldehyde. Radical lifetimes were measured by the intermittent-illumination method. Addition of t-butyl to ethylene was used to measure the relative radical concentration. The combination rate constants are  $10^{12.5}$  mole<sup>-1</sup> cm.<sup>3</sup> sec.<sup>-1</sup>. A first-order termination correction was applied.

BIRRELL and TROTMAN-DICKENSON<sup>1</sup> studied the reactions of t-butyl produced by photo-initiated chain decomposition of pivalaldehyde. The experimental rate constants were expressed relative to an assumed combination rate constant,  $k_1 = 10^{14}$  mole<sup>-1</sup> cm.<sup>3</sup> sec.<sup>-1</sup>. This paper describes the first absolute determination of this constant. It is the first absolute rate constant of a tertiary alkyl radical to be studied.

<sup>1</sup> Birrell and Trotman-Dickenson, *J.*, 1960, 4218.

The theory of intermittent illumination can be applied to any system in which the radical concentration depends on a power of the light intensity less than unity. This is realised in practice when the predominant termination reaction destroys two radicals simultaneously. A full treatment of the theory, including necessary data, is given by Melville and Burnett.<sup>2</sup> They deduce the variation of  $[\text{rad}]_i/[\text{rad}]_s$  with  $\log m$ , where  $[\text{rad}]$  is radical concentration, the subscripts *i* and *s* refer to intermittent and steady illumination, and  $m$  is a dimensionless parameter defined by:

$$m = (In \cdot k_t)^{\frac{1}{2}} \lambda, \quad (1)$$

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

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

where  $\tau_s$  is the mean radical lifetime under steady conditions. The variation of  $[\text{rad}]_i/[\text{rad}]_s$  with  $\log \lambda$  is found experimentally.

$$\text{Now} \quad \log \lambda - \log m = \log \tau_s. \quad (3)$$

Therefore the displacement between the two curves is a measure of  $\tau_s$ .

The addition of *t*-butyl to ethylene was used to measure relative radical concentration, a similar method to that employed before for the isopropyl radical.<sup>3</sup> The rate of this reaction is of first power with respect to *t*-butyl concentration. The addition rate was estimated from the formation of 2,2-dimethylbutane. Corrections to this measurement are discussed below.

In the low-temperature photolysis of pivalaldehyde there are two reactions which destroy radicals, the combination of *t*-butyl to give 2,2,3,3-tetramethylbutane:



and the disproportionation:



From reaction (i),

$$R(\text{C}_8\text{H}_{18}) = k_1[\text{C}_4\text{H}_9]^2, \quad (4)$$

where  $R(\text{C}_8\text{H}_{18})$  is the rate of formation of  $\text{C}_8$ -hydrocarbon.

$$\text{Now} \quad [\text{C}_4\text{H}_9]_s = \tau_s \cdot R(\text{C}_4\text{H}_9)_s. \quad (5)$$

Under steady conditions the rate of production and destruction of the radical are equal.

$$\begin{aligned} \text{Therefore,} \quad R(\text{C}_4\text{H}_9)_s &= 2\{R(\text{C}_8\text{H}_{18})_s + R(\text{C}_4\text{H}_8)_s\} \\ &= 2 \times 1.31 R(\text{C}_4\text{H}_9)_s \end{aligned} \quad (6)$$

since  $k_2/k_1 = 3.20$ . This value, obtained by Garcia Dominguez and Trotman-Dickenson,<sup>4</sup> using both aldehyde and ketone sources of *t*-butyl, is preferred to the higher values of Birrell and Trotman-Dickenson<sup>1</sup> and Kraus and Calvert.<sup>5</sup> Adjustment would be simple if further information supported the higher value.

$$\text{Hence} \quad k_1 = 1/\{21.97 \tau_s^2 \cdot R(\text{C}_4\text{H}_9)_s\}. \quad (7)$$

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

<sup>2</sup> Melville and Burnett, "Technique of Organic Chemistry," Interscience Publ. Inc., New York, 1953, Vol. VIII, p. 138.

<sup>3</sup> Metcalfe and Trotman-Dickenson, *J.*, 1962, 4620.

