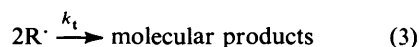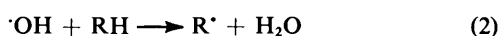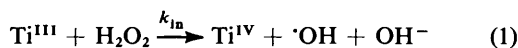# Electron Spin Resonance Studies. Part 63.[1] Selective Radical Oxidation by Titanium(IV) Complexes

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Evidence is presented that, when complexed with edta in acid solution, titanium(IV) is an effective oxidant for radicals in which tervalent carbon is bonded to a substituent of $+M$ type. A lower limit for $k(\text{Ti}^{IV}-\text{edta} + \cdot\text{CHMeOH})$ is estimated as *ca.* 10^8 dm^3 mol^{-1} s^{-1}. When the organic radicals are generated from the Ti^{III}–RO$_2$H couple (R = H or alkyl), a chain reaction operates; but stoicheiometric studies show that the chains are relatively short.

The titanium(III)–hydrogen peroxide redox couple has proved especially fruitful, in conjunction with a rapid flow-and-mixing technique, for studying the e.s.r. spectra of transient organic radicals. Under certain well defined conditions, the concentration of detected radicals is amenable to steady-state kinetic analysis, enabling rate constants to be determined. Typically, the hydroxyl radicals from the redox couple are essentially totally scavenged by an organic substrate to yield a radical R$\cdot$ which then decays bimolecularly [reactions (1)—(3)]; $2k_t$ can be evaluated. In addition, when an alternative radical–destruction process competes effectively with bimolecular decay, the rate constant of this process can be evaluated.[2] One such alternative is the one-electron oxidation of organic radicals by hydrogen peroxide; this can be important when the tervalent carbon atom is attached to a substituent of $+M$ type such as hydroxy.[3] We now report that such one-electron oxidations can also be brought about effectively in certain conditions by Ti^{IV}–edta complexes.

$$\text{Ti}^{III} + \text{H}_2\text{O}_2 \xrightarrow{k_{in}} \text{Ti}^{IV} + \cdot\text{OH} + \text{OH}^- \tag{1}$$

$$\cdot\text{OH} + \text{RH} \longrightarrow \text{R}\cdot + \text{H}_2\text{O} \tag{2}$$

$$2\text{R}\cdot \xrightarrow{k_t} \text{molecular products} \tag{3}$$

Figure 1. Variation with [edta] of [$\cdot$CHMeOH] and [$\cdot$CH$_2$CH$_2$OH] (radicals generated from EtOH with Ti^{III}–H$_2$O$_2$ at pH 2)

Results and Discussion

Rapid-flow Ti^{III}–H$_2$O$_2$ *Experiments.*—These experiments were carried out with a three-way mixing system in which aqueous solutions of titanium(III), hydrogen peroxide, and an excess of a saturated alcohol (or related substrate) were mixed *ca.* 50 ms before passage of the combined solution into the cavity of an e.s.r. spectrometer. Under these conditions essentially all the hydroxyl radicals from the redox couple react with the substrate by hydrogen-atom transfer.[2]

(i) *The effect of added edta.* The technique adopted was to monitor changes in the concentrations of alcohol-derived radicals when increasing amounts of edta were added to the titanium(III) stream, with the concentrations of the other reagents constant (typically [Ti^{III}]$_0$ 0.003, [H$_2$O$_2$]$_0$ 0.01, and [ROH]$_0$ 0.3 mol dm^{-3}). The concentration of hydrogen peroxide was sufficiently small that there was no significant contribution to the destruction of the alcohol-derived radicals by one-electron oxidation by the peroxide.[3]

With ethanol at pH *ca.* 2 in the absence of edta, the radicals $\cdot$CHMeOH and $\cdot$CH$_2$CH$_2$OH were observed in relative concentrations *ca.* 13 : 1 (*cf.* ref. 4). As [edta] was increased, [$\cdot$CHMeOH] at first decreased substantially and then levelled off when [edta] was approximately equal to the initial concentration of titanium(III) ([Ti^{III}]$_0$) (Figure 1); in contrast
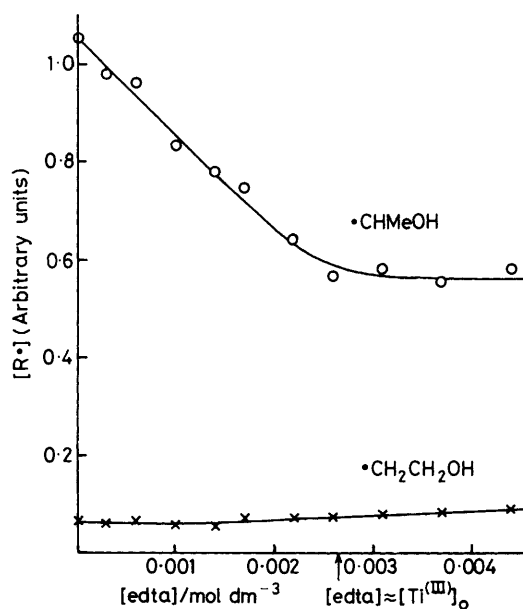
[$\cdot$CH$_2$CH$_2$OH] was relatively unaffected, though a slight increase in concentration was discernible.

Essentially similar results were obtained for other substrates whose reaction with $\cdot$OH leads to the generation of both hydroxy-conjugated and non-conjugated radicals. For example, with propan-2-ol the observed concentration of $\cdot$CH$_2$CHMeOH increased only slightly upon addition of edta whereas that of $\cdot$CMe$_2$OH decreased dramatically: the ratio of the former to the latter varied from 1 : 3.5 to 1 : 0.6 as [edta] was increased from zero to [Ti^{III}]$_0$. An analogous decrease was observed for $\cdot$CHEtOH generated from propan-1-ol, whereas signals from $\cdot$CH$_2$CH$_2$CH$_2$OH and $\cdot$CHMeCH$_2$OH remained more or less unaffected. Similarly, in the reaction of $\cdot$OH with Et$_2$O, addition of edta led to a reduction in the concentration of $\cdot$CHMeOEt, but not that of $\cdot$CH$_2$CH$_2$OEt. We also noted that, in the reaction of CH$_2$(OMe)$_2$ under identical conditions, addition of edta led to a diminution of the signal from $\cdot$CH(OMe)$_2$, compared with that from $\cdot$CH$_2$OCH$_2$OMe.

