

Electron Spin Resonance Studies. Part XXXIX.¹ A Kinetic Investigation of the Role of Radical Reduction in Metal Ion-Hydrogen Peroxide Systems

By Bruce C. Gilbert,* Richard O. C. Norman, and Roger C. Sealy, Department of Chemistry, The University of York, Heslington, York YO1 5DD

Reduction of carbonyl-conjugated radicals by Ti^{III} and Fe^{II} in aqueous solution has been investigated by e.s.r. spectroscopy and pulse radiolysis. Kinetic data have enabled the importance of such reactions in metal ion-hydrogen peroxide systems to be assessed. For example, reduction by Ti^{III} at pH 1 is negligible under typical flow system conditions whereas at pH 7 reduction by Ti^{III} -EDTA can provide an important pathway for radical termination. The dependence of reduction rates on radical structure has been investigated.

REDOX reactions of organic radicals with metal ions in solution are well known, but there have been few quantitative studies of such reactions involving small carbon radicals.^{2,3}

It has recently been suggested that the one-electron reduction by a metal ion of an organic radical conjugated to a carbonyl group may in some cases be an especially rapid process.⁴ For example, product studies of the reaction of acetone with Fenton's reagent were reported to yield a rate constant for reaction (1) of *ca.* 10^7 l mol⁻¹ s⁻¹, and it was pointed out that higher rate constants could be expected for reduction by iron(II) complexed with EDTA or by titanium(III).⁴ However, this conclusion is difficult to reconcile with the rate constant of 5.8×10^2 l mol⁻¹ s⁻¹ for the reduction of the polyacrylamide radical, $\cdot CH(CONH_2)CH_2$, with Ti^{III} in 0.08M-sulphuric acid at 25°,⁵ which shows that, at least for this radical, reduction by Ti^{III} is relatively slow. We have therefore investigated the reduction of some carbonyl-conjugated radicals by Fe^{II} and Ti^{III} ion, in some cases complexed with EDTA. Fenton's reagent and the related Ti^{III} -H₂O₂ couple were used to generate the radicals, and e.s.r. spectroscopy, complemented where appropriate by pulse radiolysis with optical detection, was employed to determine the reaction rates.



EXPERIMENTAL

E.s.r. Spectroscopy.—A Varian E-3 spectrometer with 100 kHz modulation and an X band klystron was employed in conjunction with an aqueous flat cell and a mixing chamber which enabled three reagent streams to be mixed simultaneously. Flow rates of *ca.* 6 ml s⁻¹ could be obtained with gravity feed.

Splitting constants were measured to within ± 0.01 mT, both directly and by comparison with Fremy's salt [$a(N)$ 1.3091 mT⁶], and this salt (g 2.0055⁷) was also used for determining g factors to within ± 0.0001 . Second-order corrections were made as necessary.⁸

Where possible, ratios of radical concentrations were ob-

¹ Part XXXVIII, B. C. Gilbert, D. K. C. Hodgeman, and R. O. C. Norman, *J.C.S. Perkin II*, 1973, 1748.

² R. A. Sheldon and J. K. Kochi, *Oxidation and Combustion Rev.*, 1973, **5**, 135.

³ E. T. Denisov, *Russ. Chem. Rev.*, 1971, **40**, 24.

⁴ C. Walling and G. M. El-Taliawi, *J. Amer. Chem. Soc.*, 1973, **95**, 844.

⁵ E. Collinson, F. S. Dainton, B. Mile, S. Tazuke, and D. R. Smith, *Nature*, 1963, **198**, 26.

⁶ R. J. Faber and G. K. Fraenkel, *J. Chem. Phys.*, 1967, **47**, 2462.

tained from measurements of peak amplitude and line-width.⁹ For complex line-shapes and overmodulated signals, numerical double integrations were carried out by Wyard's method.¹⁰ Absolute radical concentrations (with an estimated random error of $\pm 10\%$) were determined by comparison with a solution of vanadyl sulphate.¹¹ The procedure for computer-simulation of spectra, which allows for second-order effects, has been described.¹²

pH Measurements were made to within ± 0.1 pH units with either an Electronic Instruments model 23A or a Beckman model 72 pH meter.

Titanium(III) chloride solution was Fisons technical grade [12.5% (w/v)]. Hydrogen peroxide (100-volume), EDTA (disodium salt), sodium monohydrogen orthophosphate (anhydrous), ammonia solution (*d* 0.88), sulphuric acid (98%), cyclohexanone, ethane-1,2-diol, and diethyl ketone were Fisons laboratory reagents. Other chemicals used were acetone (Fisons analytical reagent), iron(II) sulphate (Hopkin and Williams general purpose reagent), and borate (pH 9.2), phosphate (pH 7.0), and phthalate (pH 4.0) buffers (Fisons). Oxygen-free nitrogen was from B.O.C.

For reactions at pH *ca.* 1, the reactant solutions were typically as follows. Stream (i) contained either 12.5% (w/v) titanium(III) chloride solution (3.3–23.3 ml l⁻¹; 2.7–18mm) or iron(II) sulphate (0.5–3.5 g l⁻¹; 1.9–13mm) and 98% sulphuric acid (10 ml l⁻¹). Stream (ii) contained 100-volume hydrogen peroxide solution (1–20 ml l⁻¹; 8–160mm), and stream (iii) contained the organic substrate in sufficient concentration (0.1–3M) to scavenge essentially all the hydroxyl radicals produced.

For experiments at pH above *ca.* 2.5, stream (i) contained either titanium(III) chloride solution as above or iron(II) sulphate (2 g l⁻¹; 7.5mm), together with EDTA (disodium salt) in equimolar concentration, and sufficient ammonia solution to attain the required pH. Streams (ii) and (iii) were as before.

Some experiments were carried out in phosphate buffer (pH 7.0) which was prepared from 0.1M-sodium monohydrogen orthophosphate solution and 0.1M-hydrochloric acid in the volume ratio 1.75 : 1.

