61. *The Reactions of Methoxyl Radicals with Cyclopropane and Isobutane.*

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The competitive reaction of methoxyl radicals, generated by the pyrolysis of dimethyl peroxide, with ethane and cyclopropane yields

$$\log [k(\text{ethane})/k(\text{cyclopropane})] = -0{\cdot}712 + (2650/2{\cdot}3\boldsymbol{R}T)$$

Absolute rate constants for the transfer reactions of methoxyl radicals have been derived from the study of the consumption of isobutane during the pyrolysis of dimethyl and di-t-butyl peroxide mixtures.

Shaw and Trotman-Dickenson[1] recently measured the relative rates of attack of methoxyl radicals on several hydrocarbons. Methyl nitrate and dimethyl peroxide were decomposed to yield the radicals in a flow system. The results were independent of the source of radicals except for the reactions with cyclopropane. It appeared that the radicals from methyl nitrate were more reactive than those from dimethyl peroxide, which was only used for a few experiments. Shaw and Trotman-Dickenson found cyclopropane to be 0·17 times as reactive as propane at 297°. We have used the same method, and dimethyl peroxide as the source, to compare ethane with cyclopropane between 195° and 324°. The ratio of initial ethane : cyclopropane was varied from 2 : 1 to 1 : 2. The results of eleven runs were evaluated by the method of least squares and gave:

$$\log (A_{\text{ethane}}/A_{\text{cyclopropane}}) = -0{\cdot}712 \pm 0{\cdot}119$$

$$E_{\text{ethane}} - E_{\text{cyclopropane}} = -2680 \pm 290 \text{ cal. mole}^{-1}$$

When combined with the previous results on the ethane–propane system these figures yield

$$k(\text{cyclopropane})/k(\text{propane}) = 0{\cdot}17 \text{ at } 297^\circ$$

in excellent agreement with the result obtained directly. The radicals formed from dimethyl peroxide probably attack cyclopropane only by the hydrogen-abstraction reaction: $CH_3{\cdot}O{\cdot} + C_3H_6 = CH_3{\cdot}OH + C_3H_5{\cdot}$. The reactions that occur with methyl nitrate are unknown. The abstraction of a hydrogen atom from cyclopropane by a methoxyl radical, a methyl radical,[2] a chlorine atom,[3] or the radical involved as chain carrier[4] in oxidations is slower than the abstraction of a typical primary hydrogen atom. It is, therefore, likely that the C–H bond-strength is at least 1—2 units greater than the 97 kcal. mole^{-1} normally allotted to a primary bond.

Trial runs showed that the reactivities of methoxyl radicals with hydrogen and methane could not be studied in this system. Considerable amounts of both gases were formed in the decompositions and subsequent reactions.

Some information on the absolute rates of methoxyl radical reactions has been obtained by analysing the products formed when dimethyl peroxide and di-t-butyl peroxide are decomposed in the flow system with isobutane. The results were interpreted according to the scheme:

$$(\text{MeO})_2 \longrightarrow 2\text{MeO}{\cdot} \quad \ldots \quad (1)$$

$$\left.\begin{array}{r}(\text{Bu}^t\text{O})_2 \longrightarrow 2\text{Bu}^t\text{O}{\cdot} \\ \text{Bu}^t\text{O}{\cdot} \longrightarrow \text{Me}{\cdot} + \text{Me}_2\text{CO}\end{array}\right\} \quad \ldots \quad (2)$$

$$\text{Me}{\cdot} + \text{CHMe}_3 \longrightarrow \text{Bu}^{t}{\cdot} + \text{CH}_4 \quad \ldots \quad (3)$$

$$\text{MeO}{\cdot} + \text{CHMe}_3 \longrightarrow \text{Bu}^{t}{\cdot} + \text{MeOH} \quad \ldots \quad (4)$$

$$\text{MeO}{\cdot} + \text{Me}{\cdot} \longrightarrow \text{Me}_2\text{O} \quad \ldots \quad (5)$$

$$2\text{Me}{\cdot} \longrightarrow \text{C}_2\text{H}_6 \quad \ldots \quad (6)$$

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[1] Shaw and Trotman-Dickenson, *J. Chem. Soc.*, 1960, 3210.

