

830. *The Interactions of the Lower Alkyl Radicals. Part I. Methyl, Ethyl, and n-Propyl Radicals.*

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Ratios of rate constants for disproportionation to combination (Δ) and for cross-combination to geometric mean of auto-combinations (ϕ) have been determined for the following pairs of radicals, by photolysing mixtures of ketones of azo-n-propane with a ketone: $\Delta(\text{Me}, \text{Et}) = 0.039 \pm 0.007$; $\Delta(\text{Me}, \text{Pr}^n) = 0.041 \pm 0.010$; $\Delta(\text{Et}, \text{Pr}^n) = 0.081 \pm 0.010$; $\Delta(\text{Pr}^n, \text{Et}) = 0.058 \pm 0.010$; $\phi(\text{Me}, \text{Pr}^n) = 2.08 \pm 0.15$; $\phi(\text{Et}, \text{Pr}^n) = 1.93 \pm 0.20$. Where possible the results are compared with existing values.

DESPITE much recent work on disproportionation and combination reactions of alkyl radicals^{1,2} several gaps in our knowledge of them still exist. For instance, the ratio of rate constants for cross-disproportionation to cross-combination of n-propyl and ethyl radicals, $\Delta(\text{Pr}^n, \text{Et})$, is unknown, and that for ethyl and n-propyl, $\Delta(\text{Et}, \text{Pr}^n)$, has only been reported as a preliminary result. These ratios are defined from the following reactions:



$\Delta(\text{Et}, \text{Pr}^n) = k_2/k_1$ and $\Delta(\text{Pr}^n, \text{Et}) = k_3/k_1$. This nomenclature will be used throughout.

At the same time, while many values are available, some have been obtained from experiments which were not designed specifically for their determination. The present work was undertaken, then, to determine some of the remaining unknown values, and to obtain systematically, under similar conditions, a pattern of Δ values for the lower alkyl radicals.

To ensure that the system was operating satisfactorily a few runs were done on the photolysis of diethyl ketone to measure the established value of $\Delta(\text{Et}, \text{Et})$. The results

¹ Trotman-Dickenson, *Ann. Reports*, 1958, **55**, 39.

² Kerr and Trotman-Dickenson, "Progress in Reaction Kinetics," Pergamon, Oxford, 1961, p. 105.

are shown in Table 1. Ethane was not measured as it gives no further information on Δ . The conversions are based on the non-condensable fraction. $\Delta(\text{Et},\text{Et})$ was calculated directly from $\text{C}_2\text{H}_4/\text{C}_4\text{H}_{10}$. The mean value from runs 37, 39, 41, and 42 is $\Delta(\text{Et},\text{Et}) = 0.130 \pm 0.007$, in excellent agreement with the many previous determinations, for instance

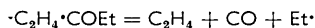
TABLE 1.
 $\Delta(\text{Et},\text{Et})$ from the photolysis of diethyl ketone.

Run *	Temp.	Time (sec.)	[COEt ₂]	% Conversion	C ₂ H ₄	n-C ₄ H ₁₀	$\Delta(\text{Et},\text{Et})$
41	115°	1200	0.39	6.8	5.26	41.6	0.126
42	119	1200	0.34	6.6	4.81	37.2	0.129
39	149	1500	0.35	6.9	4.31	34.0	0.127
37	150	1200	0.38	5.4	4.55	32.8	0.139
34	214	1200	0.37	4.5	3.98	24.6	0.162
33	215	1200	0.25	4.0	2.74	15.6	0.176

* Unfiltered light.

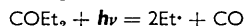
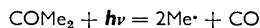
Diethyl ketone in 10^{-6} mole c.c.⁻¹. Rates of formation of products in 10^{-12} mole c.c.⁻¹ sec.⁻¹.

0.12 ± 0.01 found by Brinton and Steacie.³ At 200° decomposition of the oxopentyl radical occurs:



leading to higher values of Δ , as confirmed by runs 33 and 34.

