Electron Spin Resonance Studies. Part XL.[1] A Kinetic Investigation of the Oxidation of Oxygen-substituted Carbon Radicals by Hydrogen Peroxide

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E.s.r. spectroscopy has been employed to investigate the reaction of the hydroxyl radical with some alcohols and ethers, and the oxidation of hydroxy- and alkoxy-conjugated radicals by hydrogen peroxide. The Ti^{III}–H_2O_2 couple has been used to generate radicals, and application of a competitive kinetic method involving the steady-state approximation leads to the estimation of rate constants for some of these reactions. For example, reaction of diethyl ether with ·OH leads to the radicals ·CHMeOEt and ·CH_2CH_2OEt; the observed steady-state concentrations at low [H_2O_2] are in the ratio *ca.* 13:1. At higher concentrations of hydrogen peroxide, this ratio is reduced and we estimate that the rate constant for oxidation of ·CHMeOEt by H_2O_2 is $5{\cdot}5 \times 10^4$ l mol^{-1} s^{-1}. The influence of structural features on the oxidation of related radicals has been investigated. Evidence is also presented for oxidation and reduction processes involving radicals generated during the oxidation of 2-methoxyethanol in aqueous solution.

WE have previously employed e.s.r. spectroscopy in conjunction with a rapid-flow system to estimate the importance of radical reduction in metal ion–hydrogen peroxide systems.[1] In particular, it was possible to demonstrate that, for some carbonyl-conjugated radicals, reduction by Fe^{II} or Ti^{III}–EDTA (ethylenediamine tetra-acetate) can provide an important pathway for radical termination. Under certain well defined experimental conditions we were able to derive rate constants which were found to be in good agreement with those obtained in a parallel investigation with pulse radiolysis.

We now report a further application of the steady-state approximation to the study of short-lived radicals generated in a flow system within the cavity of an e.s.r. spectrometer.[2] A variety of hydroxy- and alkoxy-conjugated radicals have been generated; an investigation of their oxidation by hydrogen peroxide leads to a series of rate constants for acyclic radicals and for radicals with five- and six-membered rings. These and previous results are then used to provide kinetic support for the more complex mechanism of oxidation of 2-methoxyethanol, in which hydroxy-, alkoxy-, and carbonyl-conjugated radicals are involved.

EXPERIMENTAL

The e.s.r. spectrometer, spectral analysis, flow system, and experimental conditions for e.s.r. and pulse radiolysis have been described in detail.[1] For e.s.r. investigations the three reagent streams which were simultaneously mixed contained, respectively, (i) 1·6—16mM-titanium(III) chloride, (ii) 2·7—300mM-hydrogen peroxide, and (iii) the organic substrate(s) in sufficient concentration to scavenge all the hydroxyl radicals produced in the initiating reaction.[1] In order to achieve the desired pH, stream (i) contained in addition either concentrated sulphuric acid or EDTA (disodium salt) in molar concentration equal to that of Ti(III), together with ammonia solution (*d* 0·880). For pulse radiolysis studies, N_2O-saturated solutions of diethyl ether or tetrahydrofuran (10mM) at neutral pH were employed. The absorption at 260 nm was monitored; it was assumed that all primary species were scavenged during the pulse, and $G(\cdot OH + e^- + H\cdot)$ was taken as 6·2.

Commercially available chemicals used here and not reported in ref. 1 were 2-methoxyethanol, dimethoxymethane, 1,4-dioxan, and tetrahydrofuran (Fisons Laboratory Reagents), methanol and diethyl ether (Fisons Analytical Reagents), and 1,3-dioxolan (Koch–Light Laboratories).

RESULTS AND DISCUSSION

Equations (1)—(7) describe a general reaction scheme in which hydroxyl radicals, generated from the Ti^{III}-H_2O_2 couple, react with organic donors R^1H and R^2H to yield radicals $R^{1\cdot}$ and $R^{2\cdot}$, respectively, of which one ($R^{1\cdot}$) is selectively oxidised with hydrogen peroxide and with titanium(IV).

$$HO\cdot + R^1H \xrightarrow{k_1} R^{1\cdot} + H_2O \qquad (1)$$

$$HO\cdot + R^2H \xrightarrow{k_2} R^{2\cdot} + H_2O \qquad (2)$$

$$2R^{1\cdot} \xrightarrow{k_3} \text{molecular products} \qquad (3)$$

$$R^{1\cdot} + R^{2\cdot} \xrightarrow{k_4} \text{molecular products} \qquad (4)$$

$$2R^{2\cdot} \xrightarrow{k_5} \text{molecular products} \qquad (5)$$

$$R^{1\cdot} + H_2O_2 \xrightarrow{k_6} HO\cdot + \text{molecular products} \qquad (6)$$

$$R^{1\cdot} + Ti^{IV} \xrightarrow{k_7} R^+ + Ti^{III} \qquad (7)$$

The radical ·CMe_2OH is a typical example of one which, because of the attached hydroxy-group, is relatively rapidly oxidised compared with, for example, the isomeric ·$CH_2CHMeOH$; the published data[3,4] for the former indicate that, for $[H_2O_2]_0 \gg [Ti^{III}]_0$,† oxidation by Ti^{IV} [reaction (7)] should be a minor route to destruction under typical flow-system conditions. This may not be the case, however, if $[H_2O_2]_0 \not\gg [Ti^{III}]_0$ and we shall consider this possibility in greater detail later. Reactions of $R^{1\cdot}$ with R^2H, and of $R^{2\cdot}$ with R^1H, can generally be neglected for this kind of analysis.[4]

If we assume that $2k_3 = k_4 = 2k_5 = 2k$, steady-state analysis of the reaction scheme leads to equation (8),

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† Subscripts zero and *t* represent substrate concentrations on mixing and *t* s after mixing, respectively.