For studies of hydroperoxide formation, stream (ii) contained both the carbonyl compound and the hydrogen peroxide, and stream (iii) contained water only.

⁷ J. Q. Adams, S. W. Nicksic, and J. R. Thomas, *J. Chem. Phys.*, 1966, **45**, 654.

⁸ R. W. Fessenden, *J. Chem. Phys.*, 1962, **37**, 747; S. Breit and I. I. Rabi, *Phys. Rev.*, 1931, **38**, 2082.

⁹ P. B. Ayscough, 'Electron Spin Resonance in Chemistry', Methuen, London, 1967, p. 165.

¹⁰ S. J. Wyard, *J. Sci. Instr.*, 1965, **42**, 769.

¹¹ G. Czapski, A. Samuni, and D. Meisel, *J. Phys. Chem.*, 1971, **75**, 3271.

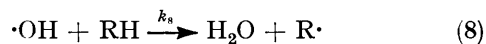
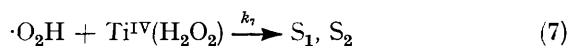
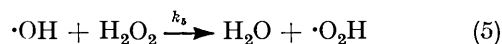
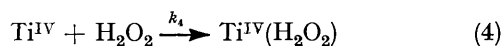
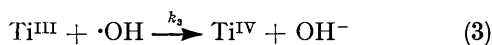
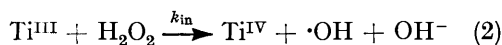
¹² B. C. Gilbert, J. P. Larkin, and R. O. C. Norman, *J.C.S. Perkin II*, 1972, 1272.

Solutions were deaerated by passing oxygen-free nitrogen for *ca.* 0.5 h.

Pulse Radiolysis.—The radiation source and experimental procedure have been described.¹³ All solutions were prepared from triply distilled water, and the pH was adjusted with sulphuric acid or ammonia solution. Reagents used were as described for the e.s.r. experiments with the exception of argon (99.995%) and nitrous oxide (medical grade) which were obtained from B.O.C.

RESULTS AND DISCUSSION

The reaction between titanium(III) ion and hydrogen peroxide is complex, involving steps (2)—(7);¹⁴ S_1 and S_2 are believed to be titanium-complexed oxyl radicals which are relatively long-lived and are observed as singlets in the e.s.r. spectrum.¹⁵ If an organic hydrogen-atom donor, RH, is also present, then reaction (8) can occur. Now, it has recently been demonstrated that, providing the resulting radicals, $R\cdot$, are short-lived (*i.e.*, have termination rate constants $> ca. 10^9$ l mol⁻¹ s⁻¹), as in the reactions we have studied, the only radicals detected by e.s.r. spectroscopy under typical flow conditions are those formed in the cavity;^{14,16} a quasi steady-state system is established, so that kinetic data pertaining to the generation and destruction of $R\cdot$ can be obtained.¹⁷



In order to simplify kinetic analysis of the systems we have investigated, the concentration of RH was made

$$[\cdot CH_2COMe] = \frac{\{k_{11}^2 [Ti^{III}]_t^2 + 8k_{10}k_{in} [Ti^{III}]_t [H_2O_2]_t\}^{\frac{1}{2}} - k_{11} [Ti^{III}]_t}{4k_{10}} \quad (12)$$

sufficiently high that essentially all the hydroxyl radicals formed in the initiation step (2) are scavenged by reaction with RH. The criterion used was that $[RH] \gg$

* Subscripts zero and *t* refer to concentrations, respectively, immediately after mixing and *t* s after mixing (usually taken to be the concentration in the cavity).

¹³ G. V. Buxton and R. M. Sellers, *J.C.S. Faraday I*, 1973, **69**, 555; K. W. Chambers, E. Collinson, F. S. Dainton, W. A. Seddon, and F. Wilkinson, *Trans. Faraday Soc.*, 1967, **63**, 1699; D. H. Ellison, G. A. Salmon, and F. Wilkinson, *Proc. Roy. Soc.*, 1972, **A**, **328**, 22.

¹⁴ G. Czapski, *J. Phys. Chem.*, 1971, **75**, 2957.

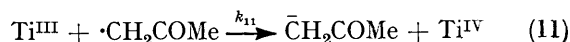
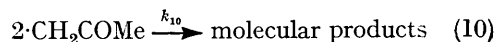
¹⁵ H. Fischer, *Ber. Bunsengesellschaft Phys. Chem.*, 1967, **71**, 685.

¹⁶ C. E. Burchill and P. W. Jones, *Canad. J. Chem.*, 1971, **49**, 4005.

$(k_3/k_8)[Ti^{III}]_t$; * k_8 was obtained from standard collections of data,^{18,19} k_3 was taken to be 3×10^9 l mol⁻¹ s⁻¹ (strictly²⁰ for 0.1M-HClO₄ solution, but unlikely to differ markedly for the solutions studied), and $[Ti^{III}]_t$ was taken as 0.5 $[Ti^{III}]_0$ (see later). As expected for efficient scavenging by RH, S_1 and S_2 were not observable under our conditions; further, increasing $[RH]$ did not result in an increase in the observed concentration of radicals.

There are three types of reaction which lead to the destruction of the radicals $R\cdot$. The first is bimolecular combination which, for the cases under consideration, has a rate constant in the range $2k$ *ca.* 10^9 — 10^{10} l mol⁻¹ s⁻¹. The second is oxidation by hydrogen peroxide, titanium(IV), or titanium(IV)-peroxide complexes; these should occur slowly enough to be neglected. Thus, for the oxidation of $\cdot CH_2OH$ by hydrogen peroxide,²¹ $k = 4 \times 10^4$ l mol⁻¹ s⁻¹; the radicals examined here lack the activating α -hydroxy-group and should be oxidised less rapidly, so that under our conditions, with $[R\cdot]$ *ca.* 4 μM and $[H_2O_2]_0$ *ca.* $10^{-2} M$, oxidation by hydrogen peroxide can make only a minor contribution to radical termination (<10% compared with bimolecular combination for $2k$ *ca.* 10^9 l mol⁻¹ s⁻¹). Oxidation by titanium(IV) species is expected to make a smaller contribution than that by hydrogen peroxide (*cf.* data for the radical $\cdot CMe_2OH$ ¹⁷). The third reaction is one-electron reduction of $R\cdot$ which we wish to investigate.

