3560

Metcalfe: The Absolute Rate of

671. The Absolute Rate of Combination of the t-Butyl Radical. By Eileen L. Metcalfe.

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 $10^{12\cdot5}$ mole⁻¹ cm.³ sec.⁻¹. A first-order termination correction was applied.

BIRRELL and TROTMAN-DICKENSON¹ studied the reactions of t-butyl produced by photoinitiated chain decomposition of pivalaldehyde. 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 this constant. It is the first absolute rate constant of a tertiary alkyl radical to be studied.

¹ Birrell and Trotman-Dickenson, J., 1960, 4218.

Combination of the t-Butyl Radical. 3561 [1963]

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.² They deduce the variation of $[rad]_i/[rad]_s$ 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:

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

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

$$m = \lambda / \tau_{\rm s},$$
 (2)

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

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

Therefore the displacement between the two curves is a measure of τ_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.³ 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 pivaladehyde there are two reactions which destroy radicals, the combination of t-butyl to give 2,2,3,3-tetramethylbutane:

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

and the disproportionation:

$$2C_4H_9 \xrightarrow{k_s} C_4H_{10} + C_4H_8 \tag{ii}$$

From reaction (i),

$$R(C_8H_{18}) = k_1[C_4H_9]^2,$$
(4)

where $R(C_8H_{18})$ is the rate of formation of C_8 -hydrocarbon.

Now
$$[C_4H_9]_s = \tau_s \cdot R(C_4H_9)_s.$$
 (5)

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

Therefore,

$$R(C_{4}H_{9})_{s} = 2\{R(C_{8}H_{18})_{s} + R(C_{4}H_{8})_{s}\}$$

$$= 2 \times 1.31R(C_{4}H_{8})_{s}$$
(6)

since $k_2/k_1 = 3.20$. This value, obtained by Garcia Dominguez and Trotman-Dickenson,⁴ using both aldehyde and ketone sources of t-butyl, is preferred to the higher values of Birrell and Trotman-Dickenson¹ and Kraus and Calvert.⁵ Adjustment would be simple if further information supported the higher value.

Hence
$$k_1 = 1/\{21.97\tau_s^2 . R(C_4H_8)_s\}.$$
 (7)

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

³ Melville and Burnett, "Technique of Organic Chemistry," Interscience Publ. Inc., New York, 1953, Vol. VIII, p. 138.

³ Metcalfe and Trotman-Dickenson, J., 1962, 4620. ⁴ Garcia Dominguez and Trotman-Dickenson, J., 1962, 3357.

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

Metcalfe: The Absolute Rate of

Experimental.—Pivalaldehyde (Koch Laboratories) was purified by wide-bore gas chromatography. The columns (450 or 150×2.5 cm.) were packed with 35% of polyethylene glycol 400 on firebrick, and were heated at 80°. 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.³ The analysis of the condensable fraction of the products was made on two columns (60×0.5 cm.) and (40×0.5 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° to 120° in 30 min.

RESULTS AND DISCUSSION

The reaction scheme has already been investigated 1 and the principal reactions below 160° are:

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

$$2C_4H_3 \cdot \xrightarrow{k_1} C_8H_{18} \tag{1}$$

$$2C_4H_9 \cdot \xrightarrow{k_8} C_4H_{10} + C_4H_8 \tag{2}$$

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

$$C_4H_9 \cdot CO \cdot \longrightarrow C_4H_9 \cdot + CO \tag{30}$$

$$C_4H_9 + C_2H_4 \xrightarrow{\gamma_4} C_6H_{13}$$
 (4)

$$C_{6}H_{13} + C_{4}H_{3} CHO \xrightarrow{\sim_{6}} C_{6}H_{14} + C_{4}H_{9} CO$$
(5)

$$C_6H_{13} + C_2H_4 \xrightarrow{\sim} C_8H_{17}$$
 (6)

$$C_6H_{13} + C_4H_9 \cdot \overset{\kappa_7}{\longrightarrow} C_6H_{14} + C_4H_8 \tag{7}$$

$$C_{6}H_{13} + C_{4}H_{9} \cdot \xrightarrow{\gamma_{3}} C_{6}H_{12} + C_{4}H_{10}$$
(8)

$$C_6H_{13} + C_4H_9 \xrightarrow{\bullet} C_{10}H_{22} \tag{9}$$

$$2C_{6}H_{13} \xrightarrow{k_{10}} C_{6}H_{14} + C_{6}H_{12}$$
(10)

$$2C_6H_{13} \xrightarrow{\kappa_{11}} C_{12}H_{26} \tag{11}$$

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

Hence

$$\frac{R(C_{6}H_{14}) = k_{4}[C_{4}H_{9}][C_{2}H_{4}]}{[C_{4}H_{9}]_{s}} = \frac{R(C_{6}H_{14})_{i}[C_{2}H_{4}]_{s}}{R(C_{6}H_{14})_{s}[C_{2}H_{4}]_{s}}$$

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 $R(C_6H_{14})$ and $[C_2H_4]$ from the steady runs. Aldehyde consumption did not exceed 5%, or ethylene consumption 1%.