Interactions of Methyl and Ethyl Radicals.—When a mixture of acetone and diethyl ketone is photolysed at temperatures above 100° the following reactions occur:



The hydrogen-abstraction reactions of the radicals need not be considered, as they will not lead to olefinic products, provided the temperature is low enough to avoid a measurable rate of decomposition of the oxopentyl radicals. It follows from the above mechanism that:

$$\Delta(\text{Me},\text{Et}) = k_8/k_5 = \text{C}_2\text{H}_4(8)/\text{C}_3\text{H}_8$$

where $\text{C}_2\text{H}_4(8)$ is equal to the rate of formation of ethylene from reaction (8) and is given by $\text{C}_2\text{H}_4(\text{total}) - \text{C}_2\text{H}_4(7)$. The rate of formation of ethylene from auto-disproportionation of ethyl radicals, $\text{C}_2\text{H}_4(7)$, can be calculated from $0.13\text{C}_4\text{H}_{10}$. The values of $\Delta(\text{Me},\text{Et})$ calculated in this way are given in Table 2, and are independent of temperature below 200°. The mean value from 110° to 166° is $\Delta(\text{Me},\text{Et}) = 0.039 \pm 0.007$.

Three previous determinations of this ratio have been reported. The first, by Ausloos and Steacie⁴ [$\Delta(\text{Me},\text{Et}) = 0.041 \pm 0.02$], agrees well with ours. The value of $\Delta(\text{Me},\text{Et}) = 0.06 \pm 0.01$ found by Heller⁵ from photolysis of acetone- $\text{CH}_3\cdot\text{CD}_2\cdot\text{CO}\cdot\text{CD}_2\cdot\text{CH}_3$ mixtures, appears to be an upper limit for two reasons: (i) $\Delta(\text{Et},\text{Et})$ was taken as 0.1, thus underestimating the C_2H_4 correction for ethyl auto-disproportionation, and (ii) it was assumed that at 90° the methane, on which the results were based, arose solely from the disproportionation reaction of $\text{CH}_3\cdot$ with $\text{CH}_3\cdot\text{CD}_2\cdot$ radicals. This assumption neglects methyl-radical attack on the ketones, which would be expected to some extent at this temperature.

³ Brinton and Steacie, *Canad. J. Chem.*, 1955, **33**, 1840.

⁴ Ausloos and Steacie, *Canad. J. Chem.*, 1955, **33**, 1062.

⁵ Heller, *J. Chem. Phys.*, 1958, **28**, 1255.

TABLE 2.

 $\Delta(\text{Me,Et})$ from the photolysis of acetone–diethyl ketone mixtures.

Run *	Temp.	Time (sec.)	[COMe ₂]	[COEt ₂]	Conversion (%)	C ₂ H ₄	C ₃ H ₈	n-C ₄ H ₁₀	$\Delta(\text{Me,Et})$
53	110°	1200	1.58	0.22	2.6	4.51	67.2	12.1	0.044
56	113	1200	1.60	0.29	2.7	4.71	76.4	16.6	0.033
46	115	1200	1.37	0.38	4.4	5.05	66.6	21.6	0.034
43	117	1200	1.72	0.27	4.6	4.34	66.9	11.8	0.042
50	137	1200	1.60	0.21	2.8	2.28	41.3	2.21	0.047
52	137	1200	1.49	0.27	3.0	5.09	82.5	15.7	0.037
51	140	1200	1.41	0.12	3.6	0.702	18.8	0.500	0.034
33	154	1500	1.37	0.23	5.3	1.77	34.4	4.23	0.035
45	158	1200	1.37	0.38	5.0	4.31	60.5	12.2	0.045
47	166	1200	1.17	0.27	5.1	1.00	21.1	2.00	0.035
35	210	1200	1.41	0.18	5.8	1.55	19.1	1.50	0.071
36	215	1500	1.16	0.19	7.0	2.02	24.8	2.11	0.070

* Unfiltered light.

Acetone and diethyl ketone in 10⁻⁶ mole c.c.⁻¹. Rates of formation of products in 10⁻¹² mole c.c.⁻¹ sec.⁻¹.

The third value of $\Delta(\text{Me,Et})$, 0.055, obtained by Thynne⁶ from the decomposition of ethyl formate sensitised by methyl radicals, although in fair agreement with the lower values, may be doubtful for reasons put forward in the following paper.

The other ratio which is of interest in radical–radical reactions is the cross-combination ratio, in this instance given by

$$k_5/(k_4 \times k_6)^{\frac{1}{2}} = \text{C}_3\text{H}_8/(\text{C}_2\text{H}_6 \times \text{C}_4\text{H}_{10})^{\frac{1}{2}}$$

and known as the ϕ factor.⁷ Unfortunately, it is not possible to calculate $\phi(\text{Me,Et})$ from the results given here, since there is an additional source of ethane, namely, ethyl-radical hydrogen-abstraction from the ketones, and the corrections involved make the calculated value of $\phi(\text{Me,Et})$ very uncertain. For this reason the ethane was not measured. Thynne reported a value of $\phi(\text{Me,Et}) = 2.02$ from the above-mentioned decomposition of ethyl formate,⁶ where the same problem of two sources of ethane exists. It is difficult to assess this value since there was no indication as to how it was calculated.