The Radical $\cdot CH_2COMe$.—From the discussion above, we should expect the reaction of acetone with the Ti^{III} - H_2O_2 system to be described for kinetic analysis by the initiating step (2) and reactions (9)—(11). For reaction (9),¹⁹ $k = 1.2 \times 10^8$ l mol⁻¹ s⁻¹.



Steady-state kinetics for the observed radical concentration, discounting negative radical concentrations, yield equation (12) which, if the reduction step (11) is of

negligible significance, simplifies to equation (13).

$$[\cdot CH_2COMe] = \left(\frac{k_{in} [H_2O_2]_t [Ti^{III}]_t}{2k_{10}} \right)^{\frac{1}{2}} \quad (13)$$

For $[H_2O_2]_0$ substantially greater than $[Ti^{III}]_0$, the decay

¹⁷ D. Meisel, G. Czapski, and A. Samuni, *J.C.S. Perkin II*, 1973, 1702.

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

¹⁹ R. L. Willson, C. L. Greenstock, G. E. Adams, R. Wageman, and L. M. Dorfman, *Internat. J. Radiation Phys. Chem.*, 1971, **3**, 211.

²⁰ A. Samuni, D. Meisel, and G. Czapski, *J.C.S. Dalton*, 1972, 1273.

²¹ C. E. Burchill and I. S. Ginns, *Canad. J. Chem.*, 1970, **48**, 2628.

of $[\text{Ti}^{\text{III}}]$ along the flow tube can be treated as an exponential process and $[\text{H}_2\text{O}_2]_t = [\text{H}_2\text{O}_2]_0$, so that equation (13) can be written as (14), where t is the time between

$$[\cdot\text{CH}_2\text{COME}] = \left(\frac{k_{\text{in}}[\text{H}_2\text{O}_2]_0[\text{Ti}^{\text{III}}]_0 e^{-k_{\text{in}}[\text{H}_2\text{O}_2]_0 t}}{2k_{10}} \right)^{\frac{1}{2}} \quad (14)$$

mixing and observation. For experiments in which t and $[\text{H}_2\text{O}_2]_0$ are kept constant, the relationship (15)

$$[\cdot\text{CH}_2\text{COME}] \propto [\text{Ti}^{\text{III}}]_0^{\frac{1}{2}} \quad (15)$$

applies. At the other extreme (*i.e.* $k_{11}^2[\text{Ti}^{\text{III}}]_t^2 \gg 8k_{10}k_{\text{in}}[\text{Ti}^{\text{III}}]_t[\text{H}_2\text{O}_2]_t$), $[\cdot\text{CH}_2\text{COME}]$ clearly approaches zero, but we can also define an intermediate region such that $k_{11}^2[\text{Ti}^{\text{III}}]_t^2 \ll 8k_{10}k_{\text{in}}[\text{Ti}^{\text{III}}]_t[\text{H}_2\text{O}_2]_t$ but $(8k_{10}k_{\text{in}}[\text{Ti}^{\text{III}}]_t[\text{H}_2\text{O}_2]_t)^{\frac{1}{2}}$ is not $\gg k_{11}[\text{Ti}^{\text{III}}]_t$, to give equation (16).

$$[\cdot\text{CH}_2\text{COME}] = \left(\frac{k_{\text{in}}[\text{Ti}^{\text{III}}]_t[\text{H}_2\text{O}_2]_t}{2k_{10}} \right)^{\frac{1}{2}} - \frac{k_{11}[\text{Ti}^{\text{III}}]_t}{4k_{10}} \quad (16)$$

We conclude, then, that if the one-electron reduction (11) makes a negligible contribution to radical termination, a plot of $[\cdot\text{CH}_2\text{COME}]$ against $[\text{Ti}^{\text{III}}]_0^{\frac{1}{2}}$ will be linear; otherwise, downward curvature will be displayed [*cf.* equation (16)] provided that the radical is present in observable concentration.

The reaction of acetone with the $\text{Ti}^{\text{III}}\text{-H}_2\text{O}_2$ system was investigated at pH 1.0 (0.1M-sulphuric acid solution) and 7.0 (with the disodium salt of EDTA as a complexing agent). The spectrum of the radical $\cdot\text{CH}_2\text{COME}$ was essentially that previously observed.²² Because of the broadening of the inner quartet at room temperature,²² the outer resonances were used to monitor the radical concentration as a function of $[\text{Ti}^{\text{III}}]_0$. The results obtained at pH 1.0 are in Table 1, and Figure 1 shows the plot of $[\cdot\text{CH}_2\text{COME}]$ against $[\text{Ti}^{\text{III}}]_0^{\frac{1}{2}}$. It is apparent from this plot that there is no detectable contribution from reaction (11); an upper limit can be put on k_{11} , assuming that a 20% reduction in $[\cdot\text{CH}_2\text{COME}]$ due to reaction (11) would be detected. For a radical concentration of *ca.* 5 μM and with $[\text{Ti}^{\text{III}}]_0 = 3.9\text{mM}$, $t = \text{ca.}$ 50 ms, $2k_{10} \text{ ca. } 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ (by analogy with $\cdot\text{CH}_2\text{CHO}$, for which²³ $2k = \text{ca. } 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$),* and $k_{\text{in}} = 590 \text{ l mol}^{-1} \text{ s}^{-1}$,¹⁷ it follows that $k_{11} \gg 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$.