<sup>4</sup> Garcia Dominguez and Trotman-Dickenson, *J.*, 1962, 3357.

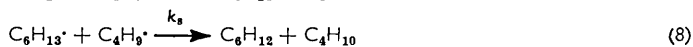
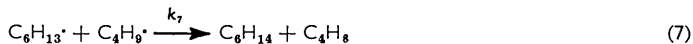
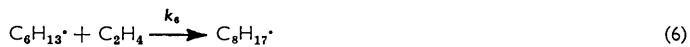
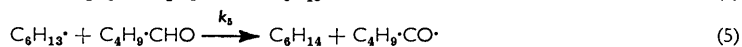
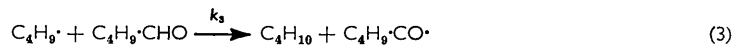
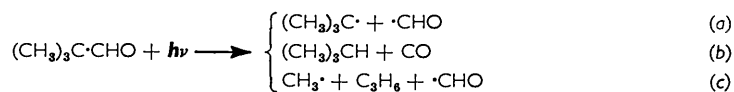
<sup>5</sup> Kraus and Calvert, *J. Amer. Chem. Soc.*, 1957, **79**, 5921.

*Experimental.*—Pivalaldehyde (Koch Laboratories) was purified by wide-bore gas chromatography. The columns ( $450$  or  $150 \times 2.5$  cm.) were packed with 35% of polyethylene glycol 400 on firebrick, and were heated at  $80^\circ$ . Gas chromatography and the nature of the photolytic products showed the aldehyde to be pure, apart from a small amount of tetramethylbutane that was removed only by repeated chromatographic fractionation. Ethylene (B.O.C.) was pure after low-temperature distillation.

The illumination, temperature control, and other apparatus and procedure were similar to those previously employed.<sup>3</sup> The analysis of the condensable fraction of the products was made on two columns ( $60 \times 0.5$  cm.) and ( $40 \times 0.5$  cm.) in series, packed with 40–60 mesh activated alumina with 1% of squalane. After hexane had passed through both columns, tetramethylbutane was eluted directly from the first column. The columns were heated during the analysis, the temperature rising from  $20^\circ$  to  $120^\circ$  in 30 min.

## RESULTS AND DISCUSSION

The reaction scheme has already been investigated<sup>1</sup> and the principal reactions below  $160^\circ$  are:



The photolytic process (c) is unimportant, the amounts of methane and propene produced being negligible. The isobutane formed by process (b) prevented the use of reaction (3) as a measure of the relative t-butyl concentration, so reaction (4) was used for this purpose. Reactions (5)—(11) show the ways in which the hexyl radical may further react. Reaction (5) predominates, and in practice the rate of formation of hexane was used to measure the t-butyl concentration. From reactions (4) and (5) we have

$$R(\text{C}_6\text{H}_{14}) = k_4[\text{C}_4\text{H}_9][\text{C}_2\text{H}_4].$$

Hence

$$\frac{[\text{C}_4\text{H}_9]_i}{[\text{C}_4\text{H}_9]_s} = \frac{R(\text{C}_6\text{H}_{14})_i[\text{C}_2\text{H}_4]_s}{R(\text{C}_6\text{H}_{14})_s[\text{C}_2\text{H}_4]_i}$$

Reaction (5) regenerates t-butyl, so the addition is not a termination reaction.

Runs with alternate steady and intermittent illumination were made. At each temperature the intermittent runs (three times as long as steady runs) were compared with mean values of  $R(\text{C}_6\text{H}_{14})$  and  $[\text{C}_2\text{H}_4]$  from the steady runs. Aldehyde consumption did not exceed 5%, or ethylene consumption 1%.

The experimental values of  $[C_4H_9]_i/[C_4H_9]_s$  were plotted against  $\log \lambda$ .  
From equation (7) we derive:

$$\log k_1 = 12 - \log 21.97 - 2 \log \tau_s - \log R(C_4H_8)_s,$$

since  $R(C_4H_9)_s$  has the units  $10^{-12}$  mole  $cm^{-3}$   $sec^{-1}$

With aldehyde concentrations of  $0.9-1.2 \times 10^{-6}$  mole  $cm^{-3}$  and ethylene con-

TABLE 1.

