663. *The Reactions of Alkyl Radicals. Part X.* The Disproportionation of Ethyl, Isopropyl, and t-Butyl Radicals.*

By J. A. Garcia Dominguez, J. A. Kerr, and A. F. Trotman-Dickenson.

The rates of all possible cross-disproportionation reactions between these radicals have been measured relative to their rates of cross-combination. The auto-disproportionation ratio of t-butyl has been found to be 3·2 which is lower than the previously accepted value.

When a mixture of di-isopropyl and di-t-butyl ketones is photolysed the following reactions occur:

$$
\begin{aligned}
(C_4H_9)_2CO + h\nu &= 2C_4H_9 + CO \\
(C_3H_7)_2CO + h\nu &= 2C_3H_7 + CO \\
2C_4H_9 &= C_8H_{18} && (1)\\
2C_3H_7 &= C_6H_{14} && (2)\\
C_4H_9 + C_3H_7 &= C_7H_{16} && (3)\\
2C_4H_9 &= C_4H_{10} + C_4H_8 && (4)\\
2C_3H_7 &= C_3H_8 + C_3H_6 && (5)\\
C_4H_9 + C_3H_7 &= C_4H_{10} + C_3H_6 && (6)\\
C_3H_7 + C_4H_9 &= C_3H_8 + C_4H_8 && (7)\\
C_4H_9 + (C_4H_9)_2CO &= C_4H_{10} + C_4H_9{\cdot}CO{\cdot}C_4H_8 \\
C_3H_7 + (C_4H_9)_2CO &= C_3H_8 + C_4H_9{\cdot}CO{\cdot}C_4H_8 \\
C_4H_9 + (C_3H_7)_2CO &= C_4H_{10} + C_3H_7{\cdot}CO{\cdot}C_3H_6 \\
C_3H_7 + (C_3H_7)_2CO &= C_3H_8 + C_3H_7{\cdot}CO{\cdot}C_3H_6
\end{aligned}
$$

A number of other reactions involving the ketone radicals must also occur but these do not affect the products measured in this study. Several relations of interest can be obtained from analyses of the hydrocarbon products.

Cross-combination.—The mechanism predicts that

$$
\begin{aligned}
\frac{R(\text{heptane})}{R^{\frac{1}{2}}(\text{hexane})\,.\,R^{\frac{1}{2}}(\text{octane})} &= \frac{k_3[C_4H_9][C_3H_7]}{k_2^{\frac{1}{2}}[C_3H_7]\,.\,k_1^{\frac{1}{2}}[C_4H_9]} \\
&= k_3/(k_1k_2)^{\frac{1}{2}},
\end{aligned}
$$

where R(heptane) is the rate of formation of heptane. According to the simple collision theory of kinetics this ratio should equal 2, and it has been found to be so for many pairs of radicals.[1]

Auto-disproportionation.—When di-t-butyl ketone is photolysed alone, the mechanism predicts that

$$R(\text{isobutene})/R(\text{octane}) = k_4/k_1.$$

This ratio is often known as the disproportionation ratio and can be written $\Delta(\text{Bu}^t,\text{Bu}^t)$. If the rate of reaction of t-butyl with the ketone is low and can be estimated with fair accuracy, then $\Delta(\text{Bu}^t,\text{Bu}^t)$ can also be found from measurements of R(isobutane); it has here been assumed that the rate of reaction is zero.

Cross-disproportionation.—The rates of reactions (6) and (7) relative to that of reaction (3) can be found from the relations:

$$k_6/k_3 = [R(\text{total propene}) - R(\text{propene from 5})]/R(\text{heptane}),$$

and

$$k_7/k_3 = [R(\text{total isobutene}) - R(\text{isobutene from 4})]/R(\text{heptane}).$$

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* Part IX, Garcia Dominguez and Trotman-Dickenson, *J.*, 1962, 940.

