645. *The Reactions of Methoxyl Radicals with Alkanes.*

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Methoxyl radicals have been produced in a circulating system by the pyrolysis of methyl nitrite and dimethyl peroxide between 200° and 400°. From measurements of the rates of disappearance of alkanes, when their mixtures with nitric oxide reacted with the methoxyl radicals, the relative reactivities of the alkanes have been deduced. It can be seen from the results that the methoxyl radical probably has a reactivity similar to that of methyl or trifluoromethyl.

GRAY[1] has recently reviewed extensively the properties and reactions of alkoxyl radicals. Despite the wealth of material available on the subject as a whole, very little is known about the kinetics of alkoxyl-radical reactions, expecially those that occur in the gas phase. Our object has been to study the hydrogen-abstraction reactions of the simplest member of the series.

The reasons for the indirect approach now employed are best understood in the light

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[1] Gray and Williams, *Chem. Rev.*, 1959, **59**, 239; *Chem. Soc. Special Publ.*, 1957, No. 9, p. 97; *Trans. Faraday Soc.*, 1956, **52**, 344; 1959, **55**, 408, 760.

of the limiting conditions and preliminary investigations. Methoxyl radicals can be formed by either photolysis or thermal decomposition. Wijnen[2] has investigated the kinetics of reaction of alkoxyl radicals produced by the photolysis of esters. Unfortunately, these systems are complicated because alkyl radicals are produced simultaneously. Thermal decomposition of nitrites was thought to yield alkoxyl radicals and nitric oxide, which although it contains an unpaired electron does not attack normal molecules. Nitrites are more readily available and more stable than symmetrical dialkyl peroxides which have the advantage that they only yield alkoxyl radicals. The abstraction of a hydrogen atom by a methoxyl radical (reaction 1) yields methanol which can readily be estimated by gas chromatography. This provides a means of following the reaction. Methoxyl radicals disproportionate to methanol and formaldehyde. The relative concentrations of methoxyl radicals in different runs could therefore be found by analysis for formaldehyde. Unfortunately formaldehyde is difficult to handle in a conventional vacuum line because of its reactivity and tendency to polymerize. Furthermore it cannot be estimated by gas chromatography without special precautions. This approach was abandoned when it had been shown that the presence of isobutane during the decomposition of methyl nitrite substantially increased the yield of methanol.

$$CH_3{\cdot}O + R^1H \longrightarrow CH_3{\cdot}OH + R^1 \qquad \text{. . . . . (1)}$$

Iodine was next added to the reaction system in order to convert radicals formed in reaction (1) into identifiable iodides. A possible advantage was that it should have made it possible to distinguish between attack on, say, the primary and secondary hydrogen atoms in propane by determination of n-propyl and isopropyl iodide produced. Considerable quantities of alkyl iodides were produced, but it was found that under the experimental conditions iodides readily isomerized.

Finally, the attempt to measure the products of the reaction was abandoned and the reactions were followed by measurements of the amounts of reactants consumed. Both methyl nitrite and dimethyl peroxide were used as sources. The relative rate constants were determined from the equation:

$$\frac{k_1}{k_2} = \frac{\log\,[R^1H]_{\text{initial}} - \log\,[R^1H]_{\text{final}}}{\log\,[R^2H]_{\text{initial}} - \log\,[R^2H]_{\text{final}}}$$

where k_2 is the rate constant of reaction (2):

$$CH_3{\cdot}O + R^2H \longrightarrow CH_3{\cdot}OH + R^2 \qquad \text{. . . . . (2)}$$

This relation can only be employed if the radicals, R^1 say, react without re-forming R^1H or producing R^2H. This condition was secured by the addition of nitric oxide. Additional nitric oxide was, of course, formed in the pyrolyses of methyl nitrite. The amounts of hydrocarbon remaining at the end of the runs were found not to depend on the quantity of nitric oxide added. For every pair of hydrocarbons, runs were done with each reactant alone to ensure that their partners were not by-products of the methoxyl attack. Although R^2H was never formed from R^1H, it was often difficult to adjust the chromatographic conditions so that the by-products from R^1H and the decompositions of the sources did not interfere with the analysis.