The combination of *t*-butyl radicals at 81°.

Run	$[C_2H_4]$	$C_4H_{10}$	$C_4H_8$	CO	$C_6H_{14}$	$[C_4H_9]_i/[C_4H_9]_s$	$\log \lambda$
35	2.13	28.5	9.13	42.3	3.91	—	—
36	2.09	6.98	2.12	11.0	1.52	0.397	2.484
37	2.08	26.2	7.93	40.1	3.75	—	—
38	2.06	5.98	1.94	11.2	1.51	0.398	2.661
39	2.10	23.5	7.43	46.2	3.73	—	—
40	2.13	6.15	2.11	11.1	1.37	0.352	2.901
41	2.14	25.0	7.87	40.1	3.77	—	—
42	2.08	5.20	1.91	9.6	1.27	0.335	1.196
44	1.99	6.58	2.25	10.3	1.00	0.275	1.000
45	2.10	6.26	2.18	11.3	1.64	0.425	2.064
46	1.97	25.4	7.98	40.3	3.94	—	—
47	2.01	5.51	2.08	10.9	1.63	0.443	3.724
48	2.08	24.6	7.52	40.3	a.f.	—	—
Mean	2.08	25.5	7.98	41.8	3.82	—	—
steady							

Rates of formation of products are given as  $10^{-12}$  mole  $cm^{-3}$   $sec^{-1}$ .  $[C_2H_4]$  is the mean ethylene concentration in  $10^{-6}$  mole  $cm^{-3}$ . The aldehyde concentration was 1.15 in  $10^{-6}$  mole  $cm^{-3}$ . a.f. = analytical failure.

TABLE 2.

The combination of *t*-butyl radicals at 115°.

Run	$[C_2H_4]$	$C_4H_{10}$	$C_4H_8$	CO	$C_6H_{14}$	$[C_4H_9]_i/[C_4H_9]_s$	$\log \lambda$
8	1.39	28.9	7.92	a.f.	4.64	—	—
9	1.41	36.9	6.41	44.3	4.41	—	—
10	1.46	6.38	1.36	11.4	2.11	0.435	2.242
11	1.43	a.f.	a.f.	48.5	4.54	—	—
12	1.46	6.85	1.96	12.3	1.92	0.396	2.478
13	1.40	24.5	a.f.	42.6	4.79	—	—
14	1.43	5.85	2.36	12.6	1.85	0.390	2.748
15	1.50	25.0	a.f.	43.4	4.77	—	—
16	1.41	5.76	1.82	11.0	1.53	0.326	1.188
17	1.54	22.6	6.99	41.7	4.74	—	—
18	1.41	5.36	1.97	10.1	1.23	0.263	1.00
19	1.18	30.8	7.35	47.3	5.01	—	—
20	1.47	5.55	1.90	12.5	2.25	0.462	3.841
21	1.47	23.5	6.22	40.0	4.67	—	—
22	1.50	5.97	2.14	9.6	1.49	0.300	1.282
Mean	1.41	25.9	6.98	44.0	4.70	—	—
steady							

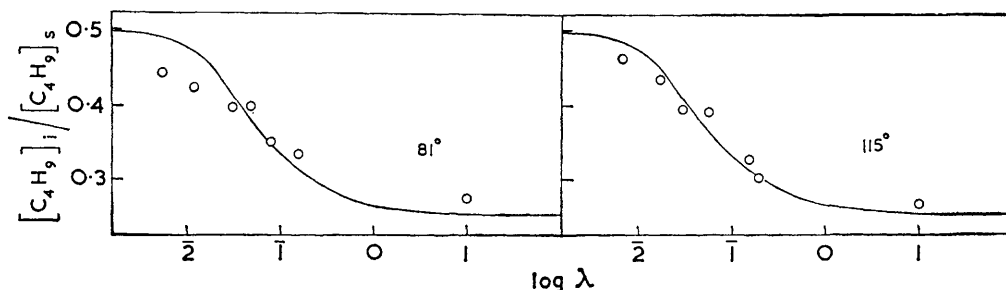
See notes under Table 1. The aldehyde concentration was 1.05 in  $10^{-6}$  mole  $cm^{-3}$ .