Interactions of Methyl and n-Propyl Radicals.—Radical–radical reactions involving n-propyl radicals have been neglected because, unlike many other alkyl radicals, they cannot be produced cleanly by photolysis of either the corresponding ketone or the aldehyde. This difficulty was overcome when it was shown that azopropane dissociates by a single photochemical process to yield nitrogen and n-propyl radicals.⁸ Preliminary experiments were carried out on the photolysis of azopropane alone to check the analysis and a few runs had to be done to “age” the reactions vessel.⁸ Eighteen experiments between 18° and 150° with filtered light yielded a mean $\Delta(\text{Pr}^n, \text{Pr}^n)$ value of 0.141 ± 0.015 , in good agreement with the value of 0.156 ± 0.01 found by Kerr and Calvert⁸ under the same conditions.

Table 3 contains the results obtained by photolysing mixtures of acetone and azopropane. $\Delta(\text{Me,Pr}^n)$ values were calculated in the same way as for $\Delta(\text{Me,Et})$, by taking $\Delta(\text{Pr}^n, \text{Pr}^n) = 0.141$; and $\phi(\text{Me,Pr}^n)$ was obtained from the rates of formation of the radical dimers. Propane was not measured since it gave no information on Δ . Azomethane was not used because of the analytical difficulty of separating it from the hexane produced. The filter used in these experiments absorbs wavelengths shorter than 3000 Å, under which conditions photolysis of azopropane proceeds as expected. Full-mercury-arc photolysis of azopropane at room temperature, however, yielded ethane, ethylene, n-butane, and n-pentane, as well as the usual C₃ and C₆ products, and the values of $\Delta(\text{Pr}^n, \text{Pr}^n)$ were then

⁶ Thynne, *Trans. Faraday Soc.*, 1962, **58**, 676.⁷ Bowles, Majer, and Robb, *Trans. Faraday Soc.*, 1962, **58**, 2394.⁸ Kerr and Calvert, *J. Amer. Chem. Soc.*, 1961, **83**, 3391.

TABLE 3.

 $\Delta(\text{Me}, \text{Pr}^n)$ from the photolysis of acetone-azopropane mixtures.

Run *	Temp.	Time (sec.)	$[(\text{Pr}^n\text{N})_2]$	$[\text{COMe}_2]$	C_2H_6	C_3H_6	$n\text{-C}_4\text{H}_{10}$	$n\text{-C}_6\text{H}_{14}$	$\Delta(\text{Me}, \text{Pr}^n)$	$\phi(\text{Me}, \text{Pr}^n)$
124	118°	3000	0.21	2.99	5.22	0.828	8.08	2.94 †	0.051	—
114	137	3000	0.19	1.63	2.29	0.977	6.80	4.55	0.049	2.11
120	137	2940	0.25	2.67	7.34	0.548	7.53	1.82	0.039	2.06
117	139	3000	0.25	0.81	0.630	2.31	6.03	15.4	0.023	1.93
121	140	3000	0.16	2.44	7.48	0.682	8.50	1.99	0.047	2.20
122	141	3000	0.17	2.38	6.76	0.574	6.81	1.48	0.054	2.14
123	141	3000	0.20	2.10	4.51	0.978	8.93	3.91	0.048	2.13
116	142	3000	0.28	1.66	2.77	1.64	10.3	9.73	0.026	1.99
115	144	3000	0.22	1.66	2.75	1.75	10.5	10.2	0.029	2.05

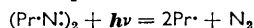
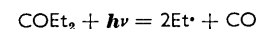
* Corning Filter No. 0616. † Hexane, not measured, but calc. from $\phi = 2$.Azopropane and acetone in 10^{-6} mole c.c.⁻¹. Rates of formation of products in 10^{-12} mole c.c.⁻¹ sec.⁻¹.

much higher than before. There appears to be no simple explanation of the full-mercury-arc photolysis of azopropane, which was not fully investigated since it was beyond the scope of the present investigation.