[1] Kerr and Trotman-Dickenson, " Progress in Reaction Kinetics," Pergamon, Oxford, 1961, p. 105.

The amounts of alkene from reactions (5) and (4) can be obtained if the autodisproportionation ratios have previously been determined and the rate of formation of the appropriate alkyl dimer has been measured. The ratios k_6/k_3 and k_7/k_3 can conveniently be designated $\Delta(\mathrm{Bu^t,Pr^i})$ and $\Delta(\mathrm{Pr^i,Bu^t})$; this notation will be employed throughout the following discussion.

The values adopted for $\Delta(\mathrm{Et,Et})$ and $\Delta(\mathrm{Pr^i,Pr^i})$ are 0·15 and 0·65, respectively. The latter value was redetermined in the course of this study in checking the calibration of the chromatography system. A value of 0·61 was found from four runs.

The results obtained in this investigation are given in Tables 1—4. The reproducibility of the runs is better than is usually found in investigations of this type. The value for $\Delta(\mathrm{Bu^t,Bu^t})$ is, on these grounds, preferred to the two best values of 4·59 [2] and 4·38,[3] though they are themselves in fair agreement. The reason for the discrepancy is not clear and one is driven to conclude that errors may have been made in the calibration of the chromatographic detectors. This can occur for isolated compounds. In the present work with isopropyl and t-butyl radicals self-consistent calibrations were obtained for hexane, heptane, and octane with standard samples. The closeness of the three cross-combination

TABLE 1.

Disproportionation of t-butyl radicals.

Run *	Temp. (°K)	Time (sec.)	DTBK or TMA †	iso-C_4H_{10} §	iso-C_4H_8 §	C_8H_{18} §	$\Delta(\mathrm{Bu^t,Bu^t})$	
							alkene	alkane
9K	323·3	900	3·2	44·3	40·8	14·5	2·81	3·05
10K	345·5	900	3·1	a.f.	41·0	13·1	3·14	—
11K	350·3	900	2·4	27·7	27·3	8·54	3·20	3·25
12K	349·8	900	2·6	27·0	28·1	9·28	3·03	2·92
15K	349·2	900	2·6	27·0	27·0	8·00	3·38	3·38
17K	350·0	240	12·6	213·4	203·2	72·9	2·79	2·93
19K	351·1	900	5·4	a.f.	52·2	16·7	3·13	—
						Mean value	3·07	
58KP ‡	351·7	3600	5·2	2·95	3·07	1·02	3·02	2·90
60KP	350·3	10,800	4·9	2·06	1·97	0·616	3·21	3·34
63KP ‡	351·3	21,600	5·2	2·77	2·65	0·785	3·38	3·53
						Mean value	3·20	
47A	353·0	900	11·9	—	20·9	6·37	3·28	—
64A ‡	347·9	1800	33·7	—	15·7	5·01	3·12	—
66A ‡	347·8	1800	32·0	—	27·8	8·33	3·34	—
67A ‡	346·8	900	49·5	—	50·8	15·1	3·36	—
68A ‡	346·4	900	52·5	—	53·3	16·0	3·33	—
						Mean value	3·29	
						Overall mean values	3·19	3·16

* K, runs done with di-t-butyl ketone; A, runs done with pivalaldehyde; P, actinic light filtered through Pyrex glass. † DTBK or TMA, di-t-ketone or pivalaldehyde (10^{-6} mole c.c.$^{-1}$). ‡ denotes a reflector placed behind the mercury arc. § 10^{-12} mole c.c.$^{-1}$ sec.$^{-1}$. a.f. = analytical failure.

TABLE 2.

Disproportionation of ethyl and isopropyl radicals.

