

Decomposition of Ethoxyl Radicals

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The thermal decomposition of the ethoxyl radical has been studied in the gas phase over the temperature range 149–176° by use of the pyrolysis of diethyl peroxide as the radical source. Arrhenius parameters of $10^{12.15}$ sec.⁻¹ and 22.1 kcal mole⁻¹ were measured for the reaction $\text{EtO} \rightarrow \text{Me} + \text{CH}_2\text{O}$. The radical has been shown to decompose by carbon–carbon bond fission about an order of magnitude more quickly than by carbon–hydrogen bond fission.

THE unimolecular decomposition of alkoxy radicals is well established and data have been reported for the decomposition of secondary and tertiary radicals.^{1–3} For primary alkoxy radicals, the situation is less satisfactory. Although they appear to be more stable towards decomposition, the few kinetic data available are in disagreement. For example, values of 13 and 21 kcal. mole⁻¹ have been suggested^{4,5} for the activation energy required for decomposition of the ethoxyl radical by carbon–carbon fission. We have now examined the thermal decomposition of the ethoxyl radical in the temperature range 149–176° using diethyl peroxide as the radical source.

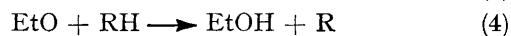
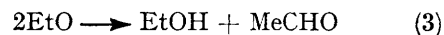
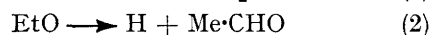
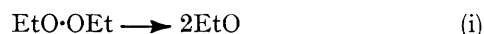
EXPERIMENTAL

Diethyl peroxide was prepared from diethyl sulphate and 30% hydrogen peroxide by Wiley's method,⁶ and purified by preparative gas chromatography. The apparatus and general technique have been described.³ Since the radicals produced in the decomposition were to be scavenged by reaction with a suitable hydrogen donor, preliminary experiments were performed with several potential donors. Hydrogen chloride, hydrogen sulphide, and methanethiol all appeared to sensitise the decomposition of the peroxide at temperatures well below its normal range for thermal decomposition and so could not be used. Cyclohexene did not induce peroxide decomposition and so was chosen as the substrate.

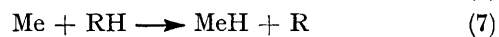
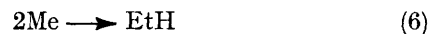
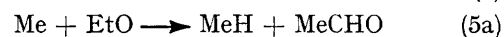
RESULTS AND DISCUSSION

Ethoxyl radicals are produced by the thermal decomposition of diethyl peroxide. These radicals may react subsequently by carbon–carbon or carbon–hydrogen bond fission, by autodisproportionation or by hydrogen atom abstraction. Our experimental observation that

methane, ethane, hydrogen, ethanol, ethyl methyl ether, and acetaldehyde are formed is evidence for the occurrence of (i) and (1)–(4).



(a) C–C Bond Fission.—Rate data for reaction (1) can be evaluated by measurement of the methyl radicals produced. These radicals can react as in (5)–(7).



If the hydrogen donor RH loses hydrogen so readily that $R_{\text{MeH}(7)} \gg R_{\text{EtH}}, R_{\text{MeOEt}},$ or $R_{\text{MeH}(5)}$ (where R_x is the rate of formation of X), then we can calculate the methyl radical yield by direct measurement of the methane yield, i.e., $R_{\text{Me}(1)} = R_{\text{MeH}(7)}$. Under such conditions relation (ii) obtains. In the presence of cyclohexene, ethane and ethyl methyl ether yields are negligible. The disproportionation : combination ratio,

$$\frac{R_{\text{EtOH}}}{R_{\text{MeH}}[\text{RH}]} = \frac{k_4}{k_1} + \frac{k_3}{k_1^2} \cdot \frac{R_{\text{MeH}}}{[\text{RH}]} \quad (\text{ii})$$

$\Delta(\text{Me}, \text{EtO}) = k_{5a}/k_5$, has not been measured, but values of 1.5 and 1.3 have been reported¹ for $\Delta(\text{Me}, \text{MeO})$ and

¹ M. J. Yee Quee and J. C. J. Thynne, *J. Phys. Chem.*, 1968, **72**, 2824.

² M. H. J. Wijnen, *J. Amer. Chem. Soc.*, 1960, **82**, 3034.

³ J. A. Gray, Thesis, London, 1950.

⁴ R. H. Wiley, U.S.P. 2,357,298/1944.

¹ P. Gray, R. Shaw, and J. C. J. Thynne, *Prog. Reaction Kinetics*, 1967, **4**, 63.

² D. L. Cox, R. A. Livermore, and L. Phillips, *J. Chem. Soc. (B)*, 1966, 245.

$\Delta(\text{Et}, \text{EtO})$ respectively. It is therefore not unreasonable to assume that $k_{5a}/k_5 = ca. 1.5$ and since only traces of ether were formed we consider that the disproportionation (5a) contributes only negligibly ($< 0.1\%$) to the total methane yield.