The mean values from Table 3 are $\Delta(\text{Me}, \text{Pr}^n) = 0.041 \pm 0.010$ and $\phi(\text{Me}, \text{Pr}^n) = 2.08 \pm 0.15$. An alternative method of dealing with the results for cross-disproportionation-combination has been suggested by Thynne.¹⁰ If $\text{C}_2\text{H}_6/\text{C}_6\text{H}_{14}$ is plotted against $\text{C}_4\text{H}_{10}/\text{C}_6\text{H}_{14}$ a straight line is obtained with a slope equal to $\Delta(\text{Me}, \text{Pr}^n)$ and the intercept equal to $\Delta(\text{Pr}^n, \text{Pr}^n)$. The results in Table 3 give rather scattered points, and the least-mean-squares line gives Δ values which do not agree very well with those obtained above by averaging the results. If, however, the intercept is fixed at $\Delta(\text{Pr}^n, \text{Pr}^n) = 0.14$, then the best line through the points corresponds to $\Delta(\text{Me}, \text{Pr}^n) = 0.047$.

Two previous determinations of $\Delta(\text{Me}, \text{Pr}^n)$ have been reported. Ausloos and Murad⁹ found from the photolysis of $\text{CH}_3\cdot\text{CO}\cdot\text{CD}_2\cdot\text{CD}_2\cdot\text{CH}_3$ at 25° a value of 0.051, which agrees reasonably with ours. A considerably higher value, 0.095, was reported by Thynne¹⁰ from the above-mentioned decomposition of *n*-propyl formate. In agreement with the results given here, Thynne found no temperature-dependence of Δ , but the difference of a factor of two between the two determinations is far from satisfactory. This point is considered in greater detail in the following paper.

Interactions of Ethyl and n-Propyl Radicals.—Azopropane having proved valuable as a source of *n*-propyl radicals for the study of disproportionation reactions, its use was extended to photolysis in admixture with diethyl ketone, to give $\Delta(\text{Et}, \text{Pr}^n)$ and $\Delta(\text{Pr}^n, \text{Et})$. Photolysis of such a mixture can be discussed in terms of the mechanism:



Reactions (1), (2), (3), (6), and (7), and



Again hydrogen abstraction reactions may be neglected if the temperature is kept low enough to avoid production of olefins from radical-decomposition reactions. From this reaction scheme the ratios of interest are defined as follows:

$$\phi(\text{Et}, \text{Pr}^n) = \text{C}_5\text{H}_{12}/(\text{C}_4\text{H}_{10} \times \text{C}_6\text{H}_{14})^{\frac{1}{2}}$$

$$\Delta(\text{Et}, \text{Pr}^n) = (\text{C}_3\text{H}_6 - 0.141\text{C}_6\text{H}_{14})/\text{C}_5\text{H}_{12}$$

$$\Delta(\text{Pr}^n, \text{Et}) = (\text{C}_2\text{H}_4 - 0.13\text{C}_4\text{H}_{10})/\text{C}_3\text{H}_{12}$$

⁹ Ausloos and Murad, *J. Amer. Chem. Soc.*, 1958, **80**, 5929.

¹⁰ Thynne, *Trans. Faraday Soc.*, 1962, **58**, 1394.

Table 4 shows the results of photolyses of mixtures of diethyl ketone and azopropane. The ethane and propane were not measured. The mean values of the ratios, calculated from the above expressions, are $\phi(\text{Et}, \text{Pr}^n) = 1.93 \pm 0.20$, $\Delta(\text{Et}, \text{Pr}^n) = 0.081 \pm 0.010$, and $\Delta(\text{Pr}^n, \text{Et}) = 0.058 \pm 0.010$. All three ratios are temperature-independent. The cross-combination ratio of ~ 2 is in keeping with the numerous other experimental values of this ratio for small alkyl radicals.^{1,2} $\Delta(\text{Pr}^n, \text{Et})$ has not previously been reported.

TABLE 4.
 $\Delta(\text{Et}, \text{Pr}^n)$ and $\Delta(\text{Pr}^n, \text{Et})$ from the photolysis of diethyl ketone-azopropane mixtures.