In contrast, the results for reaction at pH 7.0 (Table 2 and Figure 1), are consistent with a significant contribution to radical termination from reaction (11). The evaluation of the rate constant for this reaction requires that k_{in} be known for these conditions, and we estimated this as follows. It has been shown¹⁴ that, for reactions under flow-system conditions of the type used here in which a radical $\text{R}\cdot$ is generated which is comparatively unreactive towards metal ions and hydrogen peroxide, the observed concentration of $\text{R}\cdot$ is maximal when $[\text{H}_2\text{O}_2]_0$ is given approximately by $(k_{\text{in}}t)^{-1}$. The species

* Pulse radiolysis of an argon-saturated 10mM solution of acetone in 0.1M-sulphuric acid shows complicated decay kinetics of the absorption at 290 nm with a second-order component $2k = \text{ca. } 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$. Since the e.s.r. data at this pH are consistent with bimolecular termination of $\cdot\text{CH}_2\text{COME}$, with no other radicals detectable, we believe this value to be appropriate.

$\cdot\text{CH}_2\text{CMe}_2\text{OH}$ is such a radical, and we found that the values of $[\text{H}_2\text{O}_2]_0$ required to maximise the observed concentration of this radical (generated from *t*-butyl alcohol under our conditions) were in the ratio *ca.* 2 : 1 for pH 1.0 and 7.0, respectively. It follows that k_{in} (pH 7.0) $\sim 2k_{\text{in}}$ (pH 1.0) $\sim 1200 \text{ l mol}^{-1} \text{ s}^{-1}$. As a check, we measured the relative concentrations of $\cdot\text{CH}_2\text{CMe}_2\text{OH}$ at pH 1.0 and 7.0 for a fixed concentration of hydrogen peroxide ($1.0 \times 10^{-2}\text{M}$) as well as for $[\text{Ti}^{\text{III}}]_0$ ($1.6 \times 10^{-3}\text{M}$) and t (*ca.* 50 ms); the ratio observed (obtained by double integration of the first-derivative spectra, since the lines at pH 7.0 were considerably broader than at pH 1.0) was 0.83, as compared with the calculated value, based on k_{in} (pH 7.0) = $1200 \text{ l mol}^{-1} \text{ s}^{-1}$, of 0.82.

TABLE 1
Variation of $[\cdot\text{CH}_2\text{COME}]$ with $[\text{Ti}^{\text{III}}]_0$ at pH 1

$10^6[\cdot\text{CH}_2\text{COME}]/\text{M}$	$10^3[\text{Ti}^{\text{III}}]_0/\text{M}$	$10^2[\text{Ti}^{\text{III}}]_0^{\frac{1}{2}}/\text{M}^{\frac{1}{2}}$
0.00	0.0	0.0
2.07	0.7	2.6
2.18	0.9	3.0
2.94	1.2	3.5
2.96	1.6	4.0
4.34	3.2	5.7
4.29	3.2	5.7
5.15	3.9	6.2

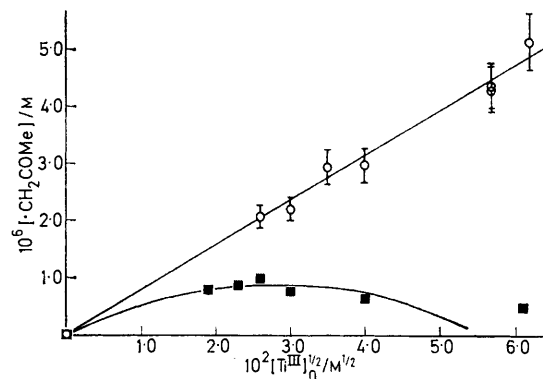


FIGURE 1 Variation of the acetylonyl radical concentration, $10^6[\cdot\text{CH}_2\text{COME}]/\text{M}$, with $10^2[\text{Ti}^{\text{III}}]_0^{\frac{1}{2}}/\text{M}^{\frac{1}{2}}$: \circ pH 1; \blacksquare pH 7

Table 2 lists values for $[\cdot\text{CH}_2\text{COME}]$, (i) calculated on the assumption that reaction (11) makes no contribution and with $k_{\text{in}} = 1200 \text{ l mol}^{-1} \text{ s}^{-1}$, and (ii) observed, obtained by comparison with a solution of vanadyl sulphate. The difference between these quantities is plotted against $[\text{Ti}^{\text{III}}]_0$ in Figure 2. From the gradient of this plot and equation (16), taking $[\text{Ti}^{\text{III}}]_t$ as $0.25[\text{Ti}^{\text{III}}]_0$ and $2k_{10} = 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$, we obtain $k_{11} = 1.4 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$. The reaction was also investigated by pulse radiolysis of an argon saturated solution of acetone (1M) at pH 7. Absorption by the $\text{Ti}^{\text{III}}\text{-EDTA}$ complex in the u.v. region led to experimental difficulties, and the decay of absorption at 390 nm was complex (the radical $\cdot\text{CMe}_2\text{OH}$ is also formed under these conditions). However, some

²² A. L. Buley, R. O. C. Norman, and R. J. Pritchett, *J. Chem. Soc. (B)*, 1966, 849.

²³ K. M. Bansal, M. Grätzel, A. Henglein, and E. Janata, *J. Phys. Chem.*, 1973, **77**, 16.

reduction was evident and a lower limit was estimated for k_{11} as *ca.* $4 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$.