If methyl or ethoxyl radicals react by addition to cyclohexene this would invalidate our suggested mechanism. Rust *et al.*⁷ have decomposed the *t*-butoxyl radical in the presence of cyclohexene. They obtained quantitative recovery of cyclohexene and observed no product such as methylcyclohexene and methylcyclohexane; they therefore concluded that methyl radical addition to the olefin did not occur. Farmer and Moore⁸ have reported that alkoxyl radicals do not react by addition to cyclohexene at a significant rate compared with their reaction by hydrogen atom abstraction. We therefore regard reactions (1), (2), (3), (4), and (7) as the predominant radical reactions in this system.

Experiments on peroxide-cyclohexene mixtures were performed in the range 149–176°. Our results are in Table 1 and, when plotted in the form suggested by equation (ii), yield least-square values for the slopes (k_3/k_1^2) and intercepts (k_4/k_1) shown in columns 2 and 3 of Table 2.

The temperature-dependences of these rate ratios are expressed by equations (iii) and (iv). The error limits represent the standard deviations of a least-mean-squares

$\log k_3/k_1^2$ (mole⁻¹ cm.³ sec.)

$$= (-11.3 \pm 1.7) - \frac{(-44,100 \pm 3400)}{2.303RT} \quad (\text{ii})$$

$\log k_4/k_1$ (mole⁻¹ cm.³)

$$= (0.2 \pm 3.0) - \frac{(-12,700 \pm 6000)}{2.303RT} \quad (\text{iv})$$

computer treatment and, in the case of the intercepts plot, are large. This may be due to some contribution to ethanol formation by abstraction from the peroxide although the absence of curvature in the plots of [ii] and the greatly enhanced ethanol yield in the peroxide-cyclohexene mixtures compared with that in the peroxide alone suggests that such a contribution is small.

The Arrhenius parameters for reaction (1) may, in principle, be obtained from either equations (iii) or (iv) if data for reactions (3) and (4) are known. No value is available for either reaction but several values of *ca.* 10^{13} mole⁻¹ cm.³ sec.⁻¹ have been estimated^{1,9} for the rate constant for the autodisproportionation of methoxyl radicals into MeOH and CH₂O. If we assume that A_3 (mole⁻¹ cm.³ sec.⁻¹) = 10^{13} and E_3 (kcal. mole⁻¹) = 0, then $\log A_1$ (sec.⁻¹) = 12.15 ± 0.85 and E_1 (kcal. mole⁻¹) = 22.1 ± 1.7 . This activation energy may be compared with values of 21 and 13 kcal. mole⁻¹ obtained from studies of the photolyses of ethyl nitrate⁵ and ethyl propionate⁴ respectively.

In Table 3 we have compared our results for the decomposition of ethoxyl radicals with those reported

TABLE 1

Product ratios obtained by the pyrolysis of diethyl peroxide (P)-cyclohexene (C) mixtures

Temp.	$\frac{[P]}{[C]}$	$10^6[C]$ (mole cm. ⁻³)	$10^{-6}R_{\text{EtOH}}$ $\frac{R_{\text{MeH}}[C]}{\text{cm.}^3}$	$10^6 R_{\text{MeH}}$ $\frac{[C]}{(\text{sec.}^{-1})}$	$\frac{R_{\text{MeH}}}{R_{\text{HH}}}$
149.3°	0.39	1.36	11.7	1.58	4.43
149.3	0.70	0.96	13.5	1.89	4.79
149.3	0.50	1.06	13.9	2.19	4.59
149.3	1.45	0.47	18.3	3.81	5.76
149.3	0.24	2.18	8.60	0.81	4.00
149.3	0.36	1.78	10.6	0.97	4.03
154.8	0.37	1.25	7.15	2.89	5.42
154.9	0.64	0.94	11.0	4.43	6.25
154.9	0.81	0.81	12.5	6.18	6.00
154.9	0.60	1.10	11.1	4.65	6.57
154.9	0.95	0.65	15.8	8.04	12.1
160.8	0.27	1.36	5.85	4.06	7.83
160.8	0.44	0.92	7.70	7.19	7.44
160.7	0.94	0.44	17.5	18.7	9.25
160.8	0.25	1.47	5.90	3.64	8.23
160.6	0.37	1.08	8.01	6.38	9.54
160.7	0.60	0.69	9.83	13.8	12.2
160.7	0.65	0.57	9.99	11.5	8.43
167.1	0.31	0.99	6.06	6.44	9.41
167.1	0.25	1.36	5.32	6.33	8.61
167.1	0.76	0.50	11.0	25.8	10.5
167.1	0.52	0.70	7.74	17.8	8.62
167.1	0.42	0.95	7.75	10.8	8.36
167.1	0.63	0.61	10.3	19.2	8.75
175.3	0.39	0.88	7.12	23.2	8.46
175.6	0.25	1.57	4.56	13.1	7.93
175.5	0.37	1.13	6.36	19.8	8.07
175.5	0.69	0.62	9.30	44.5	9.31
175.5	0.26	1.80	4.03	13.5	8.19
175.5	0.58	0.71	7.77	36.5	8.75
175.5	0.32	1.36	3.31	17.0	8.33

