

831. *The Interactions of the Lower Alkyl Radicals. Part II.¹ The Effect of the Radical Source on the Disproportionation-Combination Reactions of Methyl and n-Propyl Radicals.*

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By choice of radical sources, reasonably reproducible values for the ratio of rate constants (Δ) for the disproportionation and combination reactions of methyl and n-propyl radicals are obtained. The mean value from two reliable sources of the radicals is $\Delta(\text{Me}, \text{Pr}^n) = 0.033$. Re-investigation of the decomposition of n-propyl formate, sensitised by methyl radicals, has shown this system to be unsuitable for the study of radical-radical reactions.

It was seen from Part I of this series in conjunction with other published results that different values of the cross-disproportionation: cross-combination ratio of rate constants for the reaction of methyl and n-propyl radicals can apparently be obtained from different radical sources. This ratio is defined from the equations,



as $\Delta(\text{Me}, \text{Pr}^n) = k_2/k_1$. Thus, from the photolysis of a mixture of acetone and azopropane,¹ $\Delta(\text{Me}, \text{Pr}^n)$ was found to be 0.041, whereas from the selective photolysis of acetone in the presence of n-propyl formate² this ratio was 0.095. This is not the first instance where significantly different values of Δ for the same reactions have been observed from different radical sources. $\Delta(\text{Pr}^i, \text{Pr}^i)$ has been found to be 0.65 from aldehyde and ketone photolyses,³ while the photolysis of 1,1'-dimethylazoethane (" azoisopropane ")⁴ has yielded a value of 0.53. The interactions of methyl and n-propyl radicals were chosen for a study of the effect of different sources of the radicals on Δ because of the discrepancy in existing values, and because experience had already been gained on this system. The following series of photolytic and thermal sources of the radicals was completed:

System	Radical sources	
	Me	Pr ⁿ
Selective photolysis of acetone in presence of n-propyl formate	Photolytic	Thermal
Photolysis of acetone-azopropane mixture	Photolytic	Photolytic
Pyrolysis of di-t-butyl peroxide in presence of n-butyraldehyde	Thermal	Thermal
Selective photolysis of azopropane in presence of acetaldehyde	Thermal	Photolytic

¹ Part I, Grotewold and Kerr, preceding paper.

² Thynne, *Trans. Faraday Soc.*, 1962, **58**, 1394.

³ Kerr and Trotman-Dickenson, " Progress in Reaction Kinetics," Pergamon, Oxford, 1961, p. 105.

⁴ Riem and Kutschke, *Canad. J. Chem.*, 1960, **38**, 2332.

Pyrolysis of Di-t-butyl Peroxide in the Presence of n-Butyraldehyde.—With this system Birrell and Trotman-Dickenson⁵ measured the rate of abstraction of hydrogen atoms from the aldehyde by methyl radicals, but product analysis was insufficient to measure $\Delta(\text{Me}, \text{Pr}^n)$. The following mechanism accounts for the production of the radicals:



The pyrolysis of di-t-butyl peroxide between 120° and 170° is an established source of methyl radicals [reactions (3) and (4)]. In the presence of an aldehyde it has been shown⁵ that methyl radicals abstract the hydrogen from the aldehydic group, in this case generating a butyryl radical [reaction (5)]. There is no experimental value for the rate of decomposition of the butyryl radical but one would expect it to be fairly unstable; so reaction (6) is postulated. The remainder of the mechanism consists of the usual radical-radical reactions between methyl and n-propyl:

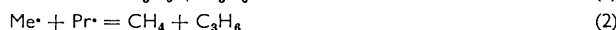


TABLE 1.

$\Delta(\text{Me}, \text{Pr}^n)$ from the pyrolysis of di-t-butyl peroxide in the presence of n-butyraldehyde.