[1] Part XXXIX, B. C. Gilbert, R. O. C. Norman, and R. C. Sealy, *J.C.S. Perkin II*, 1973, 2174.

[2] G. Czapski, *J. Phys. Chem.*, 1971, **75**, 2957.

[3] C. E. Burchill and P. W. Jones, *Canad. J. Chem.*, 1971, **49**, 4005.

[4] D. Meisel, G. Czapski, and A. Samuni, *J.C.S. Perkin II*, 1973, 1702.

where k_{in} is the rate constant for the initiating reaction of titanium(III) with hydrogen peroxide [reaction (9)].

$$k_{\text{in}}[\text{Ti}^{\text{III}}]_t[\text{H}_2\text{O}_2]_t = 2k([\text{R}^{1}\cdot] + [\text{R}^{2}\cdot])^2 \qquad (8)$$

$$\text{Ti}^{\text{III}} + \text{H}_2\text{O}_2 \xrightarrow{k_{\text{in}}} \text{Ti}^{\text{IV}} + \text{HO}\cdot + \text{HO}^- \qquad (9)$$

For $[\text{H}_2\text{O}_2]_0 \gg [\text{Ti}^{\text{III}}]_0$ we have [5,*]

$$[\text{R}^{1}\cdot] + [\text{R}^{2}\cdot] = \left\{\frac{k_{\text{in}}[\text{H}_2\text{O}_2]_0[\text{Ti}^{\text{III}}]_0 \exp\left(-k_{\text{in}}[\text{H}_2\text{O}_2]_0 t\right)}{2k}\right\}^{\frac{1}{2}} \qquad (10)$$

and

$$\frac{[\text{R}^{2}\cdot]}{[\text{R}^{1}\cdot]} = \frac{k_2[\text{R}^2\text{H}]}{k_1[\text{R}^1\text{H}]}\left(1 + k_6\left\{\frac{[\text{H}_2\text{O}_2]_0 \exp\left(k_{\text{in}}[\text{H}_2\text{O}_2]_0 t\right)}{2kk_{\text{in}}[\text{Ti}^{\text{III}}]_0}\right\}^{\frac{1}{2}}\right) \qquad (11)$$

where

$$k_6\left\{\frac{[\text{H}_2\text{O}_2]_0 \exp\left(k_{\text{in}}[\text{H}_2\text{O}_2]_0 t\right)}{2kk_{\text{in}}[\text{Ti}^{\text{III}}]_0}\right\}^{\frac{1}{2}} = \frac{k_6[\text{H}_2\text{O}_2]_0}{2k([\text{R}^{1}\cdot] + [\text{R}^{2}\cdot])} \qquad (12)$$

Equations (10)—(12) form the basis of our analysis of the e.s.r. results and of our calculations of k_6. If the analysis holds then the total radical concentration and the ratio of the concentrations of the two radicals for constant $[\text{H}_2\text{O}_2]_0$ and t should, respectively, increase and decrease with increasing $[\text{Ti}^{\text{III}}]_0$, according to equations (10) and (11).

We have investigated the following systems, for which in each case two radicals should be obtained by reaction with the hydroxyl radical; in some cases only one of the two (the oxygen-conjugated radical) is expected to be readily oxidised (for t-butyl alcohol–methanol, t-butyl alcohol–1,4-dioxan, diethyl ether, and tetrahydrofuran) and in the other cases (dimethoxymethane and 1,3-dioxolan) the di-oxygen-conjugated radical would be expected to be more readily oxidised than the mono-conjugated radical. With each system we have tested the kinetic analysis and used the following procedure to estimate k_6 for the appropriate radical: the relative radical concentrations have been measured as a function of $[\text{Ti}^{\text{III}}]_0$ (with $[\text{H}_2\text{O}_2]_0$ and t constant), a concentration calibration has been carried out to determine the rate of initiation as expressed in equation (12), and known or estimated values have been employed for $2k$.

Varying the flow rate gave no indication of a departure from steady-state conditions. The minimum dead time with the mixer assembly used is *ca.* 15 ms; Burchill and Jones have calculated [3] that, under typical flow-system conditions, a steady-state should be attained in *ca.* 1 ms for organic radicals for which $2k$ is *ca.* 10^9 l mol^{-1} s^{-1} (certainly the case for the radicals under investigation). The dependence of radical concentrations on flow rate was similar to that computed [3] for steady-state conditions.