The relative constancy of the concentration of the non-conjugated radical compared with the large decrease in that of the oxygen-conjugated radical for, *e.g.* $\cdot$CH$_2$CH$_2$OH and $\cdot$CHMeOH (see *e.g.* Figure 1) suggests that there is now a pathway additional to bimolecular termination which contributes significantly to the decay of the latter. We believe
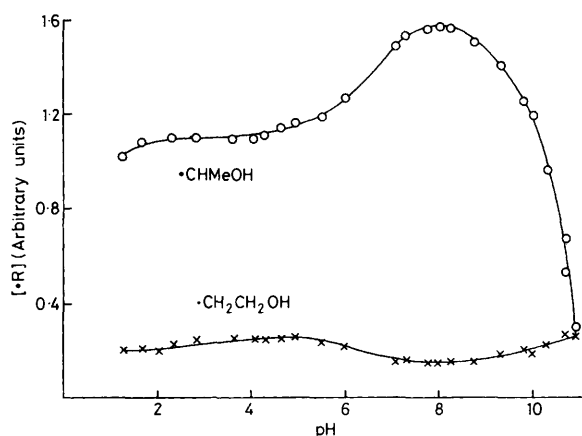
Figure 2. Variation with pH of [˙CHMeOH] and [˙CH$_2$CH$_2$OH] (radicals generated from ethanol with Ti^{III}–edta–H$_2$O$_2$)

that the reaction is one-electron oxidation by a Ti^{IV}–edta complex [e.g. reaction (4)], and this view is supported by the fact that the concentration of ˙CHMeOH (obtained from ethanol) levels off when [edta] ∼ [Ti^{III}]$_0$, i.e. when there is sufficient edta to ensure that all the Ti^{IV} is formed as its edta complex

˙CHMeOH + Ti^{IV}–edta ⟶

$^+$CHMeOH + Ti^{III}–edta   (4)
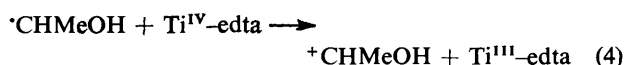
The regeneration of titanium(III) via reaction (4) would provide an increase in the rate of generation of ˙OH in the cavity, compared with its rate of generation in the absence of edta, and this may account for the slight increase in the concentration of ˙CH$_2$CH$_2$OH from ethanol (and the similar increase in ˙CH$_2$CHMeOH from propan-2-ol; see also later).

(ii) *The effect of varying pH.* Figure 2 shows the effect of varying pH on the concentrations of ˙CHMeOH and ˙CH$_2$CH$_2$OH generated from ˙OH and ethanol in the presence of edta (with [Ti^{III}]$_0$ 0.003, [edta] 0.005, and [H$_2$O$_2$]$_0$ 0.01 mol dm^{-3}.* It is notable that, as the pH is raised towards 7, the ratio [˙CHMeOH] : [˙CH$_2$CH$_2$OH] reaches approximately the same value as at low pH in the absence of edta, i.e. the ratio which reflects the relative rates of attack of ˙OH at the two sites. In the pH region 5—7 there is also a concomitant slight, but reproducible, decrease in [˙CH$_2$CH$_2$OH]. Variations of parallel type, but of more marked magnitude, were obtained for [˙CMe$_2$OH] and [˙CH$_2$CHMeOH], respectively, in the same pH range (see Figure 3).

Now, evidence has been presented [5] that complexes of Ti^{IV} with edta exist in the pH range 2—5 with a water ligand in their inner co-ordination sphere [e.g. Ti^{IV}(O)(edtaH$_2$)(H$_2$O) and Ti^{IV}(O)(edtaH)(H$_2$O)$^-$] and that, as the pH is raised, the water ligand is lost to give fully chelated complexes [e.g. Ti^{IV}(O)(edta)$^{2-}$ and Ti^{IV}(O)(edtaH)$^-$]. At higher pH (>ca. 6) titanium(IV)–edta is thought to form bi- and poly-nuclear aggregates. The pH profiles of the ratios [˙CH$_2$CH$_2$OH] : [˙CHMeOH] and [˙CH$_2$CHMeOH] : [˙CMe$_2$OH] suggest that

Figure 3. Variation with pH of the relative concentrations of the radicals obtained from ˙OH and (a) EtOH and (b) Pr^{i}OH in the presence of edta

the higher pH complexes are not such effective oxidants as their low pH counterparts.

The reduction in the concentration of the more easily oxidized radicals above pH *ca.* 9 is also of note. It is likely that this is mainly the result of the oxidation of the corresponding ketyls (e.g. by H$_2$O$_2$). This is consistent with the effect being greater for ˙CHMeOH than ˙CMe$_2$OH, since the former radical is the more acidic (˙CHMeOH has [6] pK_a 11.6, ˙CMe$_2$OH has [6] pK_a 12.2) and with the observation that the effect is small for the radical ˙CHMeOEt.

(iii) *The effect of varying* [H$_2$O$_2$]. Figure 4 shows the changes in [˙CHMeOH] and [˙CH$_2$CH$_2$OH] as [H$_2$O$_2$] was varied in experiments with EtOH (0.5 mol dm^{-3}) and Ti^{III} (0.003 mol dm^{-3}) at pH 1.5, in both the presence (0.0045 mol dm^{-3}) and absence of edta. Qualitatively similar results were obtained for ˙CMe$_2$OH and ˙CH$_2$CHMeOH from propan-2-ol.