Table 1 lists the results obtained from the investigation of propane–isobutane mixtures. The derived rate constants are plotted in Fig. 1. They do not vary with the amount of nitric oxide present or with the relative or total concentrations of the hydrocarbons. The results from the runs with dimethyl peroxide are in excellent agreement with those with methyl nitrite, though the former are more reproducible. The large quantities of by-products formed in the presence of methyl nitrite limit the extent of reaction so that the differences between the initial and final hydrocarbon concentrations are small and hence more sensitive to analytical errors. Only about 5 molecules of alkane were attacked for

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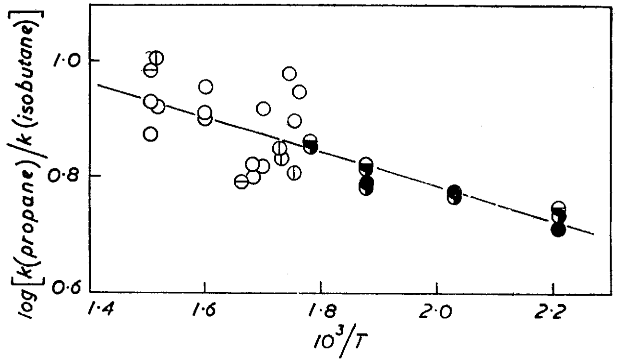
[2] Wijnen, *J. Chem. Phys.*, 1958, **28**, 939, and earlier papers.

TABLE 1. *The reaction of methoxyl radicals with propane–isobutane.*

Temp. °K	C_3H_8 (c.c.) initial	C_4H_{10} (c.c.) initial	C_3H_8 (c.c.) final	C_4H_{10} (c.c.) final	NO (c.c.) initial	k_p/k_b
(a) *Methyl nitrite source.*						
571	7·345	7·168	6·325	6·060	0	0·890
571	4·850	8·245	4·235	6·662	7	0·636
572	7·330	7·743	6·331	6·340	7	0·791
574	7·474	7·532	6·279	6·256	0	0·955
578	4·746	7·532	4·106	6·095	0	0·684
580	4·448	7·785	3·915	6·498	0	0·705
589	8·786	8·584	7·769	7·403	0	0·831
595	7·224	8·106	6·661	7·147	0	0·631
595	8·933	8·366	8·215	7·379	0	0·668
599	7·369	4·737	6·805	4·164	0	0·618
624	7·330	7·743	6·117	6·340	0	0·904
625	8·254	7·807	7·129	6·518	0	0·815
625	7·899	8·206	6·885	6·937	8	0·811
659	4·407	6·797	3·939	6·087	0	1·010
661	8·672	8·060	7·521	6·797	8	0·835
663	7·925	7·949	6·719	6·554	0	0·851
664	8·119	8·002	7·055	6·630	0	0·747
666	8·012	4·403	6·673	3·741	0	0·968
(b) *Dimethyl peroxide source.*						
453	8·314	7·324	4·093	1·863	14	0·517
453	7·709	3·875	4·395	1·434	14	0·565
454	3·715	7·941	1·600	1·729	11	0·553
454	7·778	7·900	4·088	2·439	14	0·548
493	7·973	8·245	2·878	1·499	14	0·598
493	4·048	11·68	1·397	1·922	16	0·589
532	7·964	7·900	4·771	3·595	12·5	0·652
533	9·189	8·658	4·742	2·974	12·5	0·618
533	4·704	8·110	2·013	2·013	14	0·609
533	8·788	4·551	3·712	1·234	12·5	0·661
562	8·847	4·394	5·152	2·057	14	0·712
562	3·810	8·766	1·758	3·020	14	0·726

FIG. 1. *Arrhenius plot showing the variation with temperature of the relative rates of attack of methoxyl radicals on propane and isobutane. Ratio of propane to isobutane* ● 1 : 1, ◒ 2 : 1, ◑ 1 : 2 (*source, dimethyl peroxide*); ○ 1 : 1, ⊖ 2 : 1, ⦶ 1 : 2 (*source, methyl nitrite*).



