An ESR Spectroscopic Investigation of pH-dependent Rearrangements of the Vinyl Radical formed from the Reaction between the Hydroxyl Radical and Butynedioic Acid. Routes to $^{\bullet}CH_2CO_2H$ and $^{\bullet}CH(CO_2^-)C(O)CO_2^-$, and CIDEP Effects

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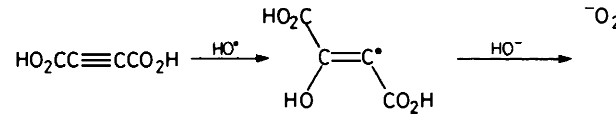
ESR experiments reveal the occurrence of two unusual rearrangements of the vinyl radical $HO_2CC(OH)=C(CO_2H)^{\bullet}$ (**1**) in aqueous solution. The formation of $^{\bullet}CH_2CO_2H$ from (**1**) at low pH is believed to result from a rapid 1,4-hydrogen shift (*k ca.* 10^4 s^{-1}) followed by ketonization, decarboxylation, and decarbonylation. Reaction to produce $^{\bullet}CH(CO_2^-)C(O)CO_2^-$ (**2**) at high pH is believed to occur *via* intramolecular deprotonation of the hydroxy group by a carboxylate function, followed by reprotonation (at carbon) of the intermediate anion radical. Rapid reduction of (**2**) and its protonated form by Ti^{III} leads to the detection of hydroxyl adducts of the corresponding enol and, at high pH, to the observation of novel CIDEP effects in the ESR spectrum of (**2**).

It has previously been noted that addition of $^{\bullet}OH$ to butynedioic acid ($HO_2CC{\equiv}CCO_2H$) at pH $\geqslant$ 8 leads to the formation of the carbonyl-conjugated radical $^{\bullet}CH(CO_2^-)C(O)CO_2^-$ (**2**), evidently *via* the first-formed vinyl radical (**1**) or its ionized counterpart [reaction (1)].[1,2] This reaction appears to be in competition with other fates for the vinyl radical which include addition to alkyne [radical (**3**) is detected at high alkyne concentrations at low pH].[1] We have also shown[3] that, at high pH in the presence of Ti^{III}–EDTA, the ESR signal from (**2**) is detected in emission, an example of the CIDEP effect the occurrence of which is ascribed[3] to the formation of a radical pair[4] [involving Ti^{III}–EDTA and (**2**)] during overall reduction of the carbonyl-conjugated radical [reaction (3)].

In the investigation described here, we set out first to determine the mechanism and scope of the base-catalysed rearrangement implied in reaction (1). Secondly, we aimed to ascertain whether other signals detected in these reactions (described below) reflect the formation of enols (*e.g.* by one-electron reduction of α-keto radicals, as shown previously for $^{\bullet}CH_2COMe$ and related species[5]). Thirdly, we intended to learn more of the factors which govern the observation of what is a very rare type of CIDEP effect involving a metal ion and an organic radical.

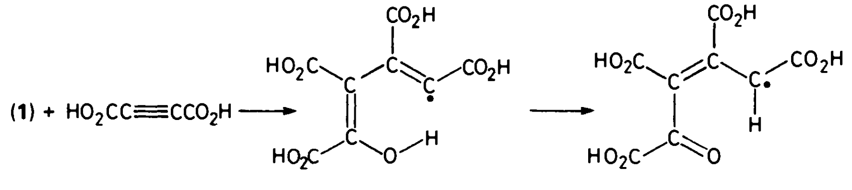
Results and Discussion

The experiments involved the use of an ESR spectrometer in conjunction with a three-stream rapid-mixing system in which solutions (normally of metal ion, peroxide, and substrate) were mixed *ca.* 30 ms before their passage through the cell in the cavity of the spectrometer. ESR spectra were recorded by scanning the magnetic field of the spectrometer under constant-flow conditions: reaction (4) was normally used for radical generation.



(1)

(**1**) (**2**)



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(**3a,b**)

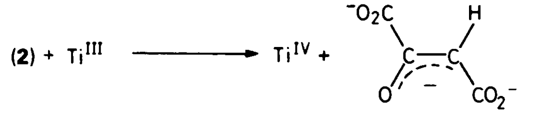

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Table 1. ESR parameters of radicals detected from the reactions of $^{\bullet}OH$ with butynedioic, propynoic, tartaric, and oxalylacetic acids.

