

324. The Reactions of Alkyl Radicals. Part IV.* The Reaction of Methyl Radicals with Isopropyl and *t*-Butyl Radicals.*

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The rates of formation of ethane, propene, and isobutane, and ethane, isobutene, and neopentane, in the photolysis of mixtures of acetone with isopropyl methyl ketone and pinacolone, respectively, have been determined. The ratio of the rate constant for the cross-disproportionation of methyl and isopropyl radicals to that for combination is 0.22; the similar ratio for *t*-butyl is 0.70. The significance of these findings is discussed.

THE autodisproportionation of ethyl, propyl, and butyl radicals has been extensively studied.¹ The results are usually expressed in terms of the ratio of the rate constant for disproportionation (k_d) to that for combination (k_c); k_d/k_c (referred to herein as Δ) is usually known as the disproportionation ratio. Although the effect of the internal energy of the radicals on the ratio Δ is not understood, there is good agreement between different groups of workers on the magnitude of the ratio for radicals in thermal equilibrium with their environment. The agreement is particularly satisfactory between results obtained by the photolysis of ketones and of aldehydes. Little is, however, known about Δ for unlike radicals and some of the values that have been reported appear doubtful. Only $\Delta(\text{Me}, \text{Et})$ which refers to the two reactions $\text{CH}_3 + \text{C}_2\text{H}_5 \rightleftharpoons \text{CH}_4 + \text{C}_2\text{H}_4$ and $\text{CH}_3 + \text{C}_2\text{H}_5 \rightleftharpoons \text{C}_3\text{H}_8$ has been reliably measured. The best value² is 0.06. We have now measured $\Delta(\text{Me}, \text{Pr}^i)$ and $\Delta(\text{Me}, \text{Bu}^t)$.

The radicals were produced by the photolysis of a mixture of acetone and either isopropyl methyl ketone or pinacolone.

$\Delta(\text{Me}, \text{Pr}^i)$ was then found in the following way:

The rate of combination of methyl radicals is given by

$$R_{\text{C}_2\text{H}_6} = k_1[\text{CH}_3]^2 \quad \dots \quad (1)$$

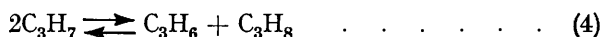
where $R_{\text{C}_2\text{H}_6}$ is the rate of formation of ethane. Furthermore,

$$R_{\text{C}_4\text{H}_{10}} = k_2[\text{C}_3\text{H}_7]^2 \quad \dots \quad (2)$$

and

$$R_{\text{C}_4\text{H}_{10}} = k_3[\text{CH}_3][\text{C}_3\text{H}_7] \quad \dots \quad (3)$$

Propene is formed both by autodisproportionation (4) and cross-disproportionation (5).



and



Hence

$$R_{\text{C}_3\text{H}_6} = k_4[\text{C}_3\text{H}_7]^2 + k_5[\text{CH}_3][\text{C}_3\text{H}_7]$$

It was not convenient to measure the rate of formation of hexane, which was found by the following method. It can be seen that $k_3/(k_1k_2)^{1/2} = R_{\text{C}_4\text{H}_{10}}/(R_{\text{C}_2\text{H}_6}R_{\text{C}_3\text{H}_6})^{1/2}$. Now this ratio can be taken as 2 because all the most reliable determinations of the rates of cross-combination of radicals approximate closely to this value; for instance, 1.9³, 2.0² (Me + Et); 1.9⁴ (Et + Prⁿ); 2.05⁵, 2.6 (Et + Prⁱ); 2.07 (Prⁿ + Buⁿ). Hence $R_{\text{C}_4\text{H}_{10}} = R_{\text{C}_2\text{H}_6}^{1/2} R_{\text{C}_3\text{H}_6}^{1/2} / 4R_{\text{C}_3\text{H}_7}$, which is equal to $k_4R_{\text{C}_3\text{H}_6}/k_2$, is found from the known^{5,8}

* Part III, preceding paper.