Temp. (°K)	Time (sec.)	PA *	IBA *	C_2H_4	C_3H_6	C_4H_{10}	C_5H_{12}	C_6H_{14}	$\Delta(\mathrm{Pr^i,Et})$	$\Delta(\mathrm{Et,Pr^i})$
321	2700	1·47	2·57	2·58	14·4	2·51	12·2	14·3	0·18	0·42
322	2880	1·80	2·82	3·14	15·9	2·99	13·2	14·9	0·20	0·47
351	2700	1·97	2·06	2·82	9·3	4·50	11·0	6·90	0·19	0·44
365	3780	1·77	1·77	3·73	11·0	7·30	15·3	7·48	0·17	0·40
374	2100	1·08	1·76	2·20	9·9	3·23	9·22	9·50	0·19	0·40
385	2760	1·25	2·11	1·94	9·2	2·05	8·50	8·68	0·19	0·42
								Mean values	0·19	0·43

Mean value $R(\text{pentane})/[R(\text{butane})^{\frac{1}{2}}R(\text{hexane})^{\frac{1}{2}}] = 1{\cdot}96$

* PA, IBA: propionaldehyde, isobutyraldehyde (10^{-6} mole c.c.$^{-1}$).
Rates of formation of products, 10^{-12} mole c.c.$^{-1}$ sec.$^{-1}$.

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[2] Kraus and Calvert, *J. Amer. Chem. Soc.*, 1957, **79**, 5921.

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

TABLE 3.

Disproportionation of ethyl and t-butyl radicals.

Temp. (°K)	Time (sec.)	DTBK*	DEK*	C_2H_6	C_2H_4	n- C_4H_{10}	i- C_4H_8	C_6H_{14}	C_8H_{18}	X ratio †	Δ(Et,Bu^t)	Δ(Bu^t,Et)
350	900	3·8	14·9			157	46·5	62·6	6·23	2·00	0·43	
354	900	3·5	15·7			179	39·9	53·9	3·93	2·03	0·51	
349	900	5·2	39·2			384	50·3	72·9	4·78	1·71	0·48	
353	1080	3·6	15·2			130	34·0	44·9	3·99	1·98	0·47	
349	900	4·4	19·2			169	42·7	73·5	5·96	1·85	0·40	
350	900	3·3	24·0			216	39·9	56·3	3·66 ^{c}	—	0·50	
353 ^{a}	900	4·0	19·4			230	50·3	68·9	5·18 ^{c}	—	0·49	
347 ^{b}	900	2·8	19·3			121	18·2	27·0	1·51 ^{c}	—	0·50	
346 ^{b}	900	3·6	22·5			129	19·8	26·6	1·38 ^{c}	—	0·50	
348 ^{b}	900	3·7	13·9			96	24·3	32·2	2·69 ^{c}	—	0·49	
										Mean value	0·48	
347	1200	4·6	2·2	9·75	5·39	3·56 ^{c}		15·8	17·5	—	0·58 ^{d}	0·31
350	600	5·0	2·2	9·15	6·30	3·26		17·6	23·1	2·03	0·49 ^{d}	0·33
350	720	6·7	5·6	a.f.	17·45	23·1		44·6	24·7	1·87	—	0·31
346	480	13·4	2·7	9·28	5·21	0·88 ^{c}		16·0	72·5	—	0·57 ^{d}	0·32
347	480	13·0	3·1	16·8	9·96	5·48 ^{c}		36·7	61·0	—	0·43 ^{d}	0·25
354	480	11·3	2·0	5·97	3·36	0·53 ^{c}		10·7	54·1	—	0·55 ^{d}	0·31
353	480	10·2	2·7	10·3	5·46	1·58 ^{c}		17·9	50·8	—	0·56 ^{d}	0·29
									Mean values	1·9	0·53 ^{d}	0·31

* DTBK, DEK, di-t-butyl ketone, diethylketone (10^{-6} mole c.c.$^{-1}$). † X ratio = the cross-combination ratio, $R(\text{hexane})/R(\text{butane})^{\frac{1}{2}}R(\text{octane})^{\frac{1}{2}}$.

Rate of formations of products 10^{-12} mole c.c.$^{-1}$ sec.$^{-1}$.