For experiments without edta, the forms of the variation of [˙CHMeOH] [Figure 4a] and of the ratio [˙CH$_2$CH$_2$OH] : [˙CHMeOH] with H$_2$O$_2$ (Figure 4b) are in accord with the preferential oxidation of ˙CHMeOH by hydrogen peroxide [reaction (5); cf. similar oxidations described in ref. 3].†

˙CHMeOH + H$_2$O$_2$ ⟶ $^+$CHMeOH + ˙OH + OH$^-$ (5)

The addition of edta causes a marked reduction in [˙CHMeOH] for values of [H$_2$O$_2$] only up to *ca.* 0.03 mol dm^{-3} (Figure 4a), suggesting that, up to this concentration, the Ti^{IV}–edta complex contributes effectively to the oxidation,

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* The pH was measured at a point in the effluent stream which was, for typical flow rates, *ca.* 1—5 s after mixing. The measured pH, especially in the range 4—7, was found to vary slightly as the flow-rate (and hence the elapsed time) was varied, presumably because of the varying degree of completion of reaction (1) with time. The pH in the cavity itself will therefore differ slightly from the measured values.
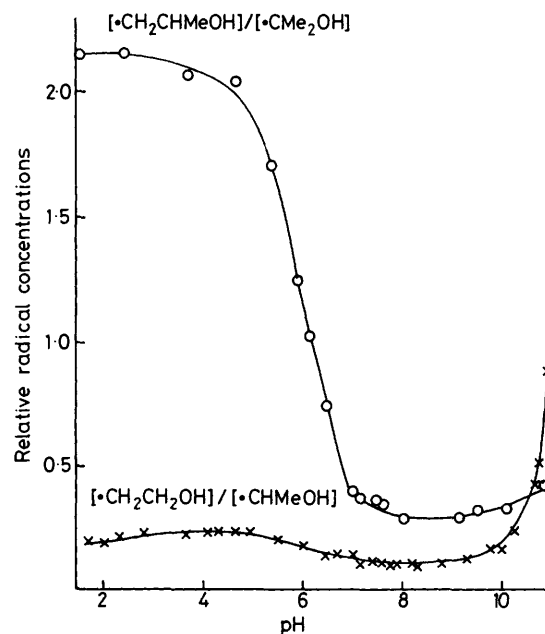
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† In this system the relationship between the concentration of the two radicals and [H$_2$O$_2$]$_0$, [Ti^{III}]$_0$, and *t*, the time between mixing and observation, is given by equation (i) where k_β and k_α are the

$$\frac{[˙CH_2CH_2OH]}{[˙CHMeOH]} = \frac{k_\beta}{k_\alpha}\left(1 + k_5\left\{\frac{[H_2O_2]_0\exp(k_{1n}[H_2O_2]_0 t)}{2k_t k_{1n}[Ti^{III}]_0}\right\}^{\frac{1}{2}}\right) \quad (i)$$

rates of attack by ˙OH to give ˙CH$_2$CH$_2$OH and ˙CHMeOH, respectively, k_{1n} is the rate constant for the reaction between Ti^{III} and H$_2$O$_2$, and k_5 refers to the oxidation [reaction (5)].[3]
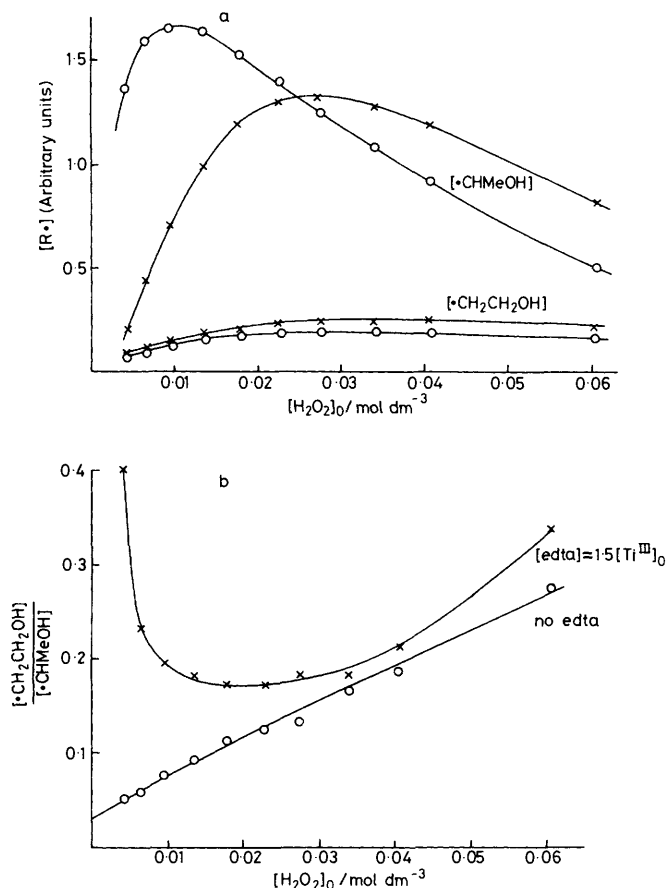
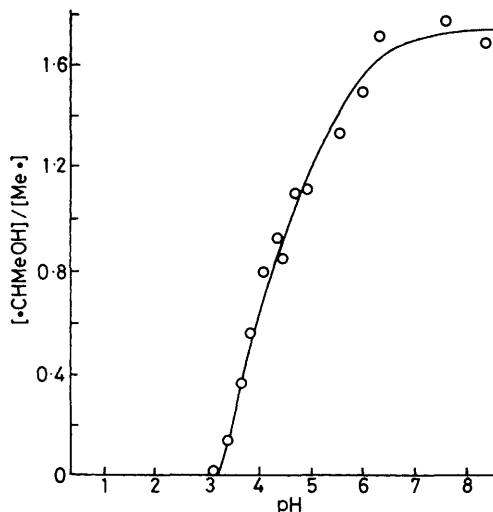Figure 4. a, Variation with [H₂O₂] of [·CHMeOH] and [·CH₂CH₂-OH], both in the presence and absence of edta: ×, edta present (0.0045 mol dm⁻³); ○, no edta present. b, Variation with [H₂O₂] of [·CH₂CH₂OH]/[·CHMeOH], both in the presence and absence of edta

Figure 5. Variation with pH of the ratio [·CHMeOH]/[Me·] (radicals generated from the reaction of Ti^III–edta with Bu^tOOH in the presence of ethanol: for concentrations of reagents, see text)

after which oxidation by the peroxide dominates. The presentation in Figure 4b demonstrates this also; at low concentrations of hydrogen peroxide, the ratio [·CH₂CH₂OH] : [·CHMeOH] is far larger when edta is present rather than absent, as compared with the value extrapolated to [H₂O₂] = zero, whereas at high concentrations of the peroxide the values are approximately the same.