[1963]

Combination of the t-Butyl Radical.

3563

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

$$\log k_1 = 12 - \log 21.97 - 2 \log \tau_s - \log R(C_4 H_8)_s,$$

since $R(C_4H_9)_8$ 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.
TUDDD	

The combination of t-butyl radicals at 81°.

				•			
Run	$[C_2H_4]$	C_4H_{10}	C_4H_8	CO	$C_{6}H_{14}$	$[C_4H_{\mathfrak{g}\mathfrak{i}}]/[C_4H_{\mathfrak{g}}]_s$	log λ
35	2.13	28.5	9· 1 3	42.3	3.91		
36	2.09	6.98	$2 \cdot 12$	11.0	1.52	0.397	$\bar{2} \cdot 484$
37	2.08	$26 \cdot 2$	7.93	40.1	3.75		
38	2.06	5.98	1.94	11.2	1.51	0.398	$\bar{2} \cdot 661$
39	$2 \cdot 10$	23.5	7.43	46.2	3.73		
40	2.13	6.15	$2 \cdot 11$	11.1	1.37	0.352	$\bar{2} \cdot 901$
41	2.14	25.0	7.87	40.1	3.77		
$\bar{42}$	2.08	5.20	1.91	9.6	1.27	0.332	ī ∙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	$\bar{2} \cdot 064$
46	1.97	25.4	7.98	40.3	3.94		
47	$\hat{2} \cdot \hat{0} \hat{1}$	5.51	2.08	10.9	1.63	0.443	$\bar{3}.724$
48	2.08	24.6	7.52	40.3	a.f.		
Mean	2.08	25.5	7.98	41.8	3.82		
steady	2 00	0					

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.

The combination of t-butyl radicals at 115°. $[C_{\boldsymbol{4}}H_{\boldsymbol{9}}]_i/[C_{\boldsymbol{4}}H_{\boldsymbol{9}}]_s$ Run $[C_2H_4]$ C_4H_8 CO C_6H_{14} log λ C4H10 28.97.921.394.648 a.f. _ ____ 4.41 9 1.41 36.96.4144.30.4352.24210 2.111.461.3611.4 6.381.4311 a.f. a.f. 48.54.542.47812.30.39612 1.466.851.961.9213 1.4024.5a.f. 42.64.79 $\bar{2}.748$ 14 1.435.852.3612.61.850.390151.5025.043.4 4.77a.f. 5.761.530.326Ī·188 16 1.41 1.8211.0 171.5422.66.9941.74.741.41 5.361.9710.11.230.2631.00 18 19 1.1830.87.3547.35.010.4623.841 20 1.475.551.9012.52.25 $\mathbf{21}$ 23.51.476.2240.04.67 $\mathbf{22}$ 0.300 1.2821.505.972.149.6 1.49 Mean 1.41 $25 \cdot 9$ 6.98**44**.0 4.70steady

TABLE 2.

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.⁴ 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⁻¹ cm.³ sec.⁻¹.

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 $R(C_4H_8)^{\frac{1}{2}}$, for, if isobutene is produced by reaction (2) only, then $R(C_4H_8)_{s^{\frac{1}{2}}}/2R(C_4H_8)_{i^{\frac{1}{3}}}$ 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 sectored runs first-order termination will be favoured. Isobutene from the secondorder 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 $2R(C_4H_8)_1^{\frac{1}{2}}$ exceeds $R(C_4H_8)_8^{\frac{1}{2}}$.

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:

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

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

 $k_3/k_1^{\frac{1}{2}}$ has been determined; $k_5/k_{11}^{\frac{1}{2}}$ has not, but it is known that this rate constant ratio is similar for ethyl,⁶ propyl,⁷ and butyl ^{1,8-10} 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-butyl⁸ and isobutyl.⁹ 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° .

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

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

Now

- Kerr and Trotman-Dickenson, J., 1960, 1611. Kerr and Trotman-Dickenson, Trans. Faraday Soc., 1959, 55, 572, 921.
- ⁸ Kerr and Trotman-Dickenson, J., 1960, 1602.
- Metcalfe and Trotman-Dickenson, J., 1960, 5072.
 Gruver and Calvert, J. Amer. Chem. Soc., 1956, 78, 5208.

[1963]

Combination of the t-Butyl Radical.

ore,
$$\begin{aligned} R(C_{10}H_{22}) &= \frac{[3\cdot35R(C_{6}H_{14})\ (5)] \cdot R(C_{8}H_{18})}{R(C_{4}H_{10})\ (3)} \text{ at } 81^{\circ}; \\ R(C_{6}H_{14})\ (5) &= [R(C_{6}H_{14})\ (total)] - [R(C_{6}H_{14})\ (7)] \\ R(C_{8}H_{18}) &= R(C_{4}H_{8})\ (2)/3\cdot2 \\ R(C_{4}H_{8})\ (2) &= [R(C_{4}H_{8})\ (total)] - [R(C_{4}H_{8})\ (7)] \\ R(C_{4}H_{10})\ (3) &= [R(C_{4}H_{10})\ (total)] - [R(C_{4}H_{8})\ (2)] - [R(C_{4}H_{10})\ (b)] \end{aligned}$$

Reasonable estimates may be made for the formation of isobutane in the photolytic process (b). The cross-disproportionation ratio, $\Delta[C_6H_{13}, (CH_3)_3C]$, which has not been determined, is assumed to be 0.5, because $\Delta[C_2H_5, (CH_3)_3C] = 0.49.4$ and $\Delta[(CH_3)_3C, C_6H_{13}]$ is assumed to be 0.3, because $\Delta[(CH_3)_3C, C_2H_5] = 0.31.4$ This assumption is discussed below. Hence $R(C_{10}H_{22}) = 2R(C_4H_8)$ (7) = $2R(C_6H_{14})$ (7). This unknown value may now be eliminated.