TABLE 2

Rate-constant ratios obtained by the decomposition of diethyl peroxide in the presence of cyclohexene

Temp.	$10^{-11}k_3/k_1^2$ (mole ⁻¹ cm. ³ sec.)	$10^{-6}k_4/k_1$ (mole ⁻¹ cm. ³)	k_1/k_2
149.3°	(3.02 ± 0.28)	(7.10 ± 0.60)	4.6
154.9	(1.56 ± 0.18)	(3.32 ± 1.01)	7.3
160.8	(0.67 ± 0.11)	(2.96 ± 0.67)	9.0
167.1	(0.27 ± 0.05)	(4.16 ± 0.82)	9.0
175.5	(0.16 ± 0.03)	(2.15 ± 0.91)	8.4

for secondary and tertiary alkoxyl radicals. The results for the last radicals were analysed by use of a Hinshelwood-Lindemann mechanism and their decomposition shown to be pressure-dependent. Such a treatment for the ethoxyl radical is not feasible because there are two sources of ethanol [reactions (3) and (4)] which leads to a somewhat intractable rate expression. We do not consider that this invalidates a comparison since the higher activation energy for the decomposition of the ethoxyl radical suggests that pressure-dependence will occur in a lower pressure region than for the other radicals. Hence it is unlikely to be apparent within the pressure range of this work (30–64 mm. Hg). In order to test this, several experiments were performed at 149° in which the total pressure was varied by the addition of carbon dioxide. The rate ratios were unaffected by the addition of up to 100 mm. of CO₂. We conclude that,

⁷ F. R. Rust, F. H. Seubold, and W. E. Vaughan, *J. Amer. Chem. Soc.*, 1950, **72**, 338.

⁸ E. H. Farmer and C. G. Moore, *J. Chem. Soc.*, 1951, 131.

⁹ J. Hecklen, Air Force Report No., SSD TR-67-68, 1967.

under our experimental conditions, the decomposition is not occurring in a 'fall-off' region.

TABLE 3

Arrhenius parameter (log A and E), enthalpies of decomposition (ΔH), and velocity constants for the decomposition of alkoxy radicals

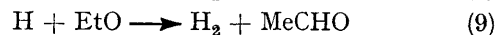
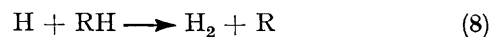
Reaction	ΔH (kcal. mole ⁻¹)	log A (sec. ⁻¹)	E (kcal. mole ⁻¹)	log k (164°) (sec. ⁻¹)	Ref.
EtO \longrightarrow Me + CH ₂ O	10	12.15	22.1	1.1	This work
Me ₂ CHO \longrightarrow Me + MeCHO	9	11.8	17.2	3.2	2
Me ₃ CO \longrightarrow Me + Me ₂ CO	2	11.2	12.0	5.2	7

Comparison of the data for the decomposition of the radicals indicates that the ease of methyl radical elimination is in the order t-butoxyl > isopropoxyl > ethoxyl, the last radical being much more stable towards decomposition. The activation energies decrease as fission becomes easier, although in view of the error limits involved and some problems in the evaluation of k_∞ and k_0 calculated from data obtained in similar regions of the fall-off curve¹⁰ the differences may not be significant. The overall pattern of decomposition is in accord with predictions based in thermochemical evidence and in column 2 of Table 3 we show the calculated enthalpies of decomposition.¹

¹⁰ E. O'Neal and S. W. Benson, *J. Chem. Phys.*, 1962, **36**, 2196.

¹¹ G. R. McMillan, *J. Amer. Chem. Soc.*, 1962, **84**, 2514.

(b) C-H Bond Fission.—Decomposition of the ethoxyl radical by (2) may lead to the formation of molecular hydrogen by reactions (8) and (9). If we assume that



few hydrogen atoms react in other ways then $R_{\text{MeH}}/R_{\text{HH}}$ can be used to give a guide to the occurrence of reaction (2), since it will be equal to k_1/k_2 . Hydrogen is a minor reaction product and so the experimental ratio is subject to appreciable fluctuations. In Table 1 we show this ratio $R_{\text{MeH}}/R_{\text{HH}}$ and in column 4, Table 2, the average value at each temperature. Part of these fluctuations may be the result of other contributions to hydrogen formation but an analysis along the lines of equation (ii) is unwarranted by the quality of our data. Our results show that carbon-carbon bond fission is faster than carbon-hydrogen fission by about an order of magnitude. Wijnen⁴ has also suggested that $k_1 \gg k_2$. Gray's results however indicate that, in the photolysis of ethyl nitrate,⁵ about 53% and 47% of the ethoxyl radicals decompose by reactions (1) and (2) respectively. The second figure is much higher than our results suggest and might be explained by the more random decomposition of photolytically produced ethoxyl radicals, since McMillan¹¹ has demonstrated the occurrence of such behaviour in systems producing alkoxy radicals.

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