However, one feature of Figure 4b is at first sight puzzling: the ratio [·CH₂CH₂OH] : [·CHMeOH] would be expected to rise monotonically with increase in H₂O₂ when edta is present, corresponding to oxidation by the peroxide additional to that by Ti^IV–edta, whereas the ratio passes through a minimum at [H₂O₂] ca. 0.02 mol dm⁻³. Now, it has recently been shown [5] that the hydrated Ti^IV–edta complexes react very rapidly with H₂O₂ at pH 2 (k ca. 5 × 10⁴ dm³ mol⁻¹ s⁻¹), so that the nature of the plot of [·CH₂CH₂OH]/[·CHMeOH] against [H₂O₂] could be accounted for if the resulting Ti^IV–edta–H₂O₂ complex were less effective as an oxidant than the original Ti^IV–edta complexes; thus, the minimum referred to would correspond to destruction of much of the latter effective oxidant without [H₂O₂] being sufficiently large itself to be significantly effective as oxidant for ·CHMeOH. Further evidence to support this interpretation is given below.

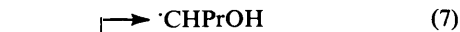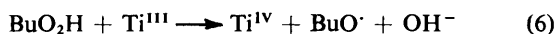(iv) Effect of added Ti^IV. In experiments in which enough edta was present to complex all Ti^III, the addition of Ti^IV–edta in the third stream (in concentrations up to ca. 0.005 mol dm⁻³) served to decrease the ratio [·CHMeOH] : [·CH₂CH₂-

OH] only slightly. Under these conditions the added Ti^IV–edta is almost completely removed between mixing and observation as a result of complexation with H₂O₂; our finding can be therefore accounted for if the resulting complex is relatively inactive as an oxidant (in contrast, when Ti^IV is generated at a steady-state concentration from Ti^III and H₂O₂ in the cavity, as it normally is,[2] oxidation of ·CHMeOH by Ti^IV–edta can successfully compete with deactivation of this complex by H₂O₂). This view is supported by the results in the following section.

Titanium(III)–Alkyl Hydroperoxide Reactions.—In order to test our hypothesis that a Ti^IV–edta complex is responsible for selective radical oxidation, we employed the one-electron reduction by Ti^III of certain alkyl hydroperoxides so as to generate mixtures of hydroxy-conjugated and non-conjugated alkyl radicals in the absence of hydrogen peroxide. When BuO₂H reacts with Ti^III in a flow system, e.s.r. signals are detected from ·CHPrOH and ·CH₂CH₂CH₂CH₂OH, which are formed by rearrangement, via formal 1,2- and 1,5-hydrogen shifts, respectively, of the first-formed (but undetectable) butoxyl radicals [reactions (6)—(8)].[7]

$$BuO_2H + Ti^{III} \longrightarrow Ti^{IV} + BuO\cdot + OH^- \quad (6)$$

$$BuO\cdot \begin{cases} \longrightarrow \cdot CHPrOH & (7) \\ \longrightarrow \cdot CH_2CH_2CH_2CH_2OH & (8) \end{cases}$$

When this reaction was carried out under typical flow-system conditions (pH 2.0, [BuO₂H]₀ 0.01, [Ti^III]₀ 0.003 mol dm⁻³) fairly intense signals from both ·CHPrOH and ·CH₂-CH₂CH₂CH₂OH were observed. However, on addition of edta (0.005 mol dm⁻³) to the Ti^III stream, the signal from ·CHPrOH was completely removed, though that from the primary radical ·CH₂CH₂CH₂CH₂OH was virtually unaffected. Similarly, in the reaction between Bu^tO₂H (0.01 mol dm⁻³) and Ti^III (0.003 mol dm⁻³) at pH 2 in the presence of ethanol, which is known to produce both Me· and ·CHMeOH [8] (by fragmentation of Bu^tO· and by its abstraction of hydrogen from ethanol, respectively), the signal from ·CHMeOH was completely removed by the addition of edta (0.005 mol dm⁻³).

These results in general correspond to those obtained with the Ti^{111}–H$_2$O$_2$ couple but the effect of adding edta is more marked; the variation with pH of the ratio [$\cdot$CHMeOH] : [Me$\cdot$] in the presence of edta (Figure 5) also parallels the results with the hydrogen peroxide system.

When the above experiments with edta at pH 2 were carried out with much smaller concentrations of titanium(III) (0.0005—0.001 mol dm^{-3}), weak signals of the hydroxy-conjugated radicals were again observed. However, the addition of a very low concentration of Ti^{IV}–edta (0.0005 mol dm^{-3}) completely quenched these signals, in accord with our views both that Ti^{IV}–edta complexes are the effective oxidising agents at low pH and that, in the Ti^{111}–H$_2$O$_2$ systems, their effectiveness is reduced by their reaction with hydrogen peroxide.

Radical Generation by Photochemical Methods.—For a further test, this time in the absence of both H$_2$O$_2$ and Ti^{111}, we explored the possibility of employing *in situ* photolytic techniques for simultaneous generation of radicals of different type (*cf.* $\cdot$CHMeOH and $\cdot$CH$_2$CH$_2$OH), in the presence and absence of Ti^{IV} and edta. In principle, this could be effected by photolysis of an aliphatic ketone of appropriate structure in the presence of an added alcohol; thus, it has previously been shown [9] that the formation of the ketone triplet [reaction (9)] may be followed by Norrish Type I fission [reaction (10)] and subsequent decarbonylation [reaction (11)] and, in the presence of added alcohol, by hydrogen-atom abstraction [*e.g.* reaction (12)].