(a) *t-Butyl alcohol–methanol.* The oxidation of mixtures of t-butyl alcohol and methanol has been recently investigated by Czapski and his co-workers [4] using low hydrogen peroxide concentrations. They assumed a termination rate constant, $2k$, in between the values previously determined [6] for $\cdot\text{CH}_2\text{OH}$ and $\cdot\text{CH}_2\text{CMe}_2\text{OH}$ separately, and obtained good agreement with the steady-state analysis [equation (11), with negligible contribution from the oxidation term]; the resulting value of 1·60 for k_{14}/k_{13} is in good agreement with that obtained from pulse radiolysis.[7]

$$\text{HO}\cdot + \text{Me}_3\text{COH} \xrightarrow{k_{13}} \cdot\text{CH}_2\text{CMe}_2\text{OH} + \text{H}_2\text{O} \qquad (13)$$

$$\text{HO}\cdot + \text{MeOH} \xrightarrow{k_{14}} \cdot\text{CH}_2\text{OH} + \text{H}_2\text{O} \qquad (14)$$

We have confirmed that the above analysis for this system holds for low peroxide concentration (2·67mM) by obtaining a linear plot of $[\cdot\text{CH}_2\text{OH}]/[\cdot\text{CH}_2\text{CMe}_2\text{OH}]$ against $[\text{MeOH}]/[\text{Bu}^t\text{OH}]$. The radical ratios were calculated both by comparison of relative peak heights (for calibration, it is assumed [4] that equal concentrations of radical are formed when t-butyl alcohol and methanol are run separately under identical conditions) and by a double integration method; [8] values were obtained for k_{14}/k_{13} of 1·55 and 1·42, respectively. The detailed results obtained with the latter method are given in Table 1.

TABLE 1

Sums and the ratios of the concentrations of $\cdot\text{CH}_2\text{OH}$ and $\cdot\text{CH}_2\text{CMe}_2\text{OH}$ obtained in the reaction of Ti^{III}–H_2O_2 with mixtures of methanol and t-butyl alcohol

$\frac{[\text{MeOH}]}{[\text{Bu}^t\text{OH}]}$	$\frac{[\cdot\text{CH}_2\text{OH}]}{[\cdot\text{CH}_2\text{CMe}_2\text{OH}]}$ [a]	$([\cdot\text{CH}_2\text{OH}] + [\cdot\text{CH}_2\text{CMe}_2\text{OH}])$ [b]
0·25	0·39	1·36
0·40	0·59	1·30
0·50	0·69	1·21
0·64	0·87	1·25
0·74	1·06	1·32
0·85	1·26	1·21
0·95	1·36	1·23

[a] Measured by double integration; see text. [b] Arbitrary units.

In order to investigate the oxidation of $\cdot\text{CH}_2\text{OH}$ by hydrogen peroxide, the concentration of the latter was increased from 2·67 to 100mM. Radical concentrations were monitored as a function of $[\text{Ti}^{\text{III}}]_0$ for fixed $[\text{Bu}^t\text{OH}]$, $[\text{MeOH}]$, $[\text{H}_2\text{O}_2]_0$, and t (*ca.* 50 ms). The required linear relations [equations (10) and (11)] were satisfactorily established; Figure 1 shows the variation of the radical ratio. A concentration calibration with VOSO_4 as standard (checked against a standard solution of Fremy's salt) yielded a rate constant for the oxidation

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[*] A more rigorous integration is given by Czapski.[2] However, under our conditions of $[\text{H}_2\text{O}_2]_0$ and t (*ca.* 50 ms), the steady-state radical concentration is close to the computed average.[2]

[5] G. Czapski, A. Samuni, and D. Meisel, *J. Phys. Chem.*, 1971, **75**, 3271.

[6] M. Simic, P. Neta, and E. Hayon, *J. Phys. Chem.*, 1969, **73**, 3794.

[7] R. L. Willson, C. L. Greenstock, G. E. Adams, R. Wageman, and L. M. Dorfman, *Internat. J. Radiation Phys. Chem.*, 1971, **3**, 211.

[8] S. J. Wyard, *J. Sci. Instr.*, 1965, **42**, 769; P. L. Hall, *J. Phys. D*, 1972, **5**, 673.

of $\cdot CH_2OH$ [reaction (6)] of $(2{\cdot}3 \pm 0{\cdot}8) \times 10^4$ l mol^{-1} s^{-1}, if we assume $2k = 2 \times 10^9$ l mol^{-1} s^{-1}, in reasonable agreement with a value of 4×10^4 l mol^{-1} s^{-1} obtained in a γ-radiolysis experiment.[9]

(b) *Diethyl ether.* Oxidation of diethyl ether with $[H_2O_2]_0$ = 6mM gave e.s.r. signals from $\cdot CHMeOEt$ and $\cdot CH_2CH_2OEt$, the hyperfine splittings being in good agreement with those recorded previously.[10,11] The latter radical was present in significantly lower concentration, which probably explains why it was not detected during some earlier investigations.[10,12] The value of $[\cdot CHMeOEt]/[\cdot CH_2CH_2OEt]$, estimated by double integration of the signals, was significantly higher than that expected from suggested reactivity data[13] together with the assumption that the three possible modes of radical coupling have the same rate coefficient. We varied $[Et_2O]$ and the pH to investigate the possibility of the occurrence of chain-transfer reactions which might affect radical concentrations; for variations in $[Et_2O]$ of *ca.* 10-fold and for pH values between 1·0 and 7·0, no significant change in the radical concentration ratio was obtained. We therefore conclude that reactions such as (15) and (16) are unimportant under these conditions.