^{a} 376 mm. nitrogen added. ^{b} Runs without reflector behind the lamp. ^{c} Rate of formation of octane or butane calculated on the assumption that the cross-combination ratio was 2. ^{d} Results based on ethane analysis which was not very reliable because the peak on the chromatogram was narrow. a.f. = analytical failure.

TABLE 4.

Disproportionation of isopropyl and t-butyl radicals.

Temp. (°K)	Time (sec.)	DTBK*	DIPK*	C_3H_6	C_3H_8	i- C_4H_8	C_6H_{14}	C_7H_{16}	C_8H_{18}	X ratio †	Δ (Pr^i,Bu^t)	Δ (Bu^t,Pr^i)
355	480	3·0	9·1			37·1	90·4	38·0	3·99 ‡	—	0·64	
353	480	2·1	12·1			26·9	125	29·6	1·75 ‡	—	0·72	
351	360	2·0	10·8			28·0	101	30·5	2·29 ‡	—	0·68	
353	480	1·3	10·3			15·8	112	18·3	0·75 ‡	—	0·73	
353	900	1·9	9·1			19·1	80·1	20·9	1·36 ‡	—	0·71	
353	300	2·0	9·1			27·0	115	30·7	2·04 ‡	—	0·67	
348	480	2·0	13·0			12·1	93·7	14·2	0·54 ‡	—	0·73	
345	1500	2·2	12·3			6·5	63·7	7·7	2·32 ‡	—	0·75	
345	900	2·0	11·2			9·0	71·4	10·8	0·41 ‡	—	0·71	
										Mean value	0·70	
352	360	12·8	2·3	12·9	13·7	—	1·25	18·1	58·5	2·12	0·71	0·67
350	360	7·1	1·2	7·1	a.f.		0·95 ‡	10·0	26·4	—	—	0·65
352	360	6·0	2·0	16·1	16·6		5·42	20·2	18·1	2·03	0·65	0·63
349	360	7·1	3·3	27·1	26·8		13·9	27·5	13·4	2·01	0·66	0·67
347	360	7·5	1·2	4·9	5·3		0·73 ‡	7·3	18·1	—	0·67	0·61
346	480	8·5	1·3	6·2	6·7		0·98 ‡	8·1	16·9	—	0·75	0·69
347	480	6·9	2·6	9·1	9·4		2·16	10·7	16·3	1·80	0·75	0·73
347	480	8·5	2·0	10·2	8·9		1·90	13·1	19·8	2·12	0·59	0·68
									Mean values	2·02	0·68	0·67

* DTBK, DIPK, di-t-butyl ketone, di-isopropyl ketone (10^{-6} mole c.c.$^{-1}$).

† X ratio = the cross-combination ratio = $R(\text{heptane})/R(\text{hexane})^{\frac{1}{2}}R(\text{octane})^{\frac{1}{2}}$.

‡ Rate of formation of hexane or octane calculated on the assumption that the cross-combination ratio was 2.

Rate of formation of products, 10^{-12} mole c.c.$^{-1}$ sec.$^{-1}$.

ratios to 2 is additional indirect evidence for the correctness of the calibrations. The similar results obtained under different conditions for pivalaldehyde and di-t-butyl ketone indicate that there is no effect that depends on the special properties of t-butyl radicals containing energy carried over from their initial formation. An independent determination with a different source of radicals would be desirable.

TABLE 5.

Disproportionation of alkyl radicals, Δ(Alk′,Alk″).