centrations of  $0.9-2.1 \times 10^{-6}$  mole  $cm^{-3}$ , determinations of  $k_1$  were made at 81°, 115°, and 159°. Tables 1 and 2 record the conditions, products, and values of  $[C_4H_9]_i/[C_4H_9]_s$  derived from the runs at 81° and 115°. For reasons discussed below, only approximate results are quoted for 159°. The amount of tetramethylbutane formed could not be estimated directly in most runs because of the persistent presence of this compound in the aldehyde. A small sample of aldehyde was purified from this contaminant and a few runs made to check the value of  $k_2/k_1$ . There was reasonable agreement with that of Garcia Dominguez and Trotman-Dickenson.<sup>4</sup> The tetramethylbutane formation was then calculated from that of isobutene. In any case, reaction (6) followed by abstraction of hydrogen produces tetramethylbutane and would complicate its measurement. 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 3 as the uncorrected rate constants. Thus within experimental error there is no temperature coefficient, and  $k_1 = 10^{13.6}$  mole<sup>-1</sup> cm.<sup>3</sup> sec.<sup>-1</sup>.

*Corrections.*—If the only reactions removing t-butyl were (1) and (2), the radical concentration would depend on the square root of the light intensity. This may be studied by means of  $R(C_4H_8)_s^{\frac{1}{2}}$ , for, if isobutene is produced by reaction (2) only, then  $R(C_4H_8)_s^{\frac{1}{2}}/2R(C_4H_8)_i^{\frac{1}{2}}$  should be 1.0. It was about 0.95.

In addition to reactions (1) and (2), t-butyl will be removed by reaction (4) if this is followed by any of reactions (7)—(11). This first-order termination alters the dependence of the radical concentration on the light intensity. Also reaction (7) produces isobutene. In sector runs first-order termination will be favoured. Isobutene from the second-order reaction (2) produced under intermittent and steady illumination should bear the



Curves obtained from rotating sector experiments at 81° and 115°.

ratio 1 : 4, but the first-order termination (7) would produce relatively more isobutene under intermittent illumination. Hence  $2R(C_4H_8)_i^{\frac{1}{2}}$  exceeds  $R(C_4H_8)_s^{\frac{1}{2}}$ .

Reaction (6) is not a termination because most of the dimethylhexyl radical will abstract formyl hydrogen from the aldehyde, regenerating t-butyl. Hexyl concentration is small compared with that of t-butyl; therefore reactions (10) and (11) will be ignored in our further discussion. Hexene could not be detected, therefore reaction (8) cannot be important. A small amount of decane, eluted as the aldehyde began to be eluted, could not have been detected if formed. The following estimation of the first-order termination was made:

$$\text{From (3),} \quad k_3/k_1^{\frac{1}{2}} = \frac{R(C_4H_{10}) (3)}{[Ald] \cdot R(C_8H_{18})^{\frac{1}{2}}}$$

$$\text{and from (5),} \quad k_5/k_{11}^{\frac{1}{2}} = \frac{R(C_6H_{14}) (5)}{[Ald] \cdot R(C_{12}H_{26})^{\frac{1}{2}}}$$

$k_3/k_1^{\frac{1}{2}}$  has been determined;<sup>1</sup>  $k_5/k_{11}^{\frac{1}{2}}$  has not, but it is known that this rate constant ratio is similar for ethyl,<sup>6</sup> propyl,<sup>7</sup> and butyl<sup>1,8-10</sup> radicals and so will probably be about the same for hexyl. For calculations it is assumed that the behaviour of the hexyl radical is intermediate between those of n-butyl<sup>8</sup> and isobutyl.<sup>9</sup> The ratio  $(k_5/k_{11}^{\frac{1}{2}})/(k_3/k_1^{\frac{1}{2}})$  was calculated on this basis, and was 0.60 at 81° and 0.75 at 115°.

$$\text{Thus} \quad [R(C_6H_{14}) (5)]/R(C_{12}H_{26})^{\frac{1}{2}} = [0.6R(C_4H_{10}) (3)]/R(C_8H_{18})^{\frac{1}{2}}.$$

$$\text{Now} \quad R(C_{10}H_{22}) = 2R(C_8H_{18})^{\frac{1}{2}} \cdot R(C_{12}H_{26})^{\frac{1}{2}}.$$

<sup>6</sup> Kerr and Trotman-Dickenson, *J.*, 1960, 1611.