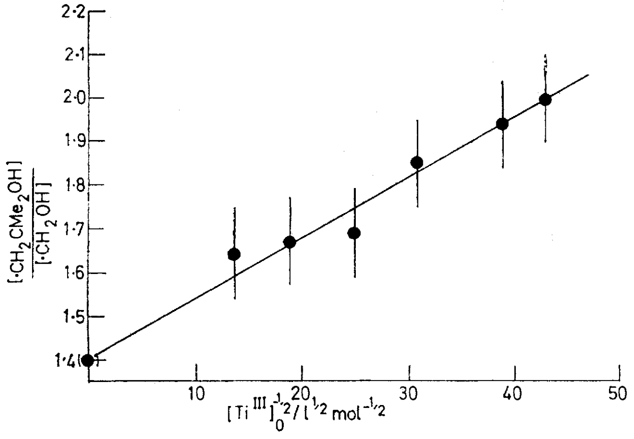


FIGURE 1 Variation of $[\cdot CH_2CMe_2OH]/[\cdot CH_2OH]$ with $[Ti^{III}]_0^{-\frac{1}{2}}/l^{\frac{1}{2}}$ mol$^{-\frac{1}{2}}$

$$\cdot CH_2CH_2OEt + Et_2O \xrightarrow{k_{15}} Et_2O + \cdot CHMeOEt \quad (15)$$

$$\cdot CH_2CH_2OEt + H^+ \xrightarrow{k_{16}} \text{unidentified species} \quad (16)$$

An increase in $[H_2O_2]_0$ to 88mM caused a significant decrease in the value of $[\cdot CHMeOEt]/[\cdot CH_2CH_2OEt]$ consistent with the radical oxidation (17). Data obtained from the variation of this parameter with $[Ti^{III}]_0$ are plotted in Figure 2. From these results, with an absolute radical concentration calibration and using a value of $2k = 2 \times 10^9$ l mol^{-1} s^{-1} measured by pulse radiolysis, we obtain $k_{17} = (5{\cdot}5 \pm 1{\cdot}1) \times 10^4$ l mol^{-1} s^{-1}, a value somewhat less than that obtained for the oxidation of $\cdot CHMeOH$ (derived as $1{\cdot}6 \times 10^5$ l mol^{-1} s^{-1} from the γ-radiolysis results in ref. 14, taking [6] for this radical $2k = 2{\cdot}3 \times 10^9$ l mol^{-1} s^{-1}).

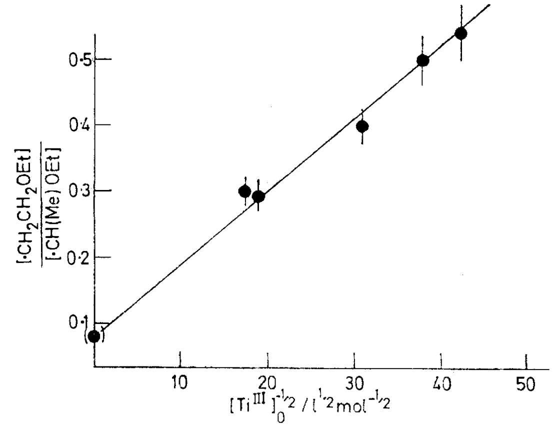
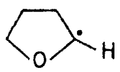


FIGURE 2 Variation of $[\cdot CH_2CH_2OEt]/[\cdot CHMeOEt]$ with $[Ti^{III}]_0^{-\frac{1}{2}}/l^{\frac{1}{2}}$ mol$^{-\frac{1}{2}}$

$$\cdot CHMeOEt + H_2O_2 \xrightarrow{k_{17}} \cdot OH + \text{molecular products} \quad (17)$$

(c) *Tetrahydrofuran.* Oxidation of tetrahydrofuran gave the two radicals previously identified[15-17] as (1) and (2), with hyperfine splittings in excellent agreement with reported values.



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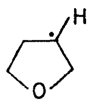

(2)

As observed for diethyl ether, the radical (2) was present in low relative concentration at low $[H_2O_2]_0$. $[Ti^{III}]_0$ was varied with a higher, constant value of $[H_2O_2]_0$ (70mM), and the relevant data are given in Table 2. The termination rate constant for the mixture of radicals (1) and (2) was obtained by pulse radiolysis as $2k = 3 \times 10^9$ l mol^{-1} s^{-1}. Combining these data, the rate constant for the oxidation of the radical (1) by hydrogen peroxide [*cf.* reaction (17)] is estimated as $3{\cdot}0 \times 10^4$ l mol^{-1} s^{-1}. On the basis of a previous investigation[3] it has been suggested that the oxidation of (1) is slow compared with that of the radical $\cdot CMe_2OH$ (5×10^5 l mol^{-1} s^{-1}). We also note here that it has been shown[18] that the lower ratio of the concentrations of (1) and (2) when the Fe^{II}–H_2O_2 system is employed,[17] com-

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[9] C. E. Burchill and I. S. Ginns, *Canad. J. Chem.*, 1970, **48**, 2628.

[10] W. T. Dixon, R. O. C. Norman, and A. L. Buley, *J. Chem. Soc.*, 1964, 3625.

[11] T. Shiga, A. Boukhors, and P. Douzou, *J. Phys. Chem.*, 1967, **71**, 3559.