TABLE 2

Variation of $[\cdot\text{CH}_2\text{COME}]$ with $[\text{Ti}^{\text{III}}]_0$ at pH 7, together with values of $[\cdot\text{CH}_2\text{COME}]$ calculated assuming negligible radical reduction

$10^6[\cdot\text{CH}_2\text{COME}]/\text{M}$		$10^3[\text{Ti}^{\text{III}}]_0/\text{M}$	$10^2[\text{Ti}^{\text{III}}]_0^{\ddagger}/\text{M}^{\ddagger}$
Observed	Calculated		
0.00	0.00	0.00	0.0
0.80	1.61	0.36	1.9
0.87	1.95	0.53	2.3
1.00	2.21	0.68	2.6
0.76	2.55	0.90	3.0
0.63	3.39	1.60	4.0
0.49	5.30	3.90	6.2

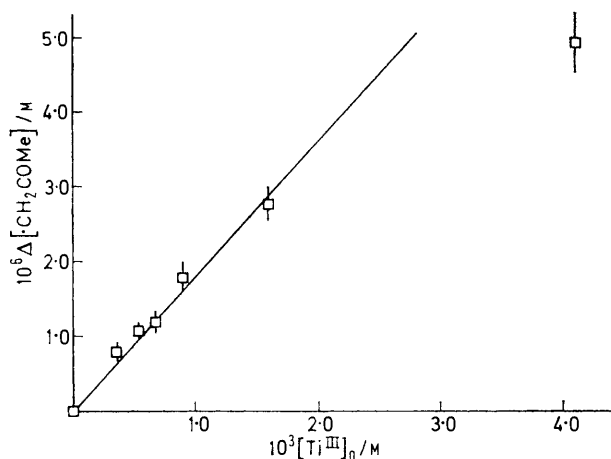
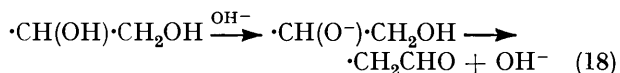
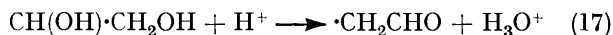


FIGURE 2 Plot of estimated reduction in concentration of $\cdot\text{CH}_2\text{COME}$; $10^5\Delta[\cdot\text{CH}_2\text{COME}]/\text{M}$ versus $10^3[\text{Ti}^{\text{III}}]_0/\text{M}$

Experiments at pH 1 employing Fenton's reagent indicated that reduction of the acetyl radical by Fe^{II} is not significant $\{[\text{Fe}^{\text{II}}]_0 = 1.9\text{--}13\text{mM}$; $[\text{H}_2\text{O}_2]_0 = 90\text{mM}\}$. Although the signal amplitude for $\cdot\text{CH}_2\text{COME}$ was observed to decrease with increasing $[\text{Fe}^{\text{II}}]_0$, this was found to be due to an increase in the linewidth.

The Radical $\cdot\text{CH}_2\text{CHO}$.—Both pulse radiolysis²³ and e.s.r.^{22,24,25} studies have shown that the oxidation of ethane-1,2-diol by the hydroxyl radical gives the species $\cdot\text{CH}(\text{OH})\text{CH}_2\text{OH}$ which undergoes acid-catalysed dehydration to the formylmethyl radical [reaction (17)]. The former technique has also demonstrated that this dehydration occurs in a diffusion-controlled reaction with hydroxide ion [reaction (18)].²³



We generated the radical $\cdot\text{CH}_2\text{CHO}$ by treating ethane-1,2-diol with the $\text{Ti}^{\text{III}}\text{--H}_2\text{O}_2$ system under conditions (pH 0.7; 0.1M-ethane-1,2-diol) in which this radical was the only one present in detectable concentration.

The variation of its concentration with $[\text{Ti}^{\text{III}}]_0$ is recorded in Table 3, and the linear relationship between its concentration and $[\text{Ti}^{\text{III}}]_0^{\ddagger}$ shows that there is no detectable contribution to radical termination from reaction (19); we estimate that $k_{19} \geq 6 \times 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$, given that $^{23} 2k_{20} = 9 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$.

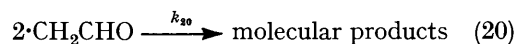
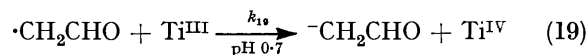


TABLE 3

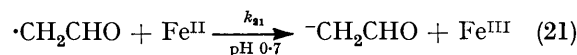
Variation of $[\cdot\text{CH}_2\text{CHO}]$ with $[\text{Ti}^{\text{III}}]_0$ at pH 0.7

$[\cdot\text{CH}_2\text{CHO}]^a$	$10^3[\text{Ti}^{\text{III}}]_0/\text{M}$	$10^2[\text{Ti}^{\text{III}}]_0^{\ddagger}/\text{M}^{\ddagger}$
3.2	1.0	3.2
3.9	1.3	3.6
4.5	2.0	4.5
4.8	2.7	5.2
7.2	4.4	6.6

^a Arbitrary units.

This result was confirmed by pulse radiolysis with optical detection. A high concentration of the diol (0.5M) was used in order to scavenge hydroxyl radicals and hydrogen atoms during the pulse (hydrated electrons are rapidly converted into hydrogen atoms at the acid concentrations used), and solutions were deoxygenated by bubbling with argon. It was found that, at pH 1, the second-order decay of the radical $\cdot\text{CH}_2\text{CHO}$, monitored at 300 nm,²³ was unaffected by the presence of $1.6 \times 10^{-2}\text{M}$ -titanium(III) ion, from which it follows that $k_{19} \geq 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$.

However, it was apparent that the decay of this radical, at pH 0.7, was significantly affected by the presence of iron(II) ion. The reaction could not be monitored at 300 nm in this case owing to the build-up of an absorption from iron(III), but it could be achieved by following the increase in $[\text{Fe}^{\text{III}}]$ at 350 nm where absorption from $\cdot\text{CH}_2\text{CHO}$ is insignificant. The rate constant derived in this way for reaction (21) was $4.5 \times 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$.



Although $\cdot\text{CH}_2\text{CHO}$ is expected to be formed from ethane-1,2-diol by way of reaction (18) at high pH,²³ no radicals could be detected by e.s.r. from the reaction of the diol with the $\text{Ti}^{\text{III}}\text{--H}_2\text{O}_2$ system at pH 9 in the presence of EDTA. We infer that $k_{22} > 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$.



This was confirmed by the pulse radiolysis of an N_2O -saturated solution of ethane-1,2-diol (0.5M) in the presence of $\text{Ti}^{\text{III}}\text{--EDTA}$ (4mM) at pH 9. Some difficulties were again encountered, but monitoring the decay in the absorption at 350 nm gave a value for k_{22} of $6 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$.