Run	Temp.	Time (sec.)	$[(\text{Bu}^t\text{O})_2]$ (10^{-6} mole c.c. ⁻¹)	$[\text{Pr}\cdot\text{CHO}]$ (10^{-6} mole c.c. ⁻¹)	C_2H_6	C_3H_8	C_3H_6	n- C_4H_{10}	n- C_6H_{14}	Δ (Me, Pr ⁿ)	ϕ (Me, Pr ⁿ)
216	139°	2205	0.41	0.15	—	0.948	0.338	6.13	1.27	0.026	—
221	145	2100	0.43	0.17	9.59	1.09	0.362	6.71	1.71	0.018	1.66
222	145	2150	0.66	0.16	14.0	—	0.084	2.34	0.086	0.031	2.13
218	146	997	0.42	0.40	6.24	2.19	0.408	6.57	1.82	0.023	1.95
219	148	2650	0.73	0.08	27.1	0.131	0.136	4.10	0.202	0.026	1.75
220	149	1005	0.55	0.07	41.4	0.300	0.269	8.55	0.370	0.025	2.18
225	169	1225	0.79	0.21	70.7	0.800	0.457	16.0	0.739	0.022	2.21
224	170	1320	0.81	0.11	77.8	0.141	0.113	4.40	0.062*	0.024	—
226	173	1250	0.66	0.13	71.1	0.160	0.143	4.61	0.074*	0.029	—
227	173	1280	0.90	0.20	72.2	0.541	0.370	14.3	0.708	0.019	2.00
Mean:										0.025	1.98

Rates of formation of products, 10^{-12} mole c.c.⁻¹ sec.⁻¹.

* Not measured; calc. from $\phi = 2$.

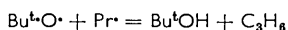
Table 1 lists the results obtained by pyrolysing di-t-butyl peroxide in the presence of n-butyraldehyde between 139° and 173°. The rate constant ratios have been calculated as follows:

$$\Delta(\text{Me}, \text{Pr}^n) = k_2/k_1 = (\text{C}_3\text{H}_6 - 0.141\text{C}_6\text{H}_{14})/\text{C}_4\text{H}_{10}$$

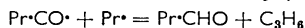
and

$$\phi(\text{Me}, \text{Pr}^n) = k_1/(k_8 \times k_7)^{\frac{1}{2}} = \text{C}_4\text{H}_{10}/(\text{C}_2\text{H}_6 \times \text{C}_6\text{H}_{14})^{\frac{1}{2}}$$

The mean values are $\Delta(\text{Me}, \text{Pr}^n) = 0.025 \pm 0.004$ and $\phi(\text{Me}, \text{Pr}^n) = 1.98 \pm 0.21$. The reproducibility of $\Delta(\text{Me}, \text{Pr}^n)$ is good for this type of measurement. The possibility of a significant disproportionation of t-butoxy or butyryl with n-propyl,



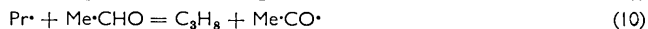
or



⁵ Birrell and Trotman-Dickenson, *J.*, 1960, 2059.

is eliminated since changes in the relative concentrations of reactants brought about no change in $\Delta(\text{Me}, \text{Pr}^n)$, thus substantiating the suggested mechanism.

Selective Photolysis of Azopropane in the Presence of Acetaldehyde.—This system is analogous to that used by Calvert and Gruver⁶ in which azomethane was selectively photolysed in the presence of acetaldehyde. By using a Pyrex cell and suitable filters the transmitted radiation is principally 3660 Å, which is close to the maximum absorption of azoalkanes. Aldehydes are transparent at wavelengths longer than 3400 Å and hence should not absorb light in the system. Experiments carried out with acetaldehyde alone in the cell produced only traces of non-condensable gases. The following mechanism is suggested for the selective photolysis:



followed by the previous sequence of methyl-n-propyl interactions. From this scheme $\Delta(\text{Me}, \text{Pr}^n)$ and $\phi(\text{Me}, \text{Pr}^n)$ are obtained as for the pyrolysis of di-t-butyl peroxide in the presence of n-butyraldehyde. Table 2 contains the results of experiments carried out between 105° and 143°. The mean values of the ratios are $\Delta(\text{Me}, \text{Pr}^n) = 0.15 \pm 0.05$ and $\phi(\text{Me}, \text{Pr}^n) = 1.5 \pm 0.4$. The results in this system are strikingly different from those of the previous investigations, but at the same time they are also very scattered. This irreproducibility probably indicates that the difference in the values of Δ is not real but the result of some peculiarity of the azopropane-acetaldehyde system. The only major

TABLE 2.

$\Delta(\text{Me}, \text{Pr}^n)$ from the selective photolysis of azopropane in the presence of acetaldehyde.