[12] P. L. Kolker, *J. Chem. Soc.*, 1964, 5929.

[13] M. Anbar, D. Meyerstein, and P. Neta, *J. Chem. Soc.* (*B*), 1966, 742.

[14] W. A. Seddon and A. O. Allen, *J. Phys. Chem.*, 1967, **71**, 1914.

[15] W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 1964, 4850.

[16] F. Sicilio, M. Dousset, R. E. Florin, and L. A. Wall, *Polym. Preprints*, 1965, **6**, 956.

[17] T. Shiga, A. Boukhors, and P. Douzou, *J. Phys. Chem.*, 1967, **71**, 4264.

[18] R. O. C. Norman and P. R. West, *J. Chem. Soc.* (*B*), 1969, 389.

pared with that for Ti^{III}–H_2O_2, is derived from preferential oxidation of the radical (1) by Fe^{III}. Under the conditions we have employed (low metal-ion concentration) no oxidation by Ti^{IV} would be expected[4] for this and similar conjugated radicals.

TABLE 2

Sums and the ratios of the concentrations of the radicals obtained in the reaction of Ti^{III}–H_2O_2 with tetrahydrofuran

$10^3[Ti^{III}]_0/M$ [a]	$[(2)]/[(1)]$	$10^6\{[(1)] + [(2)]\}/M$
0·53	0·39	0·5
0·71	0·35	0·5
1·33	0·30	0·9
1·60	0·30	0·9
2·13	0·26	1·0
2·67	0·27	1·2
4·00	0·24	1·5
5·34	0·23	1·7

[a] For other experimental conditions, see text.

(d) *Dimethoxymethane*. Oxidation of dimethoxymethane with the Ti^{III}–H_2O_2 couple gave rise to detectable e.s.r. signals from $\cdot CH(OMe)_2$ and $\cdot CH_2OCH_2OMe$, with the latter in the higher concentration. This system has been investigated previously by both flow[19] and photolytic techniques,[3,20] and our observed hyperfine splittings are in good accord with the published data.

The kinetic analysis for dimethoxymethane is less straightforward than that for the other ethers studied since we have to consider oxidation of both radicals, by H_2O_2 and by Ti^{IV} [reactions (18)—(21)]. We should expect the secondary radical to be more easily oxidised than the primary radical, on account of the increased electron-donating ability due to the two adjacent oxygen atoms, and, indeed, the preferential oxidation of $\cdot CH(OMe)_2$ by hydrogen peroxide has already been suggested.[3]

$$\cdot CH(OMe)_2 + H_2O_2 \xrightarrow{k_{18}} HO\cdot + \text{molecular products} \quad (18)$$

$$\cdot CH(OMe)_2 + Ti^{IV} \xrightarrow{k_{19}} {}^{+}CH(OMe)_2 + Ti^{III} \quad (19)$$

$$\cdot CH_2OCH_2OMe + H_2O_2 \xrightarrow{k_{20}} HO\cdot + \text{molecular products} \quad (20)$$

$$\cdot CH_2OCH_2OMe + Ti^{IV} \xrightarrow{k_{21}} {}^{+}CH_2OCH_2OMe + Ti^{III} \quad (21)$$

We have not measured the rate of oxidation of a primary ether radical with hydrogen peroxide [*cf.* reaction (20)] but since the rate constant for oxidation of $\cdot CHMeOEt$ is less than that for the oxidation of $\cdot CHMeOH$ we feel that it is reasonable to assume that k_{20} is less than that for the oxidation of $\cdot CH_2OH$, *viz.* $2{\cdot}3 \times 10^4$ l mol^{-1} s^{-1}. For $[H_2O_2]_0 = 24$mM (the highest concentration of hydrogen peroxide used in this series of experiments) and a minimum radical concentration of *ca.* $1{\cdot}4 \times 10^{-6}$M, oxidation of $\cdot CH_2OCH_2OCH_3$ should contribute to its termination to only a small extent (<20%). Reaction (21) will make a correspondingly smaller contribution owing to the small concentrations of Ti^{IV} produced.

If we now include reactions (18) and (19), but not (20) or (21), in a kinetic scheme [*cf.* equation (11)] we obtain (22), where *a* and *b* are constants for constant $[H_2O_2]_0$

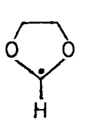
$$\frac{[\cdot CH_2OCH_2OMe]}{[\cdot CH(OMe)_2]} = \frac{k_2}{k_1} \left\{1 + \frac{ak_{18}}{[Ti^{III}]_0^{\frac{1}{2}}} + bk_{19}[Ti^{III}]_0^{\frac{1}{2}}\right\} \quad (22)$$

and *t*. Available evidence[3,4] suggests that $k_{18} \simeq k_{19}$, from which it can be shown that, when $[H_2O_2]_0 \gg [Ti^{III}]_0$, $a[Ti^{III}]_0^{-\frac{1}{2}} \gg b[Ti^{III}]_0^{\frac{1}{2}}$. Reaction (19) is then expected to have little effect on the gradient of the radical concentration ratio plot, provided that the above criterion is applied, but the intercept may be an overestimate of k_2/k_1.