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

²⁵ R. Livingston and H. Zeldes, *J. Amer. Chem. Soc.*, 1966, **88**, 4333.

The Radicals ·CHMeCOEt and ·CH₂CH₂COEt.—The reaction of the hydroxyl radical with diethyl ketone is expected to give the radicals ·CHMeCOEt and ·CH₂CH₂COEt. We investigated the oxidation of the ketone with the Ti^{III}–H₂O₂ system at pH 1.0 and 7.0. In each case the e.s.r. spectrum was in accord with the presence of these two carbon radicals; there were, in addition, some weak, unassignable lines. Hyperfine splittings and *g* factors are in Table 4, and are in good agreement with previous results for these and related radicals.^{22,24,26} At both pH values the ratio of the concentrations of the two carbon radicals was not significantly changed by a substantial increase in [Ti^{III}]₀ (Table 5), from which we infer that reaction (23) is unimportant in each case.



TABLE 4

Hyperfine splitting constants (mT) and *g* factors for radicals derived from diethyl ketone and cyclohexanone

Radical	<i>a</i> (α-H)	<i>a</i> (β-H)	<i>a</i> (γ-H)	<i>g</i>	Relative concentration
·CHMeCOEt	1.86	2.25	0.27	2.0040	2
·CH ₂ CH ₂ COEt	2.21	2.48		2.0026	1
(α)	1.75	3.43	0.20	2.0041	0.25
(β)	2.16	2.78		2.0026	0.67
(γ)	2.16	2.76		2.0025	0.33
·CH ₂ [CH ₂] ₄ CO ₂ H	2.16	2.79		2.0025	0.40 ^a

^a Approximate value relative to the sum of (β) and (γ) (1.0); the radical (α) was not observed under the conditions used (see text).

TABLE 5

Variation of concentration of radicals from diethyl ketone with pH and [Ti^{III}]₀

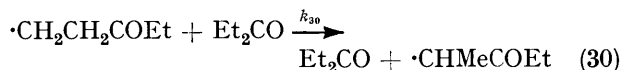
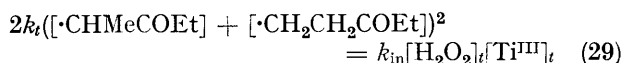
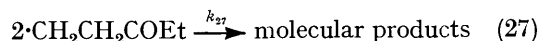
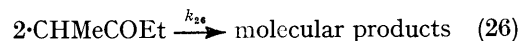
[Ti ^{III}] ₀ /mM	pH	[·CHMeCOEt] ^a		Total [R] ^{a, b}	
		[·CH ₂ CH ₂ COEt]	Observed	Predicted	
2.67	1.0	2.0	1.0	(1.0)	
6.32	1.0	2.2	1.47	1.53	
2.67	7.0	1.9	1.0	(1.0)	
6.32	7.0	2.0	1.66	1.53	

^a ±10%. ^b Arbitrary units; results for pH 1 and 7 are not in the same arbitrary units.

If the reaction of diethyl ketone is essentially described by steps (24)–(28), then, assuming $2k_{26} = 2k_{27} = k_{28} = 2k_t$, equation (29) should hold; it follows that, for $[\text{H}_2\text{O}_2]_0 \gg [\text{Ti}^{\text{III}}]_0$, the sum of the radical concentrations, $[\cdot\text{CHMeCOEt}] + [\cdot\text{CH}_2\text{CH}_2\text{COEt}]$, should be proportional to $[\text{Ti}^{\text{III}}]_0^{\frac{1}{2}}$. The sums of the radical concentrations predicted on this basis are in reasonably good agreement with the observed values (Table 5), and we conclude that $k_{23} \gg 6 \times 10^5$ (pH 1.0) and $\gg 1.2 \times 10^6$ l mol⁻¹ s⁻¹ (pH 7.0), assuming $2k_t = 10^9$ l mol⁻¹ s⁻¹.

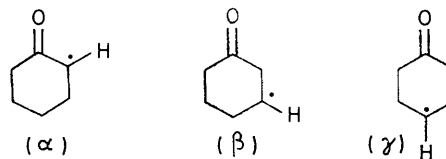
Now, reaction (30) should not make a significant contribution to the termination of ·CH₂CH₂COEt under our conditions ($k_{30} < 10^3$ l mol⁻¹ s⁻¹). We infer that the observed value of $[\cdot\text{CHMeCOEt}]/[\cdot\text{CH}_2\text{CH}_2\text{COEt}]$ is that for conditions in which termination is solely by bimolecular radical combination. If the assumption that

$2k_{26} = 2k_{27} = k_{28}$ is valid, then this ratio (2:1) is that for the rate constants of reactions (24) and (25), and we discuss this further in the sequel.



Radicals from Cyclohexanone.—The oxidation of cyclohexanone by both Fenton's reagent and the Ti^{III}–H₂O₂ system has been studied by the e.s.r. method by Shiga and his colleagues.²⁷ They suggested that either two or three radicals are formed with the former system and that one of these is absent when the latter system is used.

We have found that the reaction of cyclohexanone with the Ti^{III}–H₂O₂ system gives a complex spectrum comprising an approximate doublet of quintets attributed previously to either radical (β), or radical (γ), or a mixture,²⁷ together with a previously unreported spectrum the central lines of which are subject to selective broadening. The hyperfine splittings for the latter, together with the *g* factor (2.0041) (*cf.* ref. 28) indicate that the spectrum is that of radical (α). The broadening of the central lines could not be fully accounted for on the basis of second-order effects, and presumably the residual broadening is due to an incompletely averaged inequivalence of the β-protons. The 'doublet of quintets' is subject to second-order effects; in addition, the asymmetry of the outermost lines must be assigned to overlapping resonances from two radicals. The second-order spectrum of this mixture was satisfactorily simulated with the parameters listed in Table 4. The radical with the lower *g* is confidently expected to be radical (γ) since it is present in lower concentration. No variation of radical ratios with [Ti^{III}]₀ was observed at this pH, indicating that reduction of radical (α) is not significant under these conditions.