¹ For a review see Trotman-Dickenson, *Ann. Reports*, 1959, **55**, 36.

² Heller, *J. Chem. Phys.*, 1958, **28**, 1255.

³ Ausloos and Steacie, *Canad. J. Chem.*, 1955, **33**, 1062.

⁴ Kerr and Trotman-Dickenson, *Trans. Faraday Soc.*, 1959, **55**, 572.

⁵ *Idem, ibid.*, p. 921.

⁶ Wijnen, *Canad. J. Chem.*, 1958, **36**, 691.

⁷ Kerr and Trotman-Dickenson, *J.*, 1959, preceding paper.

⁸ Heller and Gordon, *J. Phys. Chem.*, 1956, **60**, 1315.

value (0.64) of k_4/k_2 . $k_5[\text{CH}_3][\text{C}_3\text{H}_7]$ is then found by subtraction, and the required ratio from the formula $\Delta(\text{Me}, \text{Pr}^i) = k_5/k_3 = (R_{\text{C}_3\text{H}_7} - 0.64R_{\text{C}_3\text{H}_7})/R_{\text{C}_3\text{H}_7}$. The results so obtained are shown in Table 1; those obtained for the cross-disproportionation of methyl and t-butyl by similar methods are shown in Table 2. $[\Delta(\text{Bu}^t, \text{Bu}^t)]$ was taken⁹ as 4.59.]

TABLE 1. *The photolysis of mixtures of acetone and isopropyl methyl ketone.* (All concentrations are in $\mu\text{mole cm.}^{-3}$ and all rates of formation in 10^{-12} mole cm.^3 sec.⁻¹.)

Temp. (°C)	80°	91°	104°	114°	146°	150°
Time (sec.)	1800	1500	1800	2400	1800	1500
Me ₂ CO	2.53	2.26	2.22	1.48	1.89	1.85
MeCOPr ⁱ	0.930	1.06	0.865	1.05	0.920	1.00
C ₂ H ₆	18.1	21.8	30.2	23.7	24.6	23.4
C ₃ H ₈ (total)	3.42	3.01	3.30	3.55	3.49	4.03
C ₄ H ₁₀	10.9	11.1	13.4	12.6	10.5	12.1
C ₃ H ₈ (auto)	1.05	0.91	0.95	1.06	0.72	1.00
C ₃ H ₈ (cross)	2.37	2.10	2.35	2.49	2.77	3.03
$\Delta(\text{Me}, \text{Pr}^i)$	0.218	0.189	0.175	0.198	0.264	0.254

$$\text{Mean } \Delta(\text{Me}, \text{Pr}^i) = 0.216 \pm 0.032.$$

TABLE 2. *The photolysis of mixtures of acetone and pinacolone.* (All concentrations are in $\mu\text{mole cm.}^{-3}$ and all rates of formation in 10^{-12} mole cm.^3 sec.⁻¹.)

Temp. (°C)	80°	98°	129°	152°	188°
Time (sec.)	1800	2040	2100	1860	1800
Me ₂ CO	4.44	4.07	3.55	3.45	3.08
MeCOBu ^t	1.19	1.14	1.08	0.973	0.903
C ₂ H ₆	36.8	58.3	56.5	58.8	39.2
C ₄ H ₈ (total)	10.8	10.8	10.6	9.65	9.75
C ₅ H ₁₂	10.4	11.2	11.9	10.9	9.75
C ₄ H ₈ (auto)	3.36	2.48	2.88	2.32	2.79
C ₄ H ₈ (cross)	7.44	8.32	7.72	7.33	6.96
$\Delta(\text{Me}, \text{Bu}^t)$	0.715	0.743	0.650	0.672	0.715

$$\text{Mean } \Delta(\text{Me}, \text{Bu}^t) = 0.699 \pm 0.037.$$

In all runs the acetone was in considerable excess. This precaution reduced the size of the second term of the numerator, which is equal to the expression olefin(auto) in the Tables. Hence, small errors in the rate constants for cross-combination and auto-disproportionation have little effect on the final value of $\Delta(\text{Me}, \text{Alk})$.