We carried out experiments at three concentrations of hydrogen peroxide ($[H_2O_2]_0 = 24$, 12, and 8mM), $[Ti^{III}]_0$ being varied in each case. The measured radical concentration ratios were plotted according to the modification of equation (22) described above (*i.e.* the term involving k_{19} is ignored); the differences in the gradients of the three plots were in good agreement with predicted behaviour and the extrapolated intercepts were identical within experimental error. We therefore believe that our data are consistent with a mechanism involving oxidation of the radical $\cdot CH(OMe)_2$ by hydrogen peroxide; from the gradient of the graphs, an absolute concentration calibration, and the assumption that $2k = 2 \times 10^9$ l mol^{-1} s^{-1}, we obtain $k_{18} = (1{\cdot}1 \pm 0{\cdot}3) \times 10^6$ l mol^{-1} s^{-1}.

(e) 1,3-*Dioxolan*. E.s.r. signals from radicals (3) and (4), derived by hydrogen-atom abstraction from 1,3-dioxolan, have previously been observed[17,21] during investigations of the oxidation of 1,3-dioxolan with Ti^{III}–H_2O_2; with Fenton's reagent as the initiating system only the radical (4) was detected.[17]

Using low concentrations of hydrogen peroxide (*ca.* 3·5mM) and with $[Ti^{III}]_0 = 4{\cdot}4$mM, we have confirmed that both (3) and (4) are detectable (with splitting constants in good agreement with previous reports); the two radicals were present in similar concentrations, $[(4)]/[(3)] = 1{\cdot}18$. An increase in $[H_2O_2]_0$ resulted in an increase in this ratio (*e.g.* to 2·15 for $[H_2O_2]_0 = 5 \times 10^{-2}$M). We have determined the radical concentrations as a function of $[Ti^{III}]_0$ using a fairly low hydrogen peroxide concentration ($1{\cdot}6 \times 10^{-2}$M) at which oxidation



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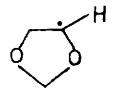

(4)

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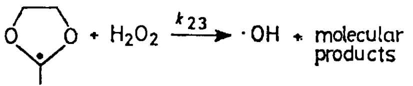
[19] E. L. Lewis and F. Sicilio, *J. Phys. Chem.*, 1969, **73**, 2590.

[20] A. Hudson and K. D. J. Root, *Tetrahedron*, 1969, **25**, 5311.

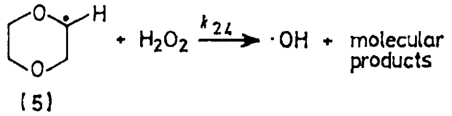
[21] A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *J. Chem. Soc. (A)*, 1971, 124.

of (4) should be slight [we assume that the rate constant for oxidation of this radical with H_2O_2 is similar to that for the oxidation of radical (1) from tetrahydrofuran]. This procedure leads to a value for k_{23} of 6×10^4 l mol^{-1} s^{-1}, assuming a value for $2k$ of 3×10^9 l mol^{-1} s^{-1}. Although this should realistically be regarded as a lower limit [since reaction of (4) with peroxide has been disregarded], it is clear that k_{23} is considerably less than k_{18}.



(23)

(f) 1,4-*Dioxan*. The 1,4-dioxanyl radical (5), obtained by reaction of the hydroxyl radical with the parent compound, had e.s.r. parameters in good agreement with those reported previously.[15] In order to estimate k_{24} a competition method similar to that employed to determine the rate constant for the oxidation of $\cdot CH_2OH$ was used. Mixtures of 1,4-dioxan and t-butyl alcohol were oxidised and, from experiments at low $[H_2O_2]_0$, such that the oxidation term in equation (11) can be neglected, we obtained a value for k_{25}/k_{13} of 3·5. This value can be compared with those from



(24)

(5)

$$\cdot OH + \text{dioxan} \xrightarrow{k_{25}} (5) + H_2O \qquad (25)$$

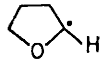
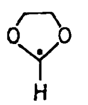
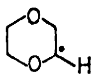
γ-radiolysis experiments with thymine and PNDA (p-nitrosodimethylaniline) as competitors for hydroxyl of 2·9 and 3·9, respectively.[22] As described previously for $\cdot CH_2OH$, we investigated the selective oxidation of (5), with $[H_2O_2]_0 = 7 \times 10^{-2}$M, and estimate a value for k_{24} of $(3\cdot0 \pm 0\cdot6) \times 10^4$ l mol^{-1} s^{-1}.

Correlation of Rate Constants with Structure.—(a) *Reaction of radicals with hydrogen peroxide*. The rate constants for the oxidation of hydroxy- and alkoxy-conjugated radicals with hydrogen peroxide obtained in this investigation are summarised in Table 3, which also includes other relevant results. Certain trends may be recognised: thus, the rate constant increases with increasing alkyl-group substitution of the radical centre, and di-alkoxy-conjugated radicals are more susceptible to oxidation than structurally similar mono-alkoxy-conjugated radicals. These observations are consistent with a mechanism which involves partial charge transfer, from the radical to hydrogen peroxide, in the transition state.