$$R_2C{=}O \xrightarrow{hv} R_2\dot{C}{-}\dot{O} \tag{9}$$

$$R_2\dot{C}{-}\dot{O} \xrightarrow{k_{10}} R\dot{C}O + R\cdot \tag{10}$$

$$R\dot{C}O \xrightarrow{k_{11}} R\cdot + CO \tag{11}$$

$$R_2\dot{C}{-}\dot{O} + Me_2CHOH \longrightarrow R_2\dot{C}OH + Me_2\dot{C}OH \tag{12}$$
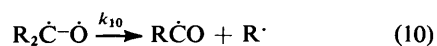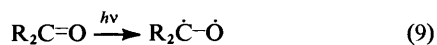
Photolysis experiments were conducted *in situ* with a flow system in order to prevent the build-up of photoproducts and to minimize the depletion of reagents in the cavity; a flow-rate of 0.3 cm^3 s^{-1} was typically employed (for most of the reactions studied, the radicals detected and their relative concentrations did not vary significantly with the flow rate although some exceptions are noted below). Photolysis of an aqueous solution containing both propanone (*ca.* 0.4 mol dm^{-3}) and propan-2-ol (2.5 mol dm^{-3}) led to the detection solely of the e.s.r. signal from $\cdot$CMe$_2$OH; evidently the fission reaction (10; R = Me) is not sufficiently rapid to compete with hydrogen-atom transfer [reaction (12)] under these conditions. On the other hand, photolysis of an aqueous solution of pentan-3-one (0.4 mol dm^{-3}) and propan-2-ol (2.5 mol dm^{-3}) under similar conditions led to the detection of both Et$\cdot$ and $\cdot$CMe$_2$OH in the concentration ratio *ca.* 10 : 1. [This reflects, at least in part, the greater rate of the fragmentation reaction (10; R = Et) than that for (10; R = Me), although differences in the reactivity of the triplets toward hydrogen-atom abstraction may also be important.]

These results led us to photolyse a mixture of propanone and pentan-3-one in the presence of propan-2-ol. Strong signals from both Et$\cdot$ and $\cdot$CMe$_2$OH were obtained, as expected from the predominant occurrence of reactions (10; R = Et) and (12; R = Me) for Et$_2$$\dot{C}$–$\dot{O}$ and Me$_2$$\dot{C}$–$\dot{O}$ respectively. For example, when a ratio of [Me$_2$CO] : [Et$_2$-CO] : [Me$_2$CHOH] of 1 : 0.75 : 5 was employed in experiments at pH *ca.* 1.9, [Et$\cdot$] : [$\cdot$CMe$_2$OH] was found to be *ca.* 0.4. The ratio of the radical concentrations remained virtually un-
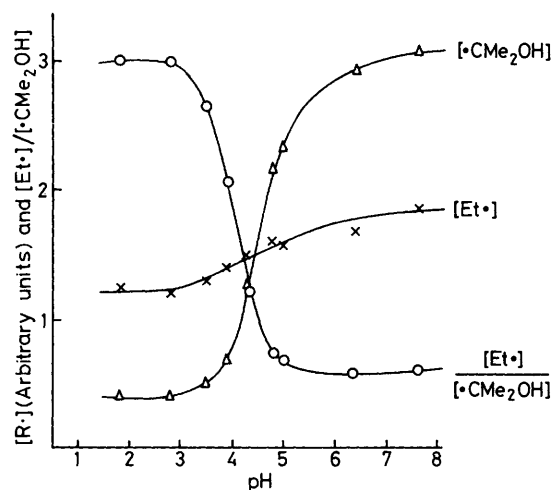

Figure 6. Variation with pH of [Et$\cdot$], [$\cdot$CMe$_2$OH], and the ratio [Et$\cdot$]/[$\cdot$CMe$_2$OH] when these radicals were generated in photolytic experiments employing pentan-3-one, propanone, and propan-2-ol (for concentrations of reagents, see text)
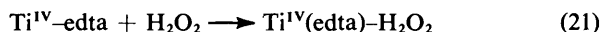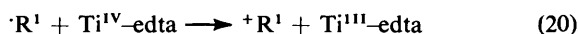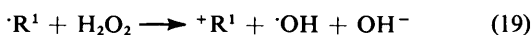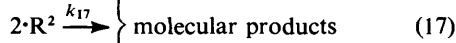
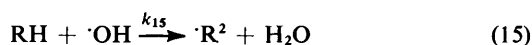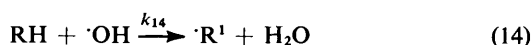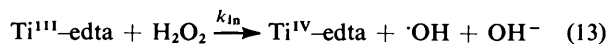changed when either titanium(IV) chloride (6 × 10^{-4} mol dm^{-3}) or edta (10^{-3} mol dm^{-3}) was added separately, but when Ti^{IV}–edta (6 × 10^{-4} mol dm^{-3}) was added (in experiments with a flow rate of *ca.* 0.3 cm^3 s^{-1}), the observed concentration of $\cdot$CMe$_2$OH fell dramatically, from *ca.* 2 × 10^{-6} to 3.5 × 10^{-7} mol dm^{-3}, whereas that of Et$\cdot$ was only slightly reduced, from *ca.* 8.5 × 10^{-7} to 6.5 × 10^{-7} mol dm^{-3}, with a resulting ratio of [Et$\cdot$] : [$\cdot$CMe$_2$OH] 1.8 : 1. For a given set of conditions, the concentration of $\cdot$CMe$_2$OH increased as the flow-rate was reduced.

Although it is possible that Ti^{IV}–edta complexes serve to absorb some of the incident radiation or to affect the photochemical processes (*e.g.* by reaction with the ketone triplets), the fact that the concentration of Et$\cdot$ remains largely unaffected suggests that such interactions are of relatively minor importance. The results thus provide further evidence that hydroxy-conjugated (oxidizable) radicals (in this case $\cdot$CMe$_2$-OH) are removed by reaction with Ti^{IV}–edta complexes; the increase in [$\cdot$CMe$_2$OH] with decrease in flow-rate in the experiment with added Ti^{IV}–edta is also consistent with this interpretation, since this reaction results in the depletion of [Ti^{IV}–edta] along that part of the flow-tube which is in the light path. It is also notable that the pH profile of the ratio of the concentrations of alkyl and hydroxyalkyl radicals in experiments in which other variables were held constant (Figure 6) shows a *general* similarity to the results obtained in the corresponding Ti^{111}–H$_2$O$_2$ experiments (although for the photolysis experiments, as with those conducted using the flow system, the pH could only be monitored *outside* the cavity, so that the precise pH pertaining to the point of observation, and hence a strict comparison with the flow results, is impossible to achieve).