every 100 molecules of methyl nitrite decomposed. Furthermore the by-products complicate the analysis. Consequently, the rate constants obtained with dimethyl peroxide are more precise. The results obtained with each pair of hydrocarbons with methyl nitrite and dimethyl peroxide are summarized in Tables 2 and 3, respectively. The errors calculated by the method of least squares show the considerable scatter of the results obtained with methyl nitrite. Nevertheless, no trends were observed when the conditions were changed, and the mean points for each pair of alkanes at 350° fall as close to the Arrhenius plots drawn from the dimethyl peroxide results as do the peroxide points themselves. Results with cyclopropane differ markedly. Since the unreactivity of cyclopropane towards the peroxide is in keeping with its behaviour with other radicals, it may be that at 350° cyclopropane is removed by reactions in addition to hydrogen abstraction. More experiments are needed.

TABLE 2. *Arrhenius parameters and rate constants relative to propane, methyl nitrite being used as source of methoxyl radicals between* 300° C *and* 400° C.

Hydrocarbon	Runs	log A	E	k at 250° c
Propane	—	0		1·00
Ethane	18	$+0·08 \pm 0·23$	$+1200 \pm 700$	0·46
n-Butane	5	$-0·96 \pm 0·61$	-3000 ± 1700	1·21
Isobutane	18	$-0·38 \pm 0·17$	-1300 ± 500	1·24
Neopentane	9	$-1·77 \pm 0·15$	-4700 ± 400	0·77
Cyclopropane	7	$-0·63 \pm 0·25$	-1100 ± 700	0·59

TABLE 3. *Arrhenius parameters and rate constants relative to propane, dimethyl peroxide being used as source of methoxyl radicals between* 200° C *and* 300° C.

Hydrocarbon	Runs	log A	E	k at 250° c
Propane	—	0	0	1·00
Ethane	7	+0·24	+1830	0·30
n-Butane	7	−0·75	−2300	1·61
Isobutane	12	−0·27	−1110	1·56
Neopentane	9	+0·55	+2130	0·46
Cyclopropane	2	—	—	0·17 at 297° c

The more accurate results with peroxide show that the variations of the A factors are small, as would be expected on theoretical grounds. Probably the experimental errors are too great to warrant a detailed comparison of the values with those deduced from transition-state theory. It was to be expected that ethane and neopentane would have activation energies similar to, and greater than, those of propane for hydrogen abstraction, as they only contain primary hydrogen atoms. n-Butane was expected to have a slightly lower activation energy than propane but not lower than isobutane. The results are probably not sufficiently accurate for these comparisons either, so discussion may most profitably be focussed on the rate constants at 250°, relative to that for attack on propane, which were directly determined. The relative rate constant for attack on a single hydrogen atom in ethane is 0·30/6 = 0·050, and in neopentane is 0·46/12 = 0·038, giving a mean of 0·044. Hence, if all primary hydrogens have the mean reactivity, secondary hydrogen atoms have specific rate constants of 0·37 (propane) and 0·34 (n-butane), and tertiary hydrogen atoms of 1·16 (isobutane). It is likely that this last figure is an underestimate as the primary hydrogens in isobutane probably resemble those in neopentane more than those in ethane. If the primary atoms in isobutane have relative rate constants of 0·40, then the tertiary constant should be 1·20. These rate constants are in the ratio 1 : 8 : 27, for primary, secondary, and tertiary hydrogens, respectively. These reactivities are compared in Table 4 with those found for other radicals in the gas phase. The reactivities for each radical increase as the C–H bond attacked becomes weaker, as might have been expected on general grounds. Also in line with expectations is the observation that the differences between the relative reactivities of the C–H bonds increase with decreasing reactivity of the attacking radical. The reactivity of the radical X can conveniently be correlated with the activation energy of its attack on ethane (column 7), which roughly follows the order of the strength of the X–H bond that is formed. On the other hand, the figures can also be used, along with others, to show that bond strength is not of overwhelming importance in determining activation energies.[3]

Consideration of the activation energies for the attack of the various radicals on ethane suggests that the value for methoxyl should be about 9 kcal. mole^{-1}. The only activation energy reported for the abstraction of a hydrogen atom by methoxyl is the reaction with

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[3] Trotman-Dickenson, " Free Radicals," Methuen, London, 1959.

TABLE 4. *Relative rate constants for* $X + RH \longrightarrow XH + R$.