			Hyperfine splittings/mT[b]			
Radical	Substrate[a]	pH	α-H	β-H	others	*g* value[c]
$HO_2CC(O)\text{–}C(CO_2H)\text{=}C(CO_2H)\text{–}\dot{C}HCO_2H$, (**3**)[d]	A	1.35	1.47 (1 H)	—	—	2.0028
			1.35 (1 H)	—	—	2.0029
$^{\bullet}CH_2CO_2H$	A	1.35	2.115 (2 H)	—	—	2.003 35
$HO_2CC(O)\text{–}\dot{C}HCO_2H$, (**2**)	A,B	2.0	1.825 (1 H)	—	—	2.0045
		7.0	1.775 (1 H)	—	—	2.0045
$HO_2CC(OH)_2\text{–}\dot{C}HCO_2H$, (**5**)	A,B	2.0	2.065 (1 H)	—	—	2.0031
		7.0	2.075 (1 H)	—	—	2.0031
$HO_2CCH(OH)\text{–}\dot{C}(OH)CO_2H$, (**6**)	A,B,C	2.0	—	0.36 (1 H)	0.16 (1 H)	2.0035
		7.0	—	0.245 (1 H)	0.105 (1 H)	2.0035
$HO_2CC(O)\text{–}CH\text{=}CH\text{–}\dot{C}HCO_2H$	D	1.3	1.25 (1 H) 1.15 (1 H)	0.375 (1 H)	—	2.0036
		6.75	1.215 (1 H) 1.11 (1 H)	0.370 (1 H)	—	2.003 65
$HC(O)\text{–}C(CO_2H)\text{=}CH\text{–}\dot{C}HCO_2H$	D	1.3	1.15 (1 H)	0.39 (1 H)	—	2.0038
		6.75	1.14 (1 H)	0.35 (1 H)	0.105 (1 H)	2.0038

[a] A butynedioic acid, B oxalylacetic acid, C tartaric acid, D propynoic acid. [b] ±0.005 mT. [c] ± 0.000 05. [d] Geometrical isomers, see the text.

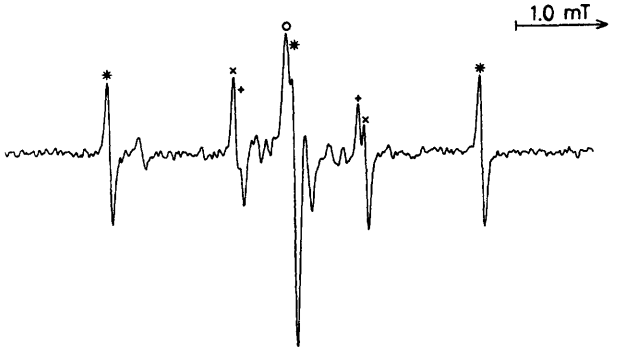


Figure 1. ESR spectra of $^{\bullet}CH_2CO_2H$(*), the pentadienyl species (**3a**) and (**3b**) [(×) and (+), respectively], and a vinyl radical (○) detected during the oxidation of $HO_2CC{\equiv}CCO_2H$ with $^{\bullet}OH$ at pH 1.35 (with [butynedioic acid]$_0$ 0.0033, [Ti^{III}]$_0$ 0.0017, [H_2O_2]$_0$ 0.0083 mol dm^{-3}).

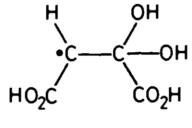
$$Ti^{III} + H_2O_2 \longrightarrow Ti^{IV} + HO^- + {}^{\bullet}OH \qquad (4)$$