Run*	Temp.	Time (sec.)	$[(\text{Pr}\cdot\text{N})_2]$	$[\text{COEt}_2]$	C_2H_4	C_3H_6	n- C_4H_{10}	n- C_5H_{12}	n- C_6H_{14}	Δ (Et, Pr ⁿ)	Δ (Pr ⁿ , Et)	Δ (Et, Pr ⁿ)
145	61°	2500	0.96	7.40	0.457	—	1.97	2.73	—	—	0.074	—
143	65	2100	0.38	1.99	0.343	—	0.575	4.72	9.62	—	0.057	2.01
144	68	3600	0.62	0.95	0.286	—	0.231	5.61	—	—	0.046	—
141	95	3600	0.50	2.31	0.365	—	0.687	4.83	—	—	0.057	—
138	96	4500	0.061	2.99	0.677	0.270	4.21	2.49	0.459	0.082	0.052	1.79
140	98	3600	0.43	2.87	0.379	—	0.677	4.21	5.93	—	0.069	2.10
139	99	1800	0.47	3.03	0.449	—	1.29	5.09	6.16	—	0.055	1.81
134	99	3000	0.18	2.77	—	0.619	1.92	3.69	2.10	0.088	—	1.84
133	99	3000	0.19	2.49	—	0.653	1.94	4.22	2.31	0.078	—	2.00
135	99	3000	0.21	1.57	0.382	0.844	0.795	4.01	4.06	0.068	0.070	2.23
137	99	3000	0.18	2.91	0.554	0.661	2.52	4.32	2.47	0.073	0.052	1.74
142	99	3540	0.55	1.81	0.291	—	0.489	4.51	—	—	0.050	—
132	100	3000	0.16	2.68	—	0.619	1.86	3.37	2.20	0.092	—	1.67
129	125	3600	0.16	3.57	—	0.537	2.19	3.42	1.45	0.097	—	1.92
127	129	2400	0.18	1.83	—	0.852	9.04	8.42	1.69	0.073	—	2.15

* Corning filter No. 0616.

Azopropane and diethyl ketone in 10^{-6} mole c.c.⁻¹. Rates of formation of products in 10^{-12} mole c.c.⁻¹ sec.⁻¹.

Thynne¹¹ found, from single experiments, the preliminary values $\Delta(\text{Et}, \text{Pr}^n) = 0.21$ and 0.14 . It is impossible to compare these results with the present investigation as details have not yet been given. The graphical method gives results for Δ which agree with the mean values only when the intercept is fixed at the known value for the auto-disproportionation ratio. It is concluded that this method can only be applied with very accurate results, which are difficult to obtain when the values of Δ are small.

EXPERIMENTAL

Apparatus and Procedure.—Photolyses were carried out in a 166 c.c. quartz cell contained in a co-axial cylindrical furnace maintained at $\pm 1^\circ$ during a run, with a temperature gradient of less than $\pm 2^\circ$ along the length of the cell. A mercury manometer was attached to the cell, which was isolated from a conventional high-vacuum line by mercury cut-off valves. The cell was illuminated by the light from a 125-w medium-pressure mercury arc, either unfiltered or in conjunction with Corning filters as indicated in the Tables.

The analytical system consisted of a low-temperature distillation train and a gas-chromatographic unit. After photolysis the products and unused starting materials were separated into non-condensable and condensable portions by a series of traps cooled in carbon dioxide-acetone, liquid air, and liquid air boiling under reduced pressure. The non-condensable gases, consisting of mixtures of nitrogen, carbon monoxide, and methane were pumped into a gas-burette and their total volume was measured. This fraction was not analysed further.

The condensable fraction was then transferred to the gas-chromatographic injection trap which was cooled in liquid air boiling under reduced pressure. Analysis was performed on a temperature-controlled column,¹² 4–12 ft. long, packed with 40–60 mesh activated alumina poisoned with 2–5% of squalane. The flow of hydrogen carrier gas was kept constant by a flow-controller. The detector, a Gow-Mac thermal conductivity cell of type 9285, was coupled

¹¹ Thynne, *Proc. Chem. Soc.*, 1961, 68.

¹² Guild, Bingham, and Aul, "Gas Chromatography," Butterworths, London, 1958, p. 226.

to a 1 mv recorder. The sensitivity of the detector was determined for each hydrocarbon by passing known volumes of the gases through the columns.

Materials.—Acetone and diethyl ketone were commercial samples which were purified by bulb-to-bulb distillation and tested by gas chromatography. Azopropane was a product of Merck, Sharp, and Dohme (Montreal), and was shown to contain about 1% of n-hexane by gas chromatography. This was removed as previously described.⁸

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