(b) *Reaction of hydroxyl with ethers*. Table 4 contains the observed steady-state ratios of radical concentrations for substrates with two sites for abstraction, these being measured under conditions where no significant radical oxidation is anticipated. The ratios are in poor agreement with those predicted from empirical reactivity data based on the *overall* reactivity of a variety of ethers;[13] in each case the observed ratio of concentrations of the oxygen-conjugated to the non-conjugated radical is considerably greater than that calculated.* Because of the apparent generality of this behaviour we incline to the view that this situation does not arise from unusual and unconsidered reactions (*e.g.* 1,2-hydrogen migration in $\cdot CH_2CH_2OEt$ to give $\cdot CHMeOEt$, or specific ring fission for certain cyclic radicals) but that the hydrogen atoms β to an alkoxy-group are subject to some significant deactivation compared with those in hydrocarbons, no allowance for which was made when the overall reactivity data were interpreted. Such deactivation is to be expected, given the $-I$ effect of an alkoxy-group and the electrophilic nature of the hydroxyl radical.

TABLE 3

Rate constants for the reactions of radicals with hydrogen peroxide [a]

Radical	k/l mol^{-1} s^{-1}	Ref. [b]
$\cdot CH_2OH$	4×10^4 $2\cdot3 \times 10^4$	c
$\cdot CHMeOH$ [d]	$1\cdot6 \times 10^5$	e
$\cdot CMe_2OH$	5×10^5	f
$\cdot CO_2^-$	7×10^5	g
	3×10^4	
	6×10^4 [h]	
	3×10^4	
$\cdot CHMeOEt$	$5\cdot5 \times 10^4$	
$\cdot CH(OMe)_2$	$1\cdot1 \times 10^6$	

[a] For limits of error, see text. [b] This work unless otherwise stated. [c] Ref. 9. [d] Our calculation, employing $2k = 2\cdot3 \times 10^9$ l mol^{-1} s^{-1}; see ref. 6. [e] Ref. 14. [f] Ref. 3. [g] G. V. Buxton and W. K. Wilmarth, *J. Phys. Chem.*, 1963, **67**, 2835. [h] Lower limit; see text.

TABLE 4

Observed and predicted steady-state concentrations of radicals derived from ethers

Ether	Radical ratio	Observed [a]	Predicted [b]
Diethyl ether	$\frac{[\cdot CHMeOEt]}{[\cdot CH_2CH_2OEt]}$	13·0	2·5
Tetrahydrofuran	$\frac{[(1)]}{[(2)]}$ [a]	6·0	0·5
1,3-Dioxolan	$\frac{[(3)]}{[(4)]}$ [a]	0·85	0·17

[a] See text. [b] Data taken from ref. 13; see text.

Oxidation of 2-Methoxyethanol.—The oxidation of 2-methoxyethanol with the Ti^{III}–H_2O_2 couple at low pH

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* Significant deviations from the assumption $2k_3 = k_4 = 2k_5$ are not expected, and in any case could not account for the magnitude of these discrepancies even if cross-combination were diffusion-controlled (k_4 *ca.* 10^{10} l mol^{-1} s^{-1}).

[22] M. Anbar and P. Neta, *Internat J. Appl. Radiation Isotopes*, 1967, **18**, 493.

has been shown [23] to give signals from $\cdot CH(OMe)CH_2OH$, $\cdot CH_2OCH_2CH_2OH$, and $\cdot CH_2CH(OH)OMe$. The last radical probably arises from the acid-catalysed reaction (26). The radical $\cdot CH(OH)CH_2OMe$ was not detected

$$MeO\dot{C}HCH_2OH + H^+ \xrightarrow{-H_2O} Me\overset{+}{O}{=}CH\dot{C}H_2 \xrightarrow{H_2O} MeO(HO)CH\dot{C}H_2 + H^+ \quad (26)$$

even though relative reactivity data [13] suggest that it should be formed more rapidly than its isomers in the reaction between hydroxyl and 2-methoxyethanol. It has been detected, however, during the low-temperature photolysis of mixtures of 2-methoxyethanol and di-t-butyl peroxide.[20]

From the kinetic data in Table **3** we should expect that oxidation of $\cdot CH_2OCH_2CH_2OH$ by hydrogen peroxide would be relatively slow ($k < 3 \times 10^4$ l mol^{-1} s^{-1}) compared with the oxidation of both $\cdot CH(OMe)CH_2OH$ and $\cdot CH(OH)CH_2OMe$, for which the rate constants should be *ca.* 5×10^4 and $1{\cdot}5 \times 10^5$ l mol^{-1} s^{-1}, respectively. However, even though the radical $\cdot CH(OH)CH_2OMe$ is expected to be oxidised the fastest of these three, the expected rate constant is not large enough to account for the failure to detect it in the Ti^{III}–H_2O_2 system at low pH. Accordingly, we investigated this problem in some detail to determine the fate of $\cdot CH(OH)CH_2OMe$ as well as to obtain kinetic support for the mechanism for rearrangement previously outlined.

We studied the oxidation of 2-methoxyethanol over an extended range of pH, with a low hydrogen peroxide concentration ($[H_2O_2]_0 = 3{\cdot}5$mM) in order to minimize possible anomalies in radical ratios arising from selective oxidation. Signals from the radical $\cdot CH(OH)CH_2OMe$ were detected, but only over a restricted pH range (*ca.* 2·9—6·5). The pH dependence of the concentrations of this and the other radicals detected is shown in Figure **3**; hyperfine parameters for all radicals showed excellent agreement with previous reports.