Run *	Temp.	Time (sec.)	$[(\text{Pr}\cdot\text{N})_2]$ (10^{-6} mole c.c. ⁻¹)	$[\text{Me}\cdot\text{CHO}]$ (10^{-6} mole c.c. ⁻¹)	C_2H_6	C_3H_6	$n\text{-C}_4\text{H}_{10}$	$n\text{-C}_6\text{H}_{14}$	$\Delta(\text{Me}, \text{Pr}^n)$	$\phi(\text{Me}, \text{Pr}^n)$
94	105°	3000	0.24	0.81	0.24	2.21	1.96	14.0	0.122	1.07
95	108	3000	0.28	1.8	1.24	1.05	2.73	6.10	0.070	0.99
96	108	3000	0.24	1.8	0.815	0.743	2.13	3.07	0.146	1.35
105	137	3000	0.25	0.98	0.662	1.46	3.83	6.86	0.128	1.80
98	138	3010	0.20	1.6	1.04	0.655	2.14	1.50	0.207	1.71
97	141	3000	0.23	1.7	1.51	1.22	4.28	3.23	0.178	1.94
100	142	3300	0.19	0.66	0.397	1.88	2.69	9.36	0.208	1.39
104	143	3000	0.26	1.9	1.39	0.943	3.45	2.83	0.158	1.74
								Mean:	0.15	1.5

Rates of formation of products, 10^{-12} mole c.c.⁻¹ sec.⁻¹.

* Corning filters Nos. 0616 and 5840 were used.

experimental difference in this system was the use of an absorbent column for the removal of aldehyde before analysis. This, however, has been successfully used by Kerr and Trotman-Dickenson⁷ in several studies, so one is led to the conclusion that the anomaly must lie in the mechanism. Since the photolysis of azopropane had been used without difficulty in the previous systems it follows that the presence of the acetaldehyde must be responsible for any peculiarity. High Δ values are most readily explained by the occurrence of additional radical-radical reactions. For instance if the acetyl radicals, produced in reaction (10), reacted with the n-propyl:



this would be an additional source of propene. Evidence on the stability of the acetyl

⁶ Calvert and Gruver, *J. Amer. Chem. Soc.*, 1958, **80**, 1313.

⁷ Kerr and Trotman-Dickenson, *Nature*, 1958, **182**, 466.

radical is conflicting. Calvert and Gruver⁶ found in the analogous azomethane-acetaldehyde study a measurable rate of decomposition of the radical at 22°, and at 130° the radical-radical products were barely detectable. More recently O'Neal and Benson⁸ reported that the acetyl radical was stable up to 200° in the photolysis of acetone in the presence of hydrogen iodide. It is possible, then, that reaction of the acetyl radicals with propyl radicals could be responsible for the anomalous results in the present system. There is no obvious explanation why this system should yield such high values of Δ , but since the results were so scattered and the values of ϕ so low, it is clearly unsuitable for the study of radical-radical reactions.

Selective Photolysis of Acetone in the Presence of n-Propyl Formate.—There still remains the question of reconciling the low values of $\Delta(\text{Me}, \text{Pr}^n)$ obtained in this investigation with the value of 0.095 reported by Thynne² from the decomposition of n-propyl formate sensitised by methyl radicals. An attempt was made to resolve this by re-investigating Thynne's system. Table 3 shows the results obtained between 74° and 152°. The condensable products consisted of ethane, propane, propene, n- and iso-butane, and, in some runs, traces of n-hexane. The non-condensable fraction contained measurable amounts of hydrogen, usually about a third to a half of the amount of propene. The absence of measurable amounts of n-hexane is not surprising since the calculated rates of formation of n-hexane (based on the ethane, and butane and the relation $\phi(\text{Me}, \text{Pr}^n) = 2$) are very low. The major differences between the present investigation and that of Thynne are as follows: (1) as shown in Table 3 the ratio $\text{C}_3\text{H}_6/\text{n-C}_4\text{H}_{10}$ is markedly dependent on temper-

TABLE 3.
 $\Delta(\text{Me}, \text{Pr}^n)$ from the selective photolysis of acetone in the presence of n-propyl formate.