Radical, R	Temp.	Rate constant				E (ethane)	D(X–H)	Note
		Me	Prim.	Sec.	Tert.			
D(R–H)		102·5	96·9	93·2	90·0			*a*
Radical, X								
F	25	0·8	1	1·2	1·4	0·3	134	*b*
Cl	250	0·03	1	3	3	1·0	103	*c*
HO_2, RO_2, or OH	350	$<$0·07	1	4	11	—	—	*d*
CF_3	182	0·08	1	6	36	7·5	102	*e*
MeO	250	—	1	8	27	—	102	*f*
Me	182	0·04	1	7	50	11	102·5	*g*
Br	98	0·002	1	250	6300	13·4	86	*h*

All energies are in kcal. mole^{-1}.

a Fettis and Trotman-Dickenson, *J. Amer. Chem. Soc.*, 1959, **81**, 5260. *b* Fettis and Trotman-Dickenson, *J.*, 1960, 1064. *c* Knox and Nelson, *Trans. Faraday Soc.*, 1959, **55**, 937; Pritchard, Pyke, and Trotman-Dickenson, *J. Amer. Chem. Soc.*, 1955, **77**, 2629. *d* Knox, Smith, and Trotman-Dickenson, *Trans. Faraday Soc.*, 1958, **54**, 1509; " Seventh Symposium on Combustion," Butterworths, London, 1959, p. 126; Falconer, Knox, and Trotman-Dickenson, unpublished results. *e* Ayscough, Polanyi, and Steacie, *Canad. J. Chem.*, 1955, **33**, 743; Ayscough and Steacie, *ibid.*, 1956, **34**, 103; Ayscough, *J. Chem. Phys.*, 1956, **24**, 944; Pritchard, Pritchard, Schiff, and Trotman-Dickenson, *Trans. Faraday Soc.*, 1956, **52**, 849. *f* This work; D(MeO–H) is higher than the value adopted by Gray, who appears to have based his calculation on an old value for the heat of formation of methyl nitrite which he now considers incorrect. *g* Trotman-Dickenson, " Gas Kinetics," Butterworths, London, 1955. *h* Kistiakowsky and Van Artsdalen, *J. Chem. Phys.*, 1944, **12**, 469; Anson, Fredricks, and Tedder, *J.*, 1959, 918; Fettis and Trotman-Dickenson, *J. Amer. Chem. Soc.*, 1959, **81**, 5260.

methyl acetate. Wijnen[4] deduced a value of about 4·5 kcal. mole^{-1}. This may be a considerable underestimate. The rate constants were obtained from the experimental results by different methods above and below 150°. Considerable reliance must have been placed on the observation that the point for 177° appears to lie on the line of points for 63°, 92°, and 143°. The point for 217° which would give a higher activation energy is neglected. The point for 177° only lies on the line because it has been taken as the mean of runs 51 and 53. Run 52 yields a much higher value and would considerably raise the point if it were included in the average. Accordingly the activation energy is not yet established and a value of, say, 7 or 8 kcal. mole^{-1} which would be in keeping with a value of 9 kcal. mole^{-1} for ethane is not ruled out.

EXPERIMENTAL

Methyl nitrite. This was prepared from methanol and nitrous acid and fractionated in a low-temperature still. It was stored in a bulb painted black; no decomposition could be detected during one month. The decomposition of the pure substance was followed by measurement of pressure changes. Good first-order plots were obtained, corresponding to the formation of two molecules of products from each molecule of reactant up to 90% decomposition. The rate constants obtained were:

$$k = 3{\cdot}5 \times 10^{-4}\ \text{sec.}^{-1}\ \text{at}\ 212°; \qquad 1{\cdot}7 \times 10^{-3}\ \text{sec.}^{-1}\ \text{at}\ 233°.$$

These rate constants are almost exactly one half Steacie and Shaw's values.[5] The latter agree well with the rate constant at 200° which we have deduced from Carter and Travers's[6] determinations of the rate of formation of nitric oxide in the decomposition. Gas-chromatographic analysis of the products showed that, contrary to the mechanism suggested by Steacie and Shaw, methanol only formed a small proportion of the final products. More methyl formate and dimethoxymethane, and an equal amount of an unidentified substance were produced. The unknown substance was eluted between dimethoxymethane and methanol from a column of Celite–diethyl phthalate–glycerol in the ratio 40 : 10 : 1, at room temperature. Furthermore, considerable quantities of nitrous oxide were formed. The apparent agreement with Carter and Travers's work therefore casts doubt on the reliability of the rate constants rather than supports them. No explanation for the discrepancies can be suggested. None of the subsequent

[4] Wijnen, *J. Chem. Phys.*, 1957, **27**, 710.