ESR Studies of the Reaction of Alkynoic acids with $^{\bullet}OH$ in the pH Range 1–9.—(*a*) *Butynedioic acid.* The complex behaviour of butynedioic acid in reactions with Ti^{III} and H_2O_2 at relatively low pH can be summarized as follows (and by reference to Table 1 and Figure 1). In experiments with, typically,* [Ti^{III}] 0.001 67, [H_2O_2] 0.0167 and [$HO_2CC{\equiv}CCO_2H$] 0.0067 mol dm^{-3} the spectra at pH 1–2 are dominated by the signals attributed to two isomeric forms of the 'dimeric' species (**3**) [identified as doublets, and as described previously: see reaction (2)]. A singlet (g = 2.0036) is believed to be an intermediate vinyl radical for which the geometry does not allow a 1,5 shift. When the concentration of the alkyne was reduced at low pH, in order to discourage attack of the first-formed vinyl radical on the alkyne [reaction (2)], the ESR spectra of (**3a**), (**3b**), and the singlet were dramatically reduced (as anticipated) and the observed spectrum (see Figure 1) was dominated by a signal [with g 2.003 35, a(2 H) 2.115 mT] attributed to the radical $^{\bullet}CH_2CO_2H$ (**4**) and identical with the signal obtained from the reaction between $^{\bullet}OH$ and ethanoic acid under these conditions. Our results, therefore, indicate that the vinyl radical (**1**) is converted into $^{\bullet}CH_2CO_2H$, at least under acidic conditions.

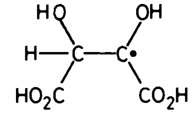
In related experiments with Ti^{III}–EDTA, H_2O_2 and butynedioic acid (with [alkyne] *ca.* 0.01 mol dm^{-3}) in which the pH was raised, it was noted that signals from $^{\bullet}CH_2CO_2H$ and the dimeric species were reduced in intensity, and other signals could be clearly detected and identified (see Figures 2 and 3). The doublet signal attributed to $^{\bullet}CH(CO_2^-)C(O)CO_2^-$ grew dramatically above pH 4 (though traces of the signal, or a protonated analogue, were also detected in the pH range 2–3): we believe that its formation involves a base-catalysed transformation of the intermediate vinyl radical (**1**) and note that attack of the ionized or, particularly, doubly ionized vinyl radical on the (charged) carboxylate anion would be expected to be significantly retarded by charge repulsion.[6] Conditions under which CIDEP effects were characterized in the ESR signal from (**2**) are described in a later section.

Other signals detected in the pH range 1–9 include a doublet [a(1 H) 2.07 mT, g 2.0031], identified as (**5**) (and its ionized form) *via* experiments in which $^{\bullet}OH$ was added to the enol form of oxalylacetic acid (see below), the radical (**6**) [with a(1 H) 0.36 mT, a(1 H) 0.16 mT, g 2.0035], similarly identified *via* experiments with tartaric acid, and an unidentified singlet (g 2.004 95).† These signals increased in intensity as the pH was raised (see Figure 3).

Use of other ligands to complex titanium(III) (nitrilotriacetic acid, NTA, and *N*-(2-hydroxyethyl)ethylenedinitrilotriacetic acid, HEDTA) gave essentially similar results both at pH 4 and 8.



(**5**)



(**6**)

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* Concentrations given in the text are those after mixing.

† The structure of the radical responsible for the singlet has not been established. Its g value and the lack of observable proton splitting suggest that the species is of semidione type, namely $^{-}O_2CC(O)\dot{C}(O^-)CO_2^-$, formed by further oxidation (*e.g.* by H_2O_2) of (**1**) or (**6**).

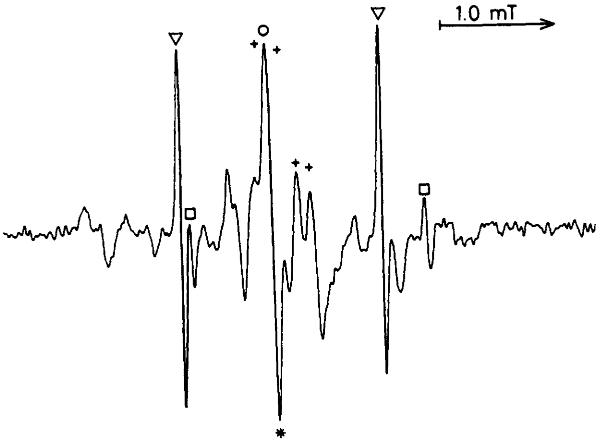


Figure 2. ESR spectrum obtained from the reaction of $^{\bullet}OH$ (from Ti^{III}–EDTA and H_2O_2) with butynedioic acid at pH 4.7: ▽, $^{\bullet}CH(CO_2^-)C(O)CO_2^-$ (**2**); □, $^{\bullet}CH(CO_2^-)C(OH)_2CO_2^-$ (**5**); +, $^{\bullet}C(OH)(CO_2^-)CH(OH)CO_2^-$ (**6**); ○, Singlet: see the text. *Reagent conditions:* [butynedioic acid]$_0$ 0.0167, $[Ti^{III}]_0$ = $[EDTA]_0$ 0.001 67, $[H_2O_2]_0$ 0.0167 mol dm^{-3}.