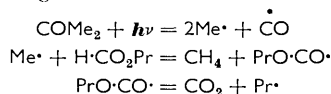
Run *	Temp.	Time (sec.)	[CoMe ₂] (10 ⁻⁶ mole c.c. ⁻¹)	[H·CO ₂ Pr] (10 ⁻⁶ mole c.c. ⁻¹)	C ₂ H ₆	C ₃ H ₈	C ₃ H ₆	iso-C ₄ H ₁₀	n-C ₄ H ₁₀	(C ₃ H ₆ /n-C ₄ H ₁₀)
237	74°	85,660	2.0	2.2	1.08 †	0.0166	0.0054	0.0019	0.0737	0.073
234	94	21,600	2.7	1.2	3.42 †	0.0276	0.0121	0.0071	0.122	0.099
241	116	12,180	4.7	2.4	6.69	0.121	0.0664	0.0276	0.208	0.319
240	117	67,680	3.1	0.44	1.56 †	—	0.0132	0.0070	0.0543	0.243
236	120	19,320	2.0	1.8	3.15 †	0.0582	0.0606	0.0246	0.188	0.322
235	121	23,760	2.2	0.67	2.86 †	0.0430	0.0361	0.0175	0.124	0.290
238	148	18,480	2.6	0.35	1.89	0.0494	0.0437	0.0143	0.0720	0.607
239	152	45,960	2.7	0.18	1.24 †	0.0389	0.0166	0.0051	0.0274	0.606

Rates of formation of products, 10⁻¹² mole c.c.⁻¹ sec.⁻¹.

* Corning filter No. 0616 was used. † Lower limit since C₂H₆ peak was out of scale on chromatogram even on lowest sensitivity.

ature. This ratio is, to a good approximation, equal to $\Delta(\text{Me}, \text{Pr}^n)$ since the propene correction for auto-disproportionation of n-propyl was usually less than 5%, owing to the small rate of formation of n-hexane. Thynne found $\Delta(\text{Me}, \text{Pr}^n)$ to be temperature-independent over much the same temperature range. (2) Isobutane was observed as a product whereas Thynne found only n-butane. Dr. Thynne considers⁹ that isobutane could have been present in his products, since he did not make a detailed search for it. (3) Here hydrogen was found in the non-condensable fraction.

Thynne suggested the following mechanism:



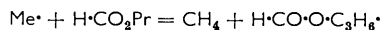
plus the usual radical-radical reactions.

This scheme accounts for neither the temperature-dependance of $\Delta(\text{Me}, \text{Pr}^n)$ nor the

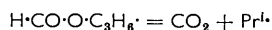
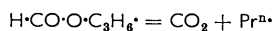
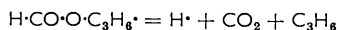
⁸ O'Neal and Benson, *J. Chem. Phys.*, 1962, **36**, 2196; **37**, 540.

⁹ Thynne, personal communication.

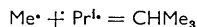
formation of isobutane. Since there is such a large discrepancy between the two studies the possibility of impurities in the reactants must be considered. The acetone had been used without trouble in the previous systems, so there is no reason to doubt its purity here. Isopropyl formate, which could account for the isobutane produced, was absent from the n-propyl formate. It is difficult to see how the $\frac{1}{2}\%$ or less of the higher-boiling impurity in the formate could be responsible for such relatively large amounts of isobutane. Runs with n-propyl formate alone yielded no products. Since the conversion of reactants was kept low the possibility of isobutane formation from secondary reactions can be eliminated. Hence we are forced to conclude that the isobutane arises from reactions involving the propyl formate. Thus, methyl radical attack may also take place on the alkyl side-chain:



and it is also possible that the resulting radical could decompose in several ways:



This would account for the temperature-dependence of the ratio $\text{C}_3\text{H}_6 : \text{n-C}_4\text{H}_{10}$ and the isobutane would result from the reaction:



This mechanism is tentatively suggested and could only be checked by the use of an isotopically labelled formate.

There are, however, several points regarding methyl radical attack on the alkyl side-chains of formates which require further discussion. Thynne¹⁰ found, in the decomposition of methyl formate sensitised by methyl radicals, that the rate of formation of methane was equal to the rate of formation of carbon dioxide. This, he rightly argued, is good evidence in favour of methyl attack exclusively at the formyl hydrogen atom in methyl formate. He extended this argument to n- and iso-propyl and n-butyl formate,¹¹ although it was not experimentally shown that the methane was equal to the carbon dioxide in these cases. He argued further that this view is supported by comparable studies with aldehydes, but in fact the rate constants for methyl attack on aldehydes are very much higher than for attack on formates. This is shown by the following comparison:

Reaction	<i>k</i> at 182° (mole c.c. ⁻¹ sec. ⁻¹)	Ref.
$\text{Me}\cdot + \text{Pr}\cdot\text{CHO} = \text{CH}_4 + \text{Pr}\cdot\text{CO}\cdot$	1.6×10^8	12
$\text{Me}\cdot + \text{H}\cdot\text{CO}_2\text{Pr} = \text{CH}_4\cdot + \text{PrO}\cdot\text{CO}\cdot$	4.0×10^6	2
$\text{Me}\cdot + \text{C}_2\text{H}_6 = \text{CH}_4\cdot + \text{Et}\cdot$	2.0×10^6	13
$\text{Me}\cdot + \text{n-C}_4\text{H}_{10} = \text{CH}_4\cdot + \text{Bu}\cdot$	1.1×10^7	13

Obviously the rate constant for the reaction of a methyl radical with n-propyl formate is more in keeping with the value for its reaction with a hydrocarbon than with that for its reaction with an aldehyde. This indicates that hydrogen abstraction from the alkyl side-chains in formates is likely, and the idea is supported by detection of hydrogen in the non-condensable products in the present study.

Finally, although the detailed mechanism of this decomposition of n-propyl formate is

¹⁰ Thynne, *Trans. Faraday Soc.*, 1962, **58**, 676.

¹¹ Thynne, *Trans. Faraday Soc.*, 1962, **58**, 1533.

¹² Kerr and Trotman-Dickenson, *Trans. Faraday Soc.*, 1959, **55**, 572.

¹³ Trotman-Dickenson, Birchard, and Steacie, *J. Chem. Phys.*, 1951, **19**, 163.

still uncertain, it is clear that under the present conditions it is of little value as a clean source of n-propyl radicals. Accordingly, results for radical-radical reactions from other formate systems are of doubtful value.

Conclusions on the Effect of the Radical Source on Δ .—Of the four Me-Prⁿ systems investigated, two have yielded self-consistent values of Δ which appear to be reliable. For these values, 0.025 ± 0.004 and 0.041 ± 0.010 , the agreement is reasonable in view of the experimental difficulties in determining such low values. The difference between them is insignificant in terms of present theoretical considerations of disproportionation-combination reactions. In conclusion it seems that by a careful choice of radical sources reasonably reproducible Δ values can be obtained.

EXPERIMENTAL

Apparatus.—The quartz cell of the apparatus described in Part I¹ was replaced by a 430 c.c. Pyrex cell. To separate hydrogen from the non-condensable fraction in the acetone-n-propyl formate experiments the carbon monoxide and methane were condensed in a trap containing silica gel at liquid-air temperature, and the hydrogen was brought back into the gas-burette and measured. The carbon dioxide produced in the formate experiments was not determined but was retained by the alumina column in the analysis of the condensable fraction. With di-t-butyl peroxide-n-butyraldehyde mixtures a trap containing aldehyde absorbent⁷ was placed between the reaction zone and the gas-chromatographic trap.

Analysis.—The major analytical column for the condensable fraction consisted of activated alumina as described in Part I.¹ For runs with di-t-butyl peroxide and n-butyraldehyde an 8 ft column packed with 60–80 mesh Celite containing 25% by weight of ethyl sebacate was placed before the alumina column to hold back the peroxide long enough to allow the n-hexane to be eluted. With the acetone-formate system the condensable fraction was analysed on a 6 ft column packed with 40–60 mesh activated alumina, poisoned with 2% of squalane and temperature controlled from 50° to 150°.

Materials.—Di-t-butyl peroxide, acetaldehyde, and n-butyraldehyde were commercial samples purified by bulb-to-bulb distillation and checked by gas chromatography. Two sources of n-propyl formate were used: (i) the B.D.H. product was distilled and a constant-boiling fraction (81–82°) collected; gas chromatography showed the presence of ca. 1% of a higher-boiling impurity; (ii) Eastman White Label n-propyl formate was twice distilled with rejection of large head and tail fractions, and the product was found to contain less than ½% of a higher-boiling impurity by gas chromatography. Further attempts to purify these materials, including preparative gas chromatography, failed. By comparing chromatograms of isopropyl formate alone and when added to the two purified materials, it was established that they did not contain this isomer. The results presented in Table 3 were mainly obtained from the purified Eastman product, but the other sample yielded the same pattern of results. Other conditions and materials were as described in Part I.

We thank Dr. J. C. J. Thynne for comments on the n-propyl formate results. Acknowledgment for a grant to J. G. is made to the donors of the Petroleum Research Fund administered by the American Chemical Society.