	Alk″						
Alk′	Et	Pr$^{\text{n}}$	Pr$^{\text{i}}$	Bu$^{\text{n}}$	Bu$^{\text{i}}$	Bu$^{\text{s}}$	Bu$^{\text{t}}$
Me	0·04[c]	0·05[cd]	0·21[b]	0·15[e]	—	0·30[f]	0·70[b]
Et	0·13[g]	0·14[h]	0·43[a]	—	—	—	0·48[a]
Pr$^{\text{n}}$	—	0·15[n]	—	—	—	—	—
Pr$^{\text{i}}$	0·19[a]	—	0·65	—	—	—	0·70[a]
Bu$^{\text{n}}$	—	—	—	0·94[k]	—	—	—
Bu$^{\text{i}}$	—	—	—	—	0·17[l]	—	—
Bu$^{\text{s}}$	—	—	—	—	—	2·3[m]	—
Bu$^{\text{t}}$	0·31[a]	—	0·67[a]	—	—	—	3·19[a]

[a] This work. [b] Kerr and Trotman-Dickenson, *J.*, 1960, 1609. [c] Kerr and Grotewold, unpublished results. [d] Ausloos and Murad, *Canad. J. Chem.*, 1955, **33**, 1062. [e] Thynne, personal communication. [f] Rabinovitch and Diesen, *J. Chem. Phys.*, 1959, **30**, 735. [g] Kerr and Trotman-Dickenson, *J.*, 1960, 1611. [h] Thynne, *Proc. Chem. Soc.*, 1961, 68. [j] Kerr and Trotman-Dickenson, *Trans. Faraday Soc.*, 1959, **55**, 921. [k] Thynne, *Proc. Chem. Soc.*, 1961, 17. [l] Metcalfe and Trotman-Dickenson, *J.*, 1960, 5072. [m] Kraus and Calvert, *J. Amer. Chem. Soc.*, 1957, **79**, 5921. [n] Kerr and Calvert, *J. Amer. Chem. Soc.*, 1961, **83**, 3391.

The cross-combination ratios for the three pairs of radicals are close to 2. They are thus in line with results on other systems of mixed alkyl radicals. The present measurements complete the determination of all the possible disproportionation ratios for methyl, ethyl, isopropyl, and t-butyl radicals. The values are collected, with those for some other systems, in Table 5. Correlations have been suggested that describe some of the results quite well[1, 4, 5] but no general principles have been found that enable us to predict disproportionation ratios to better than a factor of three or four. As the spread of values is small the achievement is not impressive. The correlation suggested by Kerr and Trotman-Dickenson[1, 4] is supported by the present results on Δ(Et,Pr$^{\text{i}}$), Δ(Pr$^{\text{i}}$,Et), Δ(Bu$^{\text{t}}$,Et) but not by the others. There is no reason to suspect the accuracy of the determinations.

EXPERIMENTAL

The apparatus was similar to that described previously. For ethyl–isopropyl work the products were analysed on a 250 cm. column of 50—60 mesh activated alumina impregnated with 2% of squalane. For ethyl–t-butyl, two columns were used, each 125 cm. long with 40—60 mesh alumina impregnated with 3% of squalane. The columns were used together to separate the low-boiling products but so arranged that only the high-boiling products passed through the first. Two columns were also used for isopropyl–t-butyl when propene had to be determined. The single column of 125 cm. served to separate isobutene, hexane, heptane, and octane. Temperature programming was used throughout.

Materials.—The propionaldehyde, isobutyraldehyde, and diethyl ketone were commercial samples which were purified by bulb-to-bulb distillation and tested by gas-chromatography. Di-isopropyl ketone was a gift from Shell Chemicals. Di-t-butyl ketone was prepared by the method of Bartlett and Schneider.[6] Koch's pivalaldehyde was purified by gas-chromatography.

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CHEMISTRY DEPARTMENT, EDINBURGH UNIVERSITY.
(A. F. T-D., J. A. K.) EDWARD DAVIES CHEMICAL LABORATORY,
ABERYSTWYTH.

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[4] Kerr and Trotman-Dickenson, *J.*, 1960, 1609.
[5] Bradley, *J. Chem. Phys.*, 1961, **35**, 748.
[6] Bartlett and Schneider, *J. Amer. Chem. Soc.*, 1945, **67**, 141.