The values of $\Delta(\text{Me}, \text{Alk})$ bear a simple relation to those for $\Delta(\text{Alk}, \text{Alk})$. In an ethyl radical there are three hydrogen atoms available for removal by disproportionation, whereas in isopropyl there are six, and in t-butyl nine. The values of Δ may be simply reduced to the same standard by division by the number of available hydrogens with the result shown in Table 3. The plot of $\log \Delta(\text{Me}, \text{Alk})$ against $\log \Delta(\text{Alk}, \text{Alk})$ is a good

TABLE 3. *Autodisproportionation and cross-disproportionation.*

Radical	Available H atoms	$\Delta(\text{Me}, \text{Alk})$	$\frac{\Delta(\text{Me}, \text{Alk})}{ \text{H} }$	$\Delta(\text{Alk}, \text{Alk})$	$\frac{\Delta(\text{Alk}, \text{Alk})}{ \text{H} }$
Et	3	0.06	0.02	0.13	0.043
Pr ⁱ	6	0.22	0.036	0.65	0.11
Bu ^t	9	0.70	0.078	4.6	0.51

straight line, though much importance should not be attached to this fact because there are only three points comparatively close together and the experimental errors are considerable. The fact that the slope is close to one-half (0.55) is of greater significance. It implies that the same factors that make t-butyl lose a hydrogen atom readily also make it equally ready to acquire a hydrogen atom. This does not involve a contradiction but it is surprising because it implies that t-butyl abstracts a hydrogen more readily than does ethyl which forms a stronger C-H bond. The slope of $\frac{1}{2}$ may indicate that in the activated complex it is not certain which of the two t-butyl radicals is to lose and which to gain a

⁹ Kraus and Calvert, *J. Amer. Chem. Soc.*, 1957, **79**, 5921.

hydrogen atom. This might occur if the radicals in the complex were loosely held together but rotated freely. It has been possible to explain the absolute A factors for the combination of methyl and the combination (and disproportionation) of ethyl radicals only by assuming complexes of this type.¹⁰

More information on cross-disproportionations must be obtained before the properties of the activated complexes can be deduced with certainty. The only extensive record is that by Boddy and Robb.¹¹ They chose a very complicated source of radicals, the mercury-photosensitized addition of hydrogen atoms to alkenes. They were therefore forced to follow the rates of disproportionation by following the rates of formation of alkanes, whereas it is more satisfactory to estimate alkenes that are unlikely to be formed in side reactions. Further difficulties arose because the addition of a hydrogen atom yields a highly activated radical. The $\Delta(\text{Alk}, \text{Alk})$ values obtained with ethyl and isopropyl did not agree very well with accepted values and the value for t-butyl did not agree at all. These $\Delta(\text{Alk}, \text{Alk})$ values had to be used to determine the cross-disproportionation values. The general reproducibility of the results does not appear to have been good, but the authors give insufficient data to permit proper tests of consistency. It is not therefore surprising that the results do not show any regularity such as that reported here.

EXPERIMENTAL

The apparatus and analytical techniques were essentially the same as those previously described in this series of papers. The light source was a 250 w medium-pressure mercury arc that gave a slightly higher light intensity than the 125 w arc, used previously. The condensable gases were analysed on a column (300 cm.) of firebrick (52—72 mesh)—20% of nitrobenzene. The flow rate of carrier gas (hydrogen) was 20 cm.³/min.

The pinacolone was carefully distilled and all the ketones were tested by gas chromatography.

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¹⁰ Marcus, *J. Chem. Phys.*, 1952, **20**, 364; Kistiakowsky and Roberts, *J. Chem. Phys.*, 1953, **21**, 1637; Ivin and Steacie, *Proc. Roy. Soc.*, 1951, *A*, **208**, 25; Trotman-Dickenson, *J. Chem. Phys.*, 1953, **21**, 211.

¹¹ Boddy and Robb, *Proc. Roy. Soc.*, 1959, *A*, **249**, 518.