When a mixture of pentan-3-one (0.4 mol dm^{-3}), propanone (0.5 mol dm^{-3}), and methanol (4.6 mol dm^{-3}) was photolysed, the e.s.r. spectrum comprised a mixture of signals from Et$\cdot$, $\cdot$CMe$_2$OH, and $\cdot$CH$_2$OH (which evidently derives from the reaction of Me$_2$$\dot{C}$–$\dot{O}$ with methanol). On the addition of a low concentration (6 × 10^{-4} mol dm^{-3}) of Ti^{IV}–edta at pH *ca.* 1.9, as described earlier, the signal from $\cdot$CMe$_2$OH was removed, there being no significant reduction in [$\cdot$CH$_2$OH]; at higher concentrations of Ti^{IV}–edta, however, the signal from $\cdot$CH$_2$OH was significantly depleted. We conclude that $\cdot$CH$_2$OH is also oxidized by Ti^{IV}–edta complexes but that the rate of

reaction is considerably less than that for $\cdot CMe_2OH$, as would be expected on the basis of the electron-donating effects of the alkyl groups in the latter [cf. also, relative rate constants for the oxidation [3] of $\cdot CH_2OH$ and $\cdot CMe_2OH$ by H_2O_2].

Kinetic Studies.—(a) Ti^{III}–H_2O_2 reactions. A general reaction scheme involving the generation of radicals by the reaction of Ti^{III} with hydrogen peroxide may be represented by equations (13)—(21). These reactions include the production of both oxidizable radicals ($\cdot R^1$) and those not significantly susceptible to oxidation ($\cdot R^2$), the selective oxidation of $\cdot R^1$ by both H_2O_2 and titanium(iv)–edta complexes, and the reaction of Ti^{IV}–edta with H_2O_2.

$$Ti^{III}\text{–edta} + H_2O_2 \xrightarrow{k_{in}} Ti^{IV}\text{–edta} + \cdot OH + OH^- \quad (13)$$

$$RH + \cdot OH \xrightarrow{k_{14}} \cdot R^1 + H_2O \quad (14)$$

$$RH + \cdot OH \xrightarrow{k_{15}} \cdot R^2 + H_2O \quad (15)$$

$$2\cdot R^1 \xrightarrow{k_{16}} \left.\begin{array}{c} \\ \\ \end{array}\right\} \quad (16)$$

$$2\cdot R^2 \xrightarrow{k_{17}} \Big\} \text{molecular products} \quad (17)$$

$$\cdot R^1 + \cdot R^2 \xrightarrow{k_{18}} \Big\} \quad (18)$$

$$\cdot R^1 + H_2O_2 \longrightarrow {}^+R^1 + \cdot OH + OH^- \quad (19)$$

$$\cdot R^1 + Ti^{IV}\text{–edta} \longrightarrow {}^+R^1 + Ti^{III}\text{–edta} \quad (20)$$

$$Ti^{IV}\text{–edta} + H_2O_2 \longrightarrow Ti^{IV}(\text{edta})\text{–}H_2O_2 \quad (21)$$

For the oxidation of EtOH in the $Ti^{III}(\text{edta})$–H_2O_2 system all the relevant rate constants have been measured, with the exception of that for the oxidation of $\cdot CHMeOH$ by Ti^{IV}–edta [reaction (20)]. We set out to determine if a kinetic analysis according to equations (13)—(21) could in principle account for the variation of $[\cdot R^1]$ and $[\cdot R^2]$ with $[H_2O_2]$ and, in particular, could provide an interpretation for the minimum observed for $[\cdot R^2]/[\cdot R^1]$ as $[H_2O_2]$ is increased in the presence of edta (see Figure 4b).

We employed a kinetic simulation program which calculates the steady-state concentrations of $\cdot R^1$, $\cdot R^2$, Ti^{III}–edta, Ti^{IV}–edta, $Ti^{IV}(\text{edta})$–H_2O_2, and H_2O_2 as a function of time after mixing for different initial concentrations of H_2O_2; the value of k_{20} was varied in order to examine the $[H_2O_2]$-dependence of $[\cdot CH_2CH_2OH]/[\cdot CHMeOH]$ for a fixed time 50 ms after mixing. The following rate constants were employed: $k_{in}(Ti^{III}$–edta + H_2O_2) 1 800 dm^3 mol^{-1} s^{-1},[10] k_{14}/k_{15} 13, $2k_{16} \simeq 2k_{17} \simeq k_{18} = 2 \times 10^9$ dm^3 mol^{-1} s^{-1} (see, e.g. refs. 3 and 6), k_{19} (pH = 1.5) = 1.6×10^5 dm^3 mol^{-1} s^{-1},[5] and [3,11] k_{21} = 1.05×10^5 dm^3 mol^{-1} s^{-1}. For calculations to simulate the behaviour of the system in the absence of edta, reactions (20) and (21) were omitted and k_{in} was taken as [10] 2 400 dm^3 mol^{-1} s^{-1}.

We found that the observed minimum for $[\cdot CH_2CH_2OH]/[\cdot CHMeOH]$ as $[H_2O_2]$ is increased in the presence of edta is qualitatively reproduced; Figure 7 shows the behaviour predicted for a value of k_{20}, the rate of oxidation of $\cdot CHMeOH$ by Ti^{IV}–edta, of 6.5×10^8 dm^{-3} mol^{-1} s^{-1}. However, while the agreement between the observed and calculated variations in $[\cdot CH_2CH_2OH]/[\cdot CHMeOH]$ is encouraging, the fit is clearly not perfect; this is perhaps not surprising in view of the inherent inaccuracies in some of the rate constants employed in the simulation. Although for this reason we cannot estimate k_{20} accurately, we infer that it is in the region 10^8—10^9 dm^3 mol^{-1} s^{-1}.