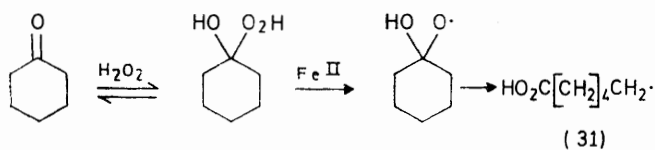
The reaction of cyclohexanone with Fenton's reagent at pH 7 (phosphate buffer) gave spectra of poorer quality.

²⁸ R. O. C. Norman and R. J. Pritchett, *Chem. and Ind.*, 1965, 2040.

²⁶ H. Fischer, *Z. Naturforsch.*, 1965, 20a, 428.

²⁷ T. Shiga, A. Boukhors, and P. Douzou, *J. Phys. Chem.*, 1967, 71, 4264.

Radical (α) was not observed, but even if it had been present in the same relative concentration as in reaction with the Ti^{III} system, its hyperfine lines would have been obscured by the noise. The additional radical reported by Shiga *et al.* could not be detected in this experiment, but it was detected when the ketone and the peroxide were contained in the same reactant stream before admixture with iron(II) ion. Its hyperfine splittings and g factor are in the regions expected for the radical $\cdot CH_2[CH_2]_4CO_2H$, and we infer the occurrence of a reaction sequence such as (31) (*cf.* refs. 29—31). This radical is also thought to be formed by photolysis of cyclohexanone–hydrogen peroxide mixtures, on the basis of a trapping experiment.³⁰



In other experiments in which the ketone and peroxide were premixed, it was found that the concentration of the radical $\cdot CH_2[CH_2]_4CO_2H$ was substantially greater on reaction with iron(II) ion than with titanium(III) ion, each at pH 7, and it could not be detected on reaction with titanium(III) ion at pH 1. These observations could reflect variations either in the rates of reaction of the intermediate peroxide with the metal ions and with pH or in those of the alkoxyl radical with the metal ions.

It is clear that premixing of peroxide and carbonyl-containing compounds can give rise to a product (probably a hydroperoxide) which may then be reduced by Ti^{III} , or Fe^{II} , or cleaved on photolysis. Mechanistic and kinetic studies employing such premixing may therefore be subject to misinterpretation; it may be that the discrepancies between our results and those reported previously for the metal ion reduction of radicals originates in the premixing technique used in the latter case.

The Significance of Radical Reduction.—The results are summarised in Table 6. They show, first, that, for a particular metal ion, the rate of one-electron reduction of a radical is sensitive to the electronic structure of the radical. Thus towards the Ti^{III} –EDTA complex the order, $\cdot CH_2CHO > \cdot CH_2COMe > \cdot CHMeCOEt$, shows that reduction is retarded as electron-releasing groups are introduced. We believe, then, that the estimated value⁴ of *ca.* 10^7 $l\ mol^{-1}\ s^{-1}$ for the reduction of $\cdot CH_2COMe$ by Fe^{II} is too high since we should expect a rate constant for this process not larger than that for reduction of $\cdot CH_2CHO$ by Fe^{II} .

Secondly, there is evidence that reduction of a particular radical by Fe^{II} is faster than by Ti^{III} ; that is, there is no correlation with metal-ion redox potentials. This is

also true of one-electron oxidations of carbon radicals by Cu^{II} and Fe^{III} ,³² and detailed studies of the mechanisms of these processes are needed to resolve the problem.

We can also consider the implications of our results on e.s.r. observations of (mono)carbonyl-conjugated radicals

TABLE 6

Reduction of carbonyl-conjugated radicals by metal ions

Metal ion	Radical	pH	$k/l\ mol^{-1}\ s^{-1}$	Method
Fe^{II}	$\cdot CH_2CHO$	0.7	4.5×10^5	P.r.
Fe^{II}	$\cdot CH_2COMe$	1.0	$> 10^5$	E.s.r.
Ti^{III}	$\cdot CH_2CHO$	0.7	$> 10^5$	P.r.
Ti^{III}	$\cdot CH_2COMe$	1.0	$> 6 \times 10^5$	E.s.r.
Ti^{III}	$\cdot CHMeCOEt$	1.0	$> 10^6$	E.s.r.
Ti^{III} –EDTA	$\cdot CH_2CHO$	9.0	$> 6 \times 10^5$	E.s.r.
Ti^{III} –EDTA	$\cdot CH_2COMe$	7.0	$> 10^7$	P.r.
Ti^{III} –EDTA	$\cdot CHMeCOEt$	7.0	$> 4 \times 10^6$	P.r.
			1.4×10^7	E.s.r.
			$> 1.2 \times 10^6$	E.s.r.

generated with Fenton's reagent or the Ti^{III} – H_2O_2 couple in a flow system. One-electron reduction by Fe^{II} at pH *ca.* 1 of such a radical from an aldehyde or ketone should not be faster than for $\cdot CH_2CHO$, *i.e.* $k \geq 4.5 \times 10^5$ $l\ mol^{-1}\ s^{-1}$. The typical concentration of Fe^{II} in one stream of a two-stream flow system is 5mM,³³ corresponding to $[Fe^{II}]_0 = 2.5$ mM, so that the concentration in the cavity is *ca.* mM. For a total observed radical concentration, $[R\cdot]$, of *ca.* μM and a termination rate constant, $2k'$, of 10^9 $l\ mol^{-1}\ s^{-1}$, $2k'[R\cdot] \geq 2\{k[Fe^{II}]\}$; the concentration of $R\cdot$ should then be reduced *at the most* by about a third of its value compared with the situation in which radical reduction is negligible. For the Ti^{III} – H_2O_2 system at pH *ca.* 1, a similar calculation for typical conditions ($[Ti^{III}]_t \sim$ mM) shows that radical reduction can be ignored.

Reactions at high pH in the presence of EDTA are in marked contrast. If a carbonyl-conjugated radical does not possess electron-donating substituents to retard reduction then the expected radical concentration may be considerably reduced (*e.g.* $\cdot CH_2CHO$ in the presence of Ti^{III} –EDTA).