Several interesting observations emerge from the Figure. First, the concentration of $\cdot CH_2OCH_2CH_2OH$ remains essentially constant over the entire pH range. From this we infer that the radical does not participate in acid- or base-catalysed reactions and that it is removed essentially only through bimolecular termination. [We have previously shown [1] that the rates of radical initiation from Ti^{III}–H_2O_2 do not differ markedly at low pH (with sulphuric acid present) and high pH (achieved with EDTA and ammonia), under typical flow-system conditions.]

Secondly, the radical $\cdot CH(OMe)CH_2OH$ does not vary in concentration over the pH range 3—8·5, whereas below pH 3 its decline in concentration is mirrored by the build-up of the radical $\cdot CH_2CH(OH)OMe$. This supports the proposed [23] acid-catalysed conversion of the former into the latter.

Thirdly, as judged by the sum of the radical concentrations, which is effectively constant except in the region where $\cdot CH(OH)CH_2OMe$ is observed, it appears that this radical must react at high and at low pH to give species which, under these conditions, are not detected. This could be because of line-broadening (to render a signal too broad for detection) or because of radical destruction by metal ions or hydrogen peroxide.

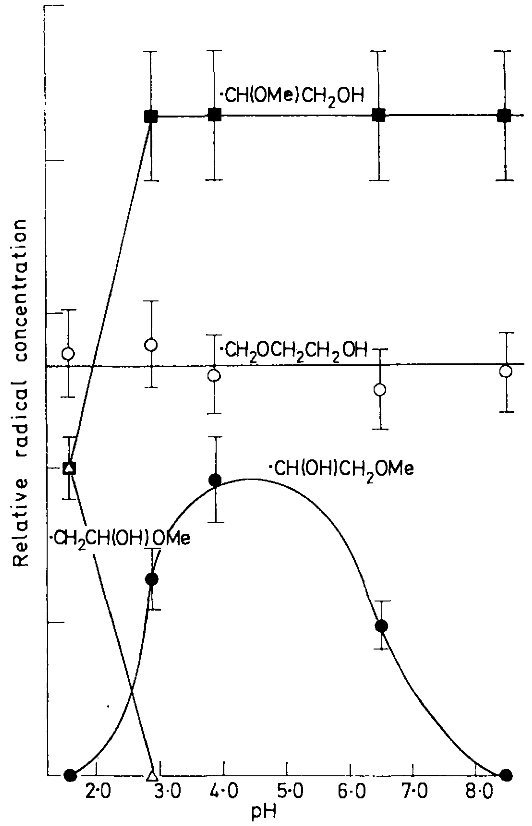

FIGURE 3 Relative concentrations of radicals from the oxidation of 2-methoxyethanol as a function of pH

By analogy with the low pH and high pH behaviour of $\cdot CH(OH)CH_2OH$ which, as demonstrated by e.s.r.[24] and pulse radiolysis,[25] is converted into $\cdot CH_2CHO$, we favour the mechanism shown in equations (27) and (28).

$$MeOCH_2\dot{C}HOH \xrightarrow[-MeOH]{H^+} \cdot CH_2CHO \quad (27)$$

$$MeOCH_2\dot{C}HOH \xrightarrow{base} MeOCH_2\dot{C}HO^- \xrightarrow[-OMe^-]{} \cdot CH_2CHO \quad (28)$$

Now, the spectrum of the radical $\cdot CH_2CHO$ is known to have broad lines and this, together with the overall complexity of the spectrum, would render its detection difficult. However, at low pH and under conditions of high gain and high modulation amplitude it was possible to locate the outer lines attributable to this radical.

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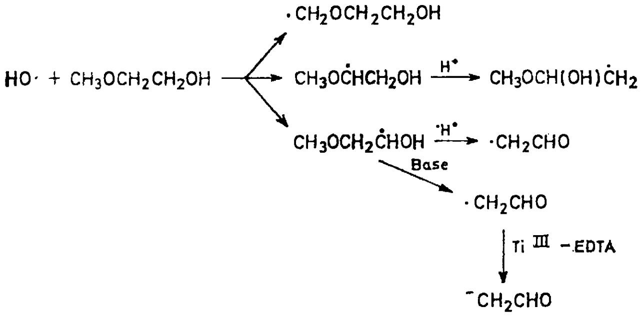
[23] D. J. Edge, B. C. Gilbert, R. O. C. Norman, and P. R. West, *J. Chem. Soc.* (*B*), 1971, 189.

[24] B. C. Gilbert, J. P. Larkin, and R. O. C. Norman, *J.C.S. Perkin II*, 1972, 794.

[25] K. M. Bansal, M. Grätzel, A. Henglein, and E. Janata, *J. Phys. Chem.*, 1973, **77**, 16.

At high pH, prolonged attempts to observe $\cdot CH_2CHO$ were unsuccessful. However, we have previously demonstrated[1] that reduction of $\cdot CH_2CHO$ by Ti^{III}–EDTA is extremely rapid ($k = 6 \times 10^7$ l mol^{-1} s^{-1} at pH 7), so that we would expect destruction of $\cdot CH_2CHO$ in this medium to render the radical concentration too small for detection by e.s.r. We therefore believe that e.s.r. results for the oxidation of 2-methoxyethanol in the Ti^{III}–H_2O_2 reaction are entirely consistent with the overall mechanism shown in the Scheme.



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