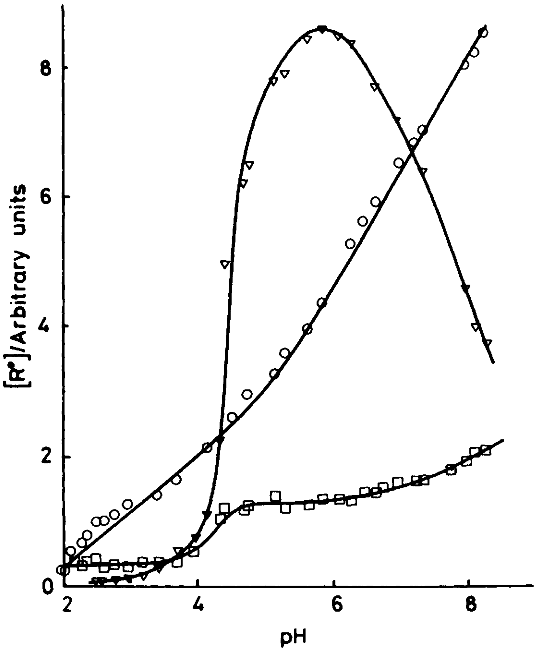
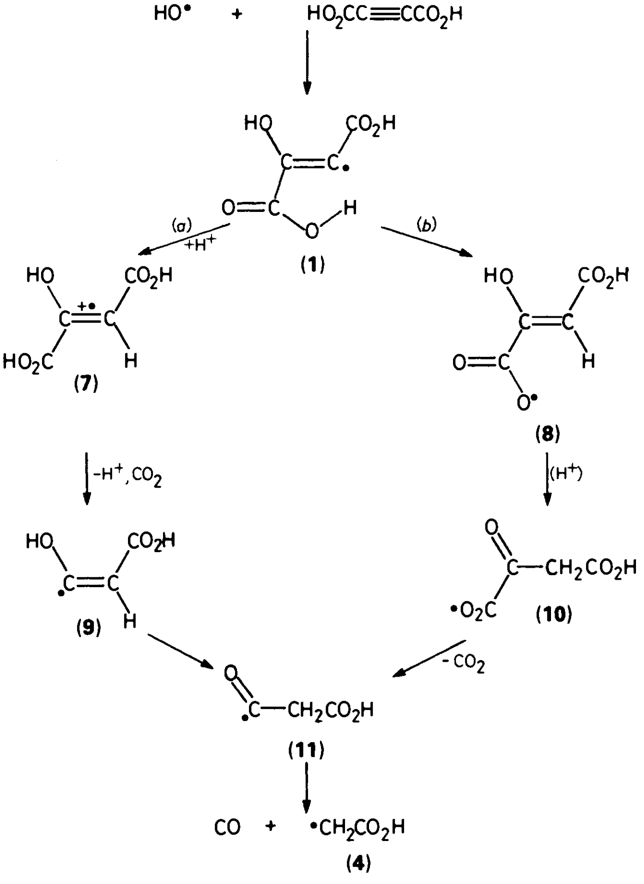


Figure 3. Variation with pH of the relative steady-state concentrations of radicals characterized by ESR spectroscopy in the reaction between $^{\bullet}OH$ (from Ti^{III}-EDTA and H_2O_2) and $HO_2CC{\equiv}CCO_2H$. Determination of the concentration of (**6**) (which was also detected) was precluded by the dominance of the signal from the singlet (○). *Reagent conditions:* [butynedioic acid]$_0$ 0.0167, $[H_2O_2]_0$ 0.0167, $[Ti^{III}]_0$ = $[EDTA]_0$ 0.001 67 mol dm^{-3}. ▽, $^{\bullet}CH(CO_2^-)C(O)CO_2^-$ (**2**); □, $^{\bullet}CH(CO_2^-)C(OH)_2CO_2^-$ (**5**); ○, singlet (see the text).