Correlations of Radical Concentrations with Kinetic Data.—It is usually possible with the e.s.r. technique to assign specific structures to each of several short-lived radicals formed from a particular molecule and in principle, therefore, through kinetic analysis, to estimate rate constants for reactions at different sites in the molecule. Other methods are not always suitable for this purpose; for instance, most organic radicals exhibit weak absorption in the same region of the u.v. spectrum, so that electronic spectroscopy may be appropriate only when the various radicals display significantly different reactivity towards a particular reagent (*cf.* oxidation of α -hydroxyl radicals by metal ions^{32,34}).

³² C. Walling and S. Kato, *J. Amer. Chem. Soc.*, 1971, **93**, 4275.

³³ H. Taniguchi, H. Hasumi, and H. Hatano, *Bull. Chem. Soc. Japan*, 1972, **45**, 3380.

³⁴ G. E. Adams and R. L. Willson, *Trans. Faraday Soc.*, 1969, **65**, 2981.

²⁹ M. S. Kharasch and W. Nudenberg, *J. Org. Chem.*, 1954, **19**, 1921.

³⁰ K. Torssell, *Tetrahedron*, 1970, **26**, 2759.

³¹ M. C. V. Sauer and J. O. Edwards, *J. Phys. Chem.*, 1971, **75**, 3004.

We can employ our data for diethyl ketone and cyclohexanone to illustrate this application of e.s.r. spectroscopy, making use of the hypothesis³⁵ that a hydrogen atom in a particular molecular site can be assigned a specific rate constant for its reaction with $\cdot\text{OH}$, the overall rate constant being the sum of these 'partial specific reaction rates'. Since most of the rate constants reported were based on a competition with *p*-nitrosodimethylaniline and assumed a value for $k(\cdot\text{OH} + \text{EtOH})$ which is an underestimate of the currently accepted value,¹⁹ we have revised these values upwards (by a factor of 1.68), to give specific rate constants (per hydrogen atom) for the methyl groups in diethyl ketone of $0.605 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ and for the methylene groups in cyclohexanone which are not adjacent to the carbonyl of $5.04 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$. With these values, together with the e.s.r. results for the relative rates of formation of the radicals $\cdot\text{CHMeCOEt}$ and $\cdot\text{CH}_2\text{CH}_2\text{COEt}$ and of radicals (α), (β), and (γ), we calculate the partial specific reaction rates for the methylene groups adjacent to carbonyl as 1.8×10^8 for diethyl ketone and $1.9 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ for cyclohexanone. Summing the specific reaction rates for the former ketone gives $1.1 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ for the overall rate constant, and this is in reasonable agreement with the value from pulse radiolysis of $1.36 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ (value revised from³⁶ $8.1 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$, based on competition with thiocyanate). In view of the approximations involved it is not possible at present to decide how much reliance can be placed upon the exactitude of the results. However, it is reasonable to expect that, with a full understanding of the $\text{Ti}^{\text{III}}-\text{H}_2\text{O}_2$ system including the extent of possible side reactions with the generating system, radical reactions involving the system may be placed on a quantitative basis. A programme exploring these possibilities is in progress.

Shapes of the Radicals from Cyclohexanone.—The sums of the hyperfine splittings for a pair of β -protons in the radicals (β) and (γ) (5.56 and 5.52 mT) are significantly larger than for the cyclohexyl radical (4.60 mT),³⁷ and that for the β -protons in the radical (α) (6.86 mT) is close to the value for the cyclopentyl radical (7.03 mT),³⁷ even though some of the spin on the tervalent carbon atom in the former should be removed by the conjugated carbonyl group. Since $a(\beta\text{-H})$ increases with $\cos^2 \theta$, where θ is the

dihedral angle between the $\beta\text{-C-H}$ bond and the singly occupied *p* orbital, we infer that the rings in the radicals (β) and (γ) are significantly flattened compared with the cyclohexyl radical. For the radical (α) we should expect that the CC bonds in the fragment $\text{CH}_2\text{-CO-}\dot{\text{C}}\text{H-CH}_2$ would tend to be coplanar so as to optimise delocalisation of the spin on to the carbonyl group. The large value of $a(\beta\text{-H})$ then suggests that the second C-C bond associated with the β -protons is also nearly in this plane, such that one $\beta\text{-C-H}$ bond has θ only slightly greater than 30° , and the other correspondingly slightly less, the average value of $\cos^2 \theta$ for the two being close to $3/4$, as it presumably is in the cyclopentyl radical.

No selective line broadening was apparent in the spectra of radicals (β) and (γ), so that interconversion of two 'flattened' chair conformations must be rapid compared with the hyperfine frequency interval between the differently sited β -protons in a particular conformation. However, there was selective broadening of the lines corresponding to $M_S = 0$ for the β -protons in radical (α), and we attribute this to the occurrence of interconversion of the near-planar conformation we have described and its mirror-image at a rate little greater than the hyperfine interval between the two β -protons. Now, we have argued that the values of θ for these protons should differ by only a small amount, so that the hyperfine interval should be small compared with that, *e.g.*, for the less 'flat' radicals (β) and (γ). We conclude, then, that the energy barrier for interconversion is higher for radical (α) than for its isomers. Possibly this is because, with the coplanar arrangement of three C-C bonds which we have suggested for the radical (α), only three of the ring bonds are able to take part in the interconversion, so that greater strains are set up as these mutually adjust than when all the ring bonds can take part in the interconversion.

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³⁶ G. E. Adams, J. W. Boag, J. Carrant, and B. D. Michael, in 'Pulse Radiolysis,' eds. J. H. Baxendale, M. Ebert, J. P. Keene, and A. J. Swallow, Academic Press, 1965, p. 131.

³⁷ R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1963, **39**, 2147.

³⁵ M. Anbar, D. Meyerstein, and P. Neta, *J. Chem. Soc. (B)*, 1966, 742.