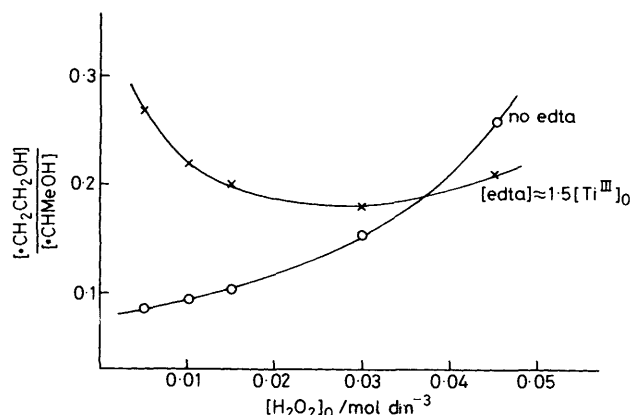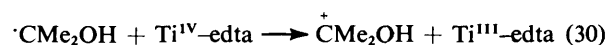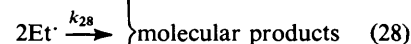Figure 7. Simulated dependence of $[\cdot CH_2CH_2OH]/[\cdot CHMeOH]$ on $[H_2O_2]$ in both the presence and absence of edta (for parameters employed, see text)

(b) *Photolysis systems.* The analysis of the steady-state concentrations of radicals obtained in the photolysis of mixture of ketones in the presence of added alcohols is based on reactions (22)—(30). In view of the very rapid decarbonylation of $Et\dot{C}O$ under these conditions, we have not included the competing bimolecular termination of this radical.

$$Et_2CO \xrightarrow[I_1]{h\nu} Et_2\dot{C} - \dot{O} \quad (22)$$

$$Et_2\dot{C} - \dot{O} \longrightarrow Et\dot{C}O + Et\cdot \quad (23)$$

$$Et\dot{C}O \longrightarrow Et\cdot + CO \quad (24)$$

$$Me_2CO \xrightarrow[I_2]{h\nu} Me_2\dot{C} - \dot{O} \quad (25)$$

$$Me_2\dot{C} - \dot{O} + Me_2CHOH \longrightarrow 2\cdot CMe_2OH \quad (26)$$

$$2\cdot CMe_2OH \xrightarrow{k_{27}} \Big\} \quad (27)$$

$$2Et\cdot \xrightarrow{k_{28}} \Big\} \text{molecular products} \quad (28)$$

$$Et\cdot + \cdot CMe_2OH \xrightarrow{k_{29}} \Big\} \quad (29)$$

$$\cdot CMe_2OH + Ti^{IV}\text{–edta} \longrightarrow {}^+CMe_2OH + Ti^{III}\text{–edta} \quad (30)$$

On the assumptions that $2k_{27} = 2k_{28} = k_{29} = 2k_t$ and that Ti^{III}–edta is not included in any significant reactions, steady-state analysis leads to the derivation of equation (31) for the ratio of concentrations of $Et\cdot$ and $\cdot CMe_2OH$.

$$\frac{[Et\cdot]}{[\cdot CMe_2OH]} = \frac{I_1}{I_2} \frac{[Et_2CO]}{[Me_2CO]} \left(1 + \frac{k_{30}[Ti^{IV}\text{–edta}]}{2k_t([Et\cdot] + [\cdot CMe_2OH])}\right) \quad (31)$$
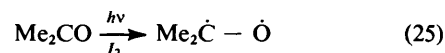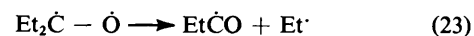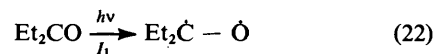
In principle, if high enough flow rates could be employed, the concentration of Ti^{IV}–edta complexes in the cavity should be the same as that added initially, i.e. with no significant depletion from the occurrence of reaction (30) along that part of the flow tube which is in the light path. The ratio $[Et\cdot] : [\cdot CMe_2OH]$ would then be independent of flow rate, so that equation (31) could be rigorously tested and k_{30} evaluated. However, we could not achieve high enough flow rates to fulfil this condition: the ratio $[Et\cdot] : [\cdot CMe_2OH]$ increased with flow-

Stoicheiometry of the Ti^{III}–RO_2H system [a]

Ti^{III}–salt	Substrate	[edta added]/ mol dm^{-3}	Stoicheiometry Ti^{III} : H_2O_2
$TiCl_3$	—	—	2.0 : 1
$TiCl_3$	EtOH	—	0.8 : 1
$TiCl_3$	EtOH	0.1	0.55 : 1
$TiCl_3$	EtOH	0.1 [b]	0.4 : 1
$TiCl_3$	Bu^tOH	0.1	1.1 : 1
$TiCl_3$	MeOH	0.1	0.8 : 1
$TiCl_3$	Pr^iOH	0.1	0.5 : 1
$Ti_2(SO_4)_3$		—	2.0 : 1
$Ti_2(SO_4)_3$	EtOH	0.1	0.5 : 1
$Ti_2(SO_4)_3$	Pr^iOH	0.1	0.5 : 1
$Ti_2(SO_4)_3$	Bu^tOH	0.1	1.0 : 1
$Ti_2(SO_4)_3$	Me_2CO	0.1	1.1 : 1
			Ti^{III} : Bu^tO_2H
$Ti_2(SO_4)_3$	Bu^tOH	0.1	1.0 : 1
$Ti_2(SO_4)_3$	Pr^iOH	0.1	0.25 : 1

[a] For conditions, see text. [b] Ti^{IV}–edta also added.

rate in an approximately linear manner. Now if on this basis we assume that $[Ti^{IV}$–edta] decreases along the flow tube in a manner linearly related to its concentration, a plot of $[Et^.]/[^.CMe_2OH]$ against $[Ti^{IV}$–edta]/$([Et^.] + [^.CMe_2OH])$ would be linear, but with an overestimate of $[Ti^{IV}$–edta] in the cavity. Such behaviour was indeed observed in a series of experiments with $[Me_2CO]$: $[Et_2CO] = 1 : 0.75$. I_1/I_2 was estimated as 0.5 from a plot of $[Et^.]/[^.CMe_2OH]$ against $[Et_2CO]/[Me_2CO]$ in the absence of Ti^{III}–edta. On the assumption that $2k_t$ is ca. 2×10^9 dm^3 mol^{-1} s^{-1}, then it follows that the lower limit for k_{30} is 10^7 dm^3 mol^{-1} s^{-1}. Since there is clearly some depletion of $[Ti^{IV}$–edta] down the flow-tube, the rate constant for the electron-transfer reaction (30) is significantly greater than this, a finding which is broadly consistent with our analysis for the analogous oxidation of $^.CHMeOH$ in the Ti^{III}–H_2O_2 system.