[5] Steacie and Shaw, *Proc. Roy. Soc.*, 1934, *A*, **146**, 388.

[6] Carter and Travers, *Proc. Roy. Soc.*, 1937, *A*, **158**, 495.

work was based on the value of the rate constant or upon the precise nature of the products formed. Different apparatus was employed for the study of the transfer reactions, so that it is unlikely that common systematic errors occur. None of the uncertainties about the decomposition of methyl nitrite invalidate the present conclusions.

Dimethyl peroxide. This was prepared, 0·05 mole at a time, by Hanst and Calvert's [7] method and stored in a blackened bulb in which no appreciable decomposition occurred during one month.

Hydrocarbons. These were normal commercial samples except for the neopentane which was supplied by the National Chemical Laboratory. The only impurities that could be detected by gas chromatography were ethylene (1·2%) in the ethane and isobutane (0·5%) in the propane. Suitable corrections were applied.

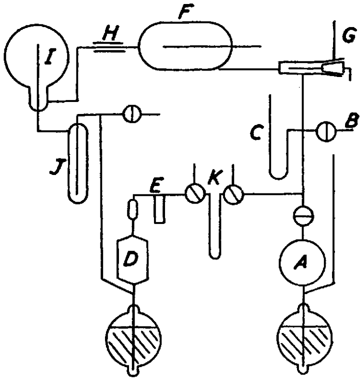

FIG. 2. *The flow system.*

Nitric oxide. This was prepared by the reaction of sodium nitrite with potassium iodide in the presence of hydrochloric acid.[8]

The reaction system (Figure 2). Appropriate amounts of the hydrocarbons were measured in the gas burette *A* and injected into the circulating system where they were mixed with nitric oxide admitted through tap *B* to a pressure measured on the manometer *C*. The gases were circulated by the automatic Toepler pump *D* protected by the anti-splash device *E*. The pump [9] displaced 45 c.c. at each stroke of 25 cm. with a period of 7 sec. Before the gases reached the reaction vessel *F*, contained in an electric furnace, they passed the capillary leak *G* through which the methoxyl source was bled. The capillary *H* controlled the residence time of the gases in the reaction zone, from which they flowed into the adjustable buffer volume *I*. The circuit was completed by the trap *J* which was normally cooled in a carbon dioxide bath to reduce the concentration of involatile by-products. At the end of the run the source leak was shut off and liquid oxygen placed round the chromatography trap *K*; the gases were circulated until the condensation was complete.

Chromatography. The chromatography system was of the conventional Janak design. The columns employed were as follows.

Methyl nitrite source: Ethane–propane—300 cm. of activated alumina (25/52 mesh), 13°. Propane–n-butane, propane–neopentane, and propane–cyclopropane—split columns, each 75 cm. of activated alumina (25/52 mesh), 20°. Propane–isobutane—300 cm. of alumina (25/52 mesh)–1% squalane, 20°.

Dimethyl peroxide source: Ethane–propane—150 cm. of alumina (25/52 mesh)–1% squalane, 20°; 20 cm. of activated charcoal (25/32 mesh), 78°. Propane–n-butane, propane–neopentane, and propane–cyclopropane—75 cm. of alumina (25/52 mesh)–1% squalane, 20°. Propane–isobutane—split columns, each 75 cm. of alumina (25/52 mesh)–1% squalane, 20°.

We are indebted to the Institute of Petroleum for a grant.

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[*Received, December 28th,* 1959.]

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

[8] Miller and Steacie, *J. Chem. Phys.*, 1951, **19**, 73.

[9] Maass, *J. Amer. Chem. Soc.*, 1919, **41**, 53.