<sup>7</sup> Kerr and Trotman-Dickenson, *Trans. Faraday Soc.*, 1959, **55**, 572, 921.

<sup>8</sup> Kerr and Trotman-Dickenson, *J.*, 1960, 1602.

<sup>9</sup> Metcalf and Trotman-Dickenson, *J.*, 1960, 5072.

<sup>10</sup> Gruver and Calvert, *J. Amer. Chem. Soc.*, 1956, **78**, 5208.

Therefore,  $R(\text{C}_{10}\text{H}_{22}) = \frac{[3 \cdot 35R(\text{C}_6\text{H}_{14}) (5)] \cdot R(\text{C}_8\text{H}_{18})}{R(\text{C}_4\text{H}_{10}) (3)}$  at 81°;

$$R(\text{C}_6\text{H}_{14}) (5) = [R(\text{C}_6\text{H}_{14}) (\text{total})] - [R(\text{C}_6\text{H}_{14}) (7)]$$

$$R(\text{C}_8\text{H}_{18}) = R(\text{C}_4\text{H}_8) (2)/3 \cdot 2$$

$$R(\text{C}_4\text{H}_8) (2) = [R(\text{C}_4\text{H}_8) (\text{total})] - [R(\text{C}_4\text{H}_8) (7)]$$

$$R(\text{C}_4\text{H}_{10}) (3) = [R(\text{C}_4\text{H}_{10}) (\text{total})] - [R(\text{C}_4\text{H}_8) (2)] - [R(\text{C}_4\text{H}_{10}) (b)]$$

Reasonable estimates may be made for the formation of isobutane in the photolytic process (b). The cross-disproportionation ratio,  $\Delta[\text{C}_6\text{H}_{13}, (\text{CH}_3)_3\text{C}]$ , which has not been determined, is assumed to be 0.5, because  $\Delta[\text{C}_2\text{H}_5, (\text{CH}_3)_3\text{C}] = 0.49$ ,<sup>4</sup> and  $\Delta[(\text{CH}_3)_3\text{C}, \text{C}_6\text{H}_{13}]$  is assumed to be 0.3, because  $\Delta[(\text{CH}_3)_3\text{C}, \text{C}_2\text{H}_5] = 0.31$ .<sup>4</sup> This assumption is discussed below. Hence  $R(\text{C}_{10}\text{H}_{22}) = 2R(\text{C}_4\text{H}_8) (7) = 2R(\text{C}_6\text{H}_{14}) (7)$ . This unknown value may now be eliminated.

At each temperature formation of decane under steady illumination was estimated. Hence, first-order termination =  $2 \times 1.8 \times R(\text{C}_{10}\text{H}_{22})$ , since each of the reactions (7)–(9) effectively destroys two *t*-butyl radicals. Therefore

$$\alpha_c = \frac{\text{first-order termination}}{\text{second-order termination}} = \frac{1.8R(\text{C}_{10}\text{H}_{22})_s}{[1.3R(\text{C}_4\text{H}_8)_s (2)]_s}$$

This value was used to derive a new theoretical curve at each temperature, Shepp's<sup>11</sup> modified theory being used which includes a first-order termination.

A small correction was made to the value of  $R(\text{C}_4\text{H}_8)_s$  used in calculating  $\log k_1$ , to allow for  $R(\text{C}_4\text{H}_8)_s (7)$ .