Stoicheiometry.—In the absence of a substrate, the stoicheiometric relationship for the reaction between Ti^{III} ion and hydrogen peroxide should be 2 : 1, corresponding to the initiation reaction (1) and the reduction of $^.OH$ by Ti^{III}. When a substrate is present which scavenges $^.OH$ to yield radicals which decay only bimolecularly, a 1 : 1 relationship would be expected. When a substrate yields a radical which is oxidised by Ti^{IV}–edta complexes, then the ratio would be expected to fall below 1 : 1. These predictions were tested by titrating hydrogen peroxide (ca. 0.1 mol dm^{-3}) against titanium(III) sulphate (ca. 0.05 mol dm^{-3}) or titanium(III) chloride (ca. 0.1 mol dm^{-3}) at pH 1.9 in the presence and absence of several substrates and of edta. The end-point was taken to be the permanent formation of the deep orange Ti^{IV}–H_2O_2 complex or the yellow Ti^{IV}–H_2O_2–edta complex. Although this was not ideal, it gave results (Table) reproducible to within 10% providing that factors such as the stirring rate were constant.

The results were in general in accord with expectation: in the two experiments with neither a substrate nor edta present, a ratio of 2.0 : 1 was obtained; with ethanol present, the ratio was lowered significantly by the addition of edta; and in the presence of edta, compounds yielding oxidizable radicals (EtOH, MeOH, Pr^iOH) gave ratios significantly less than 1 : 1 whereas those yielding essentially non-oxidizable radicals (Bu^tOH, Me_2CO) gave ratios close to 1 : 1. Moreover, with EtOH as substrate and with edta present, the stoicheiometric ratio was decreased still further by the initial addition of Ti^{IV}–edta (ca. 0.05 mol dm^{-3}). However, it is apparent that,

when oxidation of radicals by Ti^{IV}–edta complexes occurs, the chains involving Ti^{III}–Ti^{IV} cycles are short.

The stoicheiometric relationship for the reaction between Ti^{III} and t-butyl hydroperoxide was also investigated by this technique. In the presence of t-butyl alcohol, the radical product of this reaction is predominantly methyl, formed from t-butoxyl, but in the presence of propan-2-ol significant concentrations of the oxidizable radical $^.CMe_2OH$ are formed.[7] Consequently, with added edta, the stoicheiometric ratio should be 1 : 1 in the former case but <1 : 1 in the latter. These predictions were borne out (Table); and the low ratio in the experiment with propan-2-ol indicates the occurrence of somewhat longer chains with the hydroperoxide compared with the hydrogen peroxide system.

Experimental

The e.s.r. spectrometer, spectral analysis, Ti^{III}–peroxide flow system, and general experimental conditions have been described in detail.[2] For Ti^{III}–peroxide e.s.r. flow investigations the three reagent streams which were simultaneously mixed contained, respectively, (i) 1.0—5.0 × 10^{-3} mol dm^{-3} titanium(III) as sulphate or chloride, (ii) 5—70 × 10^{-3} mol dm^{-3} hydrogen peroxide or 10 × 10^{-3} mol dm^{-3} alkyl hydroperoxide, and (iii) the organic substrate in considerable excess of the concentration necessary to scavenge all the hydroxyl radicals produced in the Ti^{III}–H_2O_2 initiating reaction[2] (usually 0.3—0.5 mol dm^{-3}). Edta was added as its disodium salt to stream (i) in molar concentration in slight excess of that of Ti^{III}. The pH of stream (i) was altered by the addition of sulphuric or hydrochloric acid and ammonia or potassium carbonate.

The flow photolysis apparatus consisted of a standard flat cell through which solutions flowed, under gravity, from a reservoir continuously purged with nitrogen. The flow rate was controlled by a tap on the outflow side and could be varied from 0.03 to 3 cm^3 s^{-1} as measured by calibrated float glass flowmeters. The cell was irradiated in the cavity of the e.s.r. spectrometer by the output of an Hanovia 977B-1 1 kW mercury–xenon compact arc filtered by a cell containing distilled water and focused by a silica lens (5 cm diameter, f 10 cm). The cell was cooled by passing nitrogen through the cavity. The temperature of the solution emerging from the cell was measured by a thermocouple placed just above the cavity and could be maintained at between 398 and 399 K for flow rates >0.1 cm^3 s^{-1}. The solutions used for flow photolysis experiments were all premixed and typically contained ketone(s) (0.3—0.5 mol dm^{-3}) and alcohol (2.5—8.0 mol dm^{-3}) dissolved in distilled and deionised water.

For kinetic e.s.r. measurements, absolute radical concentrations were estimated by comparing the double integrals of the first derivative signals with those of a known concentration of $VOSO_4$ using a Datalab DL4000 microcomputer.

The titrations used to investigate the stoicheiometry of the titanium–edta–peroxide reactions were performed under nitrogen and with rapid stirring and mixing rates of ca. 0.5 cm^3 s^{-1}.

Nearly all the chemicals employed were commercially available: methanol and ethanol (James Burrough Ltd.); propan-2-ol, 2-methylpropan-2-ol, titanium(III) sulphate, hydrogen peroxide (100 mol), titanium(III) chloride, and potassium carbonate (Fisons); t-butyl hydroperoxide (Koch-Light); and the remainder from B.D.H. n-Butyl hydroperoxide was prepared according to the method of Williams and Mosher[12] and purified by low pressure distillation (b.p. 40—42 °C at 8 mmHg).

Solutions of titanium(III) and titanium(IV) used in kinetic measurements and titrations were prepared by diluting the

commercial samples. The titanium(III) solutions were kept over zinc amalgam and under nitrogen, edta being added as required, and the titanium(IV)–edta solutions were made up to pH 5 and stored under nitrogen. All these titanium solutions were estimated spectrophotometrically either as Ti^{IV}–H_2O_2 (ε_{412} 65.2 m^2 mol^{-1}) [13] or as Ti^{IV}–edta–H_2O_2 (ε_{363} 1.24 $\times$ 10^2 m^2 mol^{-1}).[5] Hydrogen peroxide solutions were determined iodometrically.

The program for the simulation of kinetic results was kindly provided by Dr. J. Lilie of the Hahn-Meitner Institüt fur Kohlenforschung, W. Berlin.

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