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

$$\alpha_{\rm c} = \frac{\text{first-order termination}}{\text{second-order termination}} = \frac{1 \cdot 8R(C_{10}H_{22})_{\rm s}}{[1 \cdot 3R(C_4H_8)_{\rm s}(2)]_{\rm s}}$$

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

A small correction was made to the value of $R(C_4H_8)_s$ used in calculating log k_1 , to allow for $R(C_4H_8)_s$ (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,

$$\frac{[C_4H_9]_i}{[C_4H_9]_s} = \frac{\{R(C_6H_{14}) + [R(C_8H_{18}) (6)] + R(C_6H_{12}) + R(C_{10}H_{22})\}_i}{\{R(C_6H_{14}) + [R(C_8H_{18}) (6)] + R(C_6H_{12}) + R(C_{10}H_{22})\}_s}$$

which closely approximates to $\frac{\{R(C_{6}H_{14}) + R(C_{10}H_{22})\}_{i}}{\{R(C_{6}H_{14}) + R(C_{10}H_{22})\}_{s}}$

 $[R(C_8H_{18})$ (6)] is small and proportional to $[R(C_6H_{14})$ (5)]; $R(C_6H_{12})$ is small and proportional to $R(C_{10}H_{22})$; 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,

$$R_{\text{termination}} = (1 + \alpha_c)$$
 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.¹ 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 α_c , but a small correction was made to $R(C_4H_8)_s$ (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

¹¹ Shepp, J. Chem. Phys., 1956, 24, 939.

3566 The Absolute Rate of Combination of the t-Butyl Radical

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
α _c	0.275	0.285	0.325
First-order termin. corrn.	-0.82	-0.84	-0.93
Corrn. to $R(C_4H_8)_8$	+0.04	+0.04	+0.02
Corrn. to $[C_4H_9]_1/[C_4H_9]_8$	-0.04	0.00	-0.05
Corrn. to $R(C_3H_7)$	-0.22	-0.22	-0.24
Corrn. for $R(C_4H_8)$ (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⁻¹. If this is real, the A factor is $10^{13\cdot2}$ mole⁻¹ cm.³ sec.⁻¹. However, within experimental error the activation energy is zero, and the A factor for combination may be estimated as $10^{12\cdot5}$ mole⁻¹ cm.³ sec.⁻¹.

The corrections applied introduce uncertainty into the rate constant. The calculation of α_c could be improved if the rate constant ratio k_5/k_{11}^{\dagger} , $\Delta[C_6H_{13}, (CH_3)_3C]$ and $\Delta[(CH_3)_3C, C_6H_{13}]$ were determined. However, the values of Δ used have relatively little effect on the calculation of α_c . If $\Delta[C_6H_{13}, (CH_3)_3C]$ were halved or doubled, α_c would be changed by only 0.03. The values of α_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 $C_4H_9 \cdot + \cdot CHO \longrightarrow C_4H_9 \cdot CHO$ takes place to a significant extent. The ratio $R(C_4H_8)^{\frac{1}{5}}/2R(C_4H_8)^{\frac{1}{5}}$ approximates closely to unity if the isobutene only from the second-order reaction (2) is considered.

If a collision diameter of $5 \cdot 20$ Å is assumed for t-butyl (that calculated by Rowlinson ¹² for isobutane), then the collision rate at 115° is $10^{14\cdot14}$ mole⁻¹ cm.³ sec.⁻¹. The experimental rate of bimolecular termination at 115° , including combination and disproportionation, is $10^{13\cdot17}$ mole⁻¹ cm.³ sec.⁻¹, 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.¹ 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.⁻¹ 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.¹³ 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

¹³ Trotman-Dickenson, J. Chem. Phys., 1953, 21, 211.

¹² Rowlinson, Quart. Rev., 1954, 8, 168

[1963]

Chipperfield and Prince.

2—4 cal. mole⁻¹ deg.⁻¹). Hence it is calculated that log A (sec.⁻¹) 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 ¹⁴ corrected by Shepp ¹¹ for methyl, of Shepp and Kutschke ¹⁵ for ethyl, of Metcalfe and Trotman-Dickenson ³ 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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[Received, December 29th, 1962.]

¹⁴ Kistiakowsky and Roberts, J. Chem. Phys., 1953, 21, 1637.
 ¹⁵ Shepp and Kutschke, J. Chem. Phys., 1957, 26, 1020.