[2] Trotman-Dickenson, "Gas Kinetics," Butterworths, London, 1955.

[3] Knox and Nelson, *Trans. Faraday Soc.*, 1959, **55**, 937.

[4] Falconer, Knox, and Trotman-Dickenson, unpublished results.

The fate of the t-butyl radicals is unknown, but they are comparatively unreactive and are unlikely to re-form isobutane in the presence of higher concentrations of other radicals. Hence we can write:

$$\frac{k_4 k_6^{\frac{1}{2}}}{k_5} = \frac{R_{C_2H_6}}{R_{Me_2O}} \cdot \left(\frac{-R_{CHMe_3}}{R^{\frac{1}{2}}_{C_2H_6}[CHMe_3]} - \frac{k_3}{k_6^{\frac{1}{2}}}\right)$$

where $R_{C_2H_6}$ is the rate of formation of ethane and $[CHMe_3]$ is the mean concentration of isobutane. The rates of formation were found from the known amount of isobutane injected into the system and from the analysis of a known fraction of the products:

$$\log k_6\ (\text{mole}^{-1}\ \text{cm.}^3\ \text{sec.}^{-1}) = 13{\cdot}345\ ^5$$

and $$\log k_3\ (\text{mole}^{-1}\ \text{cm.}^3\ \text{sec.}^{-1}) = 11{\cdot}0 - (7600/2{\cdot}3\boldsymbol{R}T)\ \ (\text{ref. } 2)$$

k_5 has not been measured but can be deduced in two ways.

Hanst and Calvert[6] found, from a study of the decomposition of dimethyl peroxide, that $\log A_1$ (sec.$^{-1}$) = 15·4. The entropy of dimethyl peroxide can be deduced from entropies of *cis*-but-2-ene[7] (71·9) and n-butane (74·1) to be about 73 cal. mole^{-1} deg.$^{-1}$. The entropy of the methoxyl radical has been taken as 54·7 cal. mole^{-1} deg.$^{-1}$ by comparison with the entropy of methyl fluoride (53·3). Hence $\log A_{-1}$ (mole^{-1} cm.^{3} sec.$^{-1}$) = 13·0. The rate constants for the combination of unlike small radicals in the gas phase have been found to be very close to twice the geometric means of the rate constants for the combination of the two like radicals for almost all the systems studied.[8] Hence $k_5 = 2(k_{-1}k_6)^{\frac{1}{2}}$. If none of the reactions has an activation energy, then:

$$\log k_5\ (\text{mole}^{-1}\ \text{cm.}^3\ \text{sec.}^{-1}) = 13{\cdot}5$$

An alternative value can be derived from Benson and Jain's value[9] of $\log A_{-5}$ (sec.$^{-1}$) = 18·1, and considerations of the entropy change similar to those given above. Then $\log k_5$ (mole^{-1} cm.^{3} sec.$^{-1}$) = 14·6. This value is probably not reliable, as A_{-5} was deduced from a complicated scheme for the chain decomposition of dimethyl ether and was not measured directly.

TABLE 1. *The pyrolysis of dimethyl and di-t-butyl peroxide in isobutane*
(R in mole c.c.$^{-1}$ sec.$^{-1}$).

Temp.	10^7 [CHMe$_3$] (average) (mole c.c.$^{-1}$)	$10^{10}R_{CHMe_3}$	$10^{10}R_{C_2H_6}$	$10^{10}R_{C_2H_6O}$	$10^{-9}k_4$
190·5°	2·25	1·81	1·65	0·30	2·12
192·5	2·44	1·75	1·37	0·27	1·93
193·0	2·00	1·69	1·67	0·30	2·55
211·0	2·00	4·53	3·15	0·69	3·65
211·0	1·83	3·23	2·97	0·69	2·75
212·0	1·97	3·77	0·95	0·39	3·06
219·0 [a]	3·17	16·29	8·77	2·78	3·90
221·0	2·11	4·23	3·17	0·77	2·98
221·5	1·98	3·97	3·62	0·73	3·27
229·0	2·53	3·95	1·81	0·76	2·82
235·0 [a]	3·23	23·13	19·19	4·10	4·80
241·0	2·55	4·53	3·29	0·51	3·80
242·0	2·29	7·94	3·20	0·56	3·01
257·0	2·64	5·70	2·10	0·47	4·07
260·0 [a]	3·08	27·50	19·20	4·34	5·61

[a] Run in small reaction vessel.