The rate of reaction (4) was followed by measuring the amounts of hexane formed; this estimates hexyl disappearing by reactions (5), (7), and (10). Reaction (11) may be ignored. However, strictly,

$$\frac{[\text{C}_4\text{H}_9]_i}{[\text{C}_4\text{H}_9]_s} = \frac{\{R(\text{C}_6\text{H}_{14}) + [R(\text{C}_8\text{H}_{18}) (6)] + R(\text{C}_6\text{H}_{12}) + R(\text{C}_{10}\text{H}_{22})\}_i}{\{R(\text{C}_6\text{H}_{14}) + [R(\text{C}_8\text{H}_{18}) (6)] + R(\text{C}_6\text{H}_{12}) + R(\text{C}_{10}\text{H}_{22})\}_s}$$

which closely approximates to  $\frac{\{R(\text{C}_6\text{H}_{14}) + R(\text{C}_{10}\text{H}_{22})\}_i}{\{R(\text{C}_6\text{H}_{14}) + R(\text{C}_{10}\text{H}_{22})\}_s}$ .

$[R(\text{C}_8\text{H}_{18}) (6)]$  is small and proportional to  $[R(\text{C}_6\text{H}_{14}) (5)]$ ;  $R(\text{C}_6\text{H}_{12})$  is small and proportional to  $R(\text{C}_{10}\text{H}_{22})$ ; therefore both can be omitted. At each temperature a ratio was calculated from mean rates of hexane and decane formation, which corresponded to a value of 0.375 for hexane 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; this proved to be small.

The rate of radical production was equated to the rate of second-order termination. More accurately,

$$R_{\text{termination}} = (1 + \alpha_c) \text{second-order termination.}$$

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

The isobutene produced by abstraction from the alkyl group of the aldehyde was estimated by using the rate constant for this reaction determined by Birrell and Trotman-Dickenson.<sup>1</sup> At 115° this was negligible; at 159° it was about 10% of the total isobutene formed. This correction had a negligible effect on the calculation of  $\alpha_c$ , but a small correction was made to  $R(\text{C}_4\text{H}_8)_s (2)$  and  $\log k_1$  at 159°.

At 115° no thermal reaction could be detected, but at 159° about 3% of hexane was produced thermally and a correction was made for this. Although the thermal reaction has a marked effect on the rate constant, the exact amount of it was difficult to measure

<sup>11</sup> Shepp, *J. Chem. Phys.*, 1956, **24**, 939.

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accurately because it was so small. Table 3 shows that the value of  $\log k_1$  at 159° is markedly different from the values at lower temperatures. If the amount of thermal reaction were 5—6%, within the limits of experimental error, the value at 159° would be raised by 0.3 log unit. Because of this uncertainty the value at 159° is disregarded.

The rate constants and the corrections applied are summarised in Table 3.

TABLE 3.

Temperature .....	81°	115°	159°
Uncorrected $\log k_1$ .....	13.53	13.57	12.89
$\alpha_c$ .....	0.275	0.285	0.325
First-order termin. corr. ....	-0.82	-0.84	-0.93
Corrn. to $R(\text{C}_4\text{H}_9)_s$ .....	+0.04	+0.04	+0.05
Corrn. to $[\text{C}_4\text{H}_9]_s/[\text{C}_4\text{H}_9]_s$ .....	-0.04	0.00	-0.02
Corrn. to $R(\text{C}_4\text{H}_9)$ .....	-0.22	-0.22	-0.24
Corrn. for $R(\text{C}_4\text{H}_9)$ (chain) .....	—	—	+0.06
Corrn. for thermal reaction .....	—	—	+0.36
Corrected $\log k_1$ .....	12.49	12.55	12.17

The results at 81° and 115° yield an activation energy of 1 kcal. mole<sup>-1</sup>. If this is real, the  $A$  factor is  $10^{13.2}$  mole<sup>-1</sup> cm.<sup>3</sup> sec.<sup>-1</sup>. However, within experimental error the activation energy is zero, and the  $A$  factor for combination may be estimated as  $10^{12.5}$  mole<sup>-1</sup> cm.<sup>3</sup> sec.<sup>-1</sup>.

The corrections applied introduce uncertainty into the rate constant. The calculation of  $\alpha_c$  could be improved if the rate constant ratio  $k_5/k_{11}^{\frac{1}{2}}$ ,  $\Delta[\text{C}_6\text{H}_{13}, (\text{CH}_3)_3\text{C}]$  and  $\Delta[(\text{CH}_3)_3\text{C}, \text{C}_6\text{H}_{13}]$  were determined. However, the values of  $\Delta$  used have relatively little effect on the calculation of  $\alpha_c$ . If  $\Delta[\text{C}_6\text{H}_{13}, (\text{CH}_3)_3\text{C}]$  were halved or doubled,  $\alpha_c$  would be changed by only 0.03. The values of  $\alpha_c$  used yielded modified theoretical curves with upper limits in good agreement with those found experimentally. This shows that no other first-order termination, such as  $\text{C}_4\text{H}_9\cdot + \cdot\text{CHO} \rightarrow \text{C}_4\text{H}_9\text{-CHO}$  takes place to a significant extent. The ratio  $R(\text{C}_4\text{H}_9)_s/2R(\text{C}_4\text{H}_9)_i$  approximates closely to unity if the isobutene only from the second-order reaction (2) is considered.

If a collision diameter of 5.20 Å is assumed for t-butyl (that calculated by Rowlinson<sup>12</sup> for isobutane), then the collision rate at 115° is  $10^{14.14}$  mole<sup>-1</sup> cm.<sup>3</sup> sec.<sup>-1</sup>. The experimental rate of bimolecular termination at 115°, including combination and disproportionation, is  $10^{13.17}$  mole<sup>-1</sup> cm.<sup>3</sup> sec.<sup>-1</sup>, giving a steric factor of about 0.1 if the activation energy is zero. This is the smallest steric factor yet found for an alkyl-radical combination, and such a bulky radical may well have steric requirements for combination. This low steric factor suggests that disproportionation proceeds through the same activated complex as combination, because a "head-to-tail" mechanism would have less stringent steric requirements.

This determination of  $k_1$  leaves unaltered the activation energies of the reactions of t-butyl, determined by Birrell and Trotman-Dickenson.<sup>1</sup> However the  $A$  factors of these reactions will be decreased by 1.5 log units. This gives the more credible  $A$  factors of  $10^{14.8}$  and  $10^{14.5}$  sec.<sup>-1</sup> for the radical decompositions. It also follows that abstraction of the formyl-hydrogen of the aldehyde by t-butyl proceeds more slowly than the analogous abstraction by other alkyl radicals. This is to be expected because the bond formed in isobutane is relatively weak, whereas the bond broken is similar in each case.

The rate constants of radical combinations are thermodynamically related to those of the symmetrical decompositions of alkanes. The relative values of the  $A$  factors for combination and decomposition can be found from the overall entropy change.<sup>13</sup> Because it is difficult to measure temperature coefficients,  $A$  factors for combination are equated to the rate constants at 100°. The entropy of the radicals is assumed to be the same as that of the hydrocarbon with one more hydrogen atom (almost certainly an underestimate by

<sup>12</sup> Rowlinson, *Quart. Rev.*, 1954, **8**, 168

<sup>13</sup> Trotman-Dickenson, *J. Chem. Phys.*, 1953, **21**, 211.

2—4 cal. mole<sup>-1</sup> deg.<sup>-1</sup>). Hence it is calculated that log  $A$  (sec.<sup>-1</sup>) for the symmetrical decompositions of ethane, n-butane, 2,3-dimethylbutane, and 2,2,3,3-tetramethylbutane are 16.3, 16.6, 18.5, and 18.5, respectively. The rate constants for the combinations are those of Kistiakowsky and Roberts<sup>14</sup> corrected by Shepp<sup>11</sup> for methyl, of Shepp and Kutschke<sup>15</sup> for ethyl, of Metcalfe and Trotman-Dickenson<sup>3</sup> for isopropyl, and of the present work for t-butyl. Estimates of the entropies of the radicals after allowance for electron degeneracy would raise these values by 0.6 unit.

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<sup>14</sup> Kistiakowsky and Roberts, *J. Chem. Phys.*, 1953, **21**, 1637.

<sup>15</sup> Shepp and Kutschke, *J. Chem. Phys.*, 1957, **26**, 1020.

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