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[5] Shepp, *J. Chem. Phys.*, 1956, **24**, 939.

[6] Hanst and Calvert, *J. Phys. Chem.*, 1959, **63**, 104.

[7] Entropies are taken from " Selected Values of Thermodynamic Properties," Circular 500, National Bureau of Standards, Washington, 1952.

[8] Trotman-Dickenson, *Ann. Rev. Phys. Chem.*, 1959, **10**, 53.

[9] Benson and Jain, *J. Chem. Phys.*, 1959, **31**, 1008.

The experimental conditions and results are summarised in Table 1, together with values of k_4 deduced from the first value of k_5. The dependence of k_4 on the volume of the reaction vessel is smaller than was expected, in view of the fact that the mean residence time of a molecule is equal to the half-life of one of the radical sources at 200° for the large and 225° for the small (one-sixth the size) reaction vessel. The results in the large and small vessels are sufficiently similar to justify confidence in the rate constants around 200°. The Arrhenius equation found with the large vessel was

$$\log k_4 \text{ (mole}^{-1}\text{ cm.}^3\text{ sec.}^{-1}) = (11{\cdot}30 \pm 0{\cdot}24) - (4100 \pm 600)/2{\cdot}3\boldsymbol{R}T$$

A_4 is of the normal magnitude for the reaction of a small radical with a moderate sized molecule. E_4 is about 3 kcal. mole^{-1} lower than the activation energy for the attack of a methyl radical on isobutane. This higher reactivity is in keeping with the lower selectivity of methoxyl radicals.[1] As has previously been pointed out, Wijnen's results [10] on the photolysis of methyl acetate can be interpreted to yield an activation energy of 7·1 kcal. mole^{-1} for the attack of methoxyl radicals on methyl acetate, as compared with 10 kcal. mole^{-1} for attack by methyl. If the present value of k_5 is accepted the A factor for the attack on methyl acetate by methoxyl is $10^{11 \cdot 6}$ mole^{-1} cm.^{3} sec.$^{-1}$ which is in line with those for the hydrocarbons shown in Table 2. The results form a self-consistent pattern except that the activation energy for n-butane appears slightly low (there is no corresponding discrepancy in the rate constant; therefore it is likely that the low value is the consequence of experimental error).

TABLE 2. *Reaction of methoxyl radicals with hydrocarbons.*

Hydro-carbon	log A (mole^{-1} cm.^{3} sec.$^{-1}$)	E (kcal. mole^{-1})	$10^{-8}k$ (250°) (mole^{-1} cm.^{3} sec.$^{-1}$)	Hydro-carbon	log A (mole^{-1} cm.^{3} sec.$^{-1}$)	E (kcal. mole^{-1})	$10^{-8}k$ (250°) (mole^{-1} cm.^{3} sec.$^{-1}$)
Ethane	11·8	7·1	7	Isobutane	11·3	4·1	38
Propane	11·6	5·2	24	Neopentane	12·1	7·3	11
n-Butane	10·8	2·9	40	Cyclopropane	12·5	9·7	3

Experimental.—The apparatus and procedure used to study the competitive attack on ethane and cyclopropane were identical with those used by Shaw and Trotman-Dickenson.[1] They were slightly modified in the experiments with isobutane to allow the injection of known amounts of di-t-butyl peroxide into the gas stream. A thermal-conductivity cell was used as a detector for the gas chromatography. In three experiments the 150 c.c. reaction vessel was replaced by one of 24 c.c. with 2 mm. capillary connecting tubes.

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[10] Wijnen, *J. Chem. Phys.*, 1957, **27**, 712.