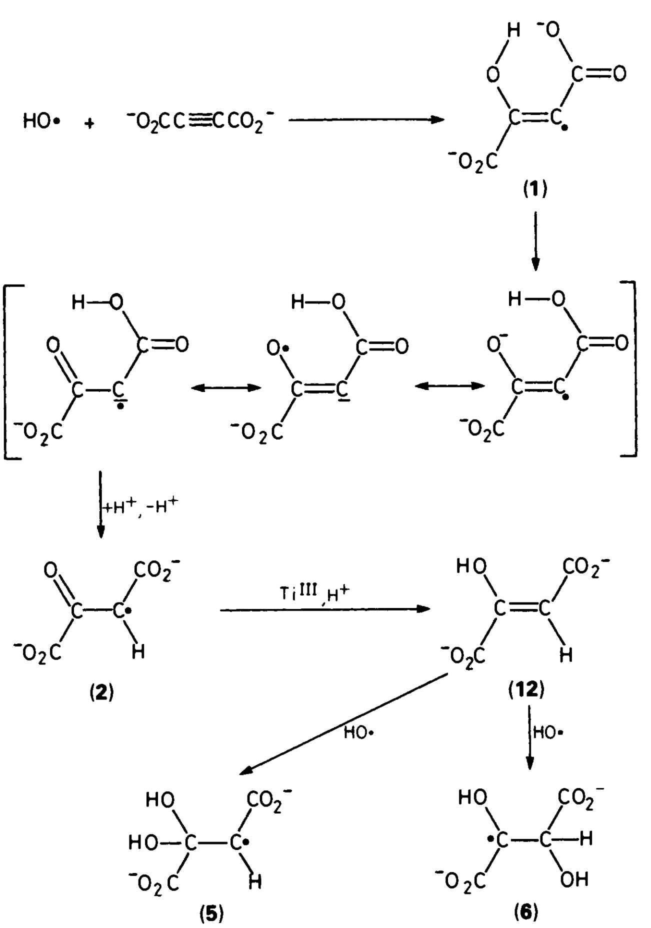
In experiments over a more limited pH range using the Fenton reaction to generate $^{\bullet}OH$ (from Fe^{II}–H_2O_2, in the presence of EDTA to complex iron and to increase the rate of radical generation[7]), signals were obtained from the 'dimeric' radicals (**3a**) and (**3b**) (in the pH range 2–4) and, above pH *ca.* 4, the carbonyl-conjugated radical (**2**). Though there were also some additional weak lines, no clear evidence for the formation of (**5**) and (**6**) could be obtained under these conditions.



Scheme 1.

Mechanism of reaction under acidic conditions. We envisage two possible mechanisms whereby the intermediate vinyl radical (**1**) is rapidly converted into (**4**) at low pH (see Scheme 1). In route (*a*), protonation of the vinyl radical gives a radical-cation (**7**) for which precedents have been proposed,[8] and for which deprotonation and decarboxylation [to (**9**)] is followed by ketonization and decarbonylation [though (**8**) may also be involved]. In route (*b*), abstraction of a carboxy hydrogen atom (*via* a 1,4-shift) to give (**8**), is followed by ketonization to (**10**), with subsequent rapid decarboxylation and decarbonylation. We believe that route (*b*) provides a more plausible pathway than route (*a*), since the presence of the carboxy groups would be expected to inhibit the formation of a radical cation; further, hydroxy-substituted radical cations are known to undergo rapid deprotonation of the hydroxy substituent (to give carbonyl-conjugated radicals).[8,9] Moreover, in each of the radicals (**1**), (**8**), (**10**), and (**11**) the unpaired electron is expected to be in a σ-(in plane) orbital (so that no symmetry-forbidden process should be involved), and numerous precedents for rapid decarbonylation[10] and decarboxylation[11] have been reported. We note, however, that the relative resistance to decarboxylation of alkene carbonyloxy radicals (**8**) (compare, for example, $MeCH{=}CHCO_2^{\bullet}$ with $MeCO_2^{\bullet}$) might well allow rapid acid-catalysed ketone formation to occur. A rate constant of 10^4 s^{-1} for the proposed 1,4-shift is estimated from its competition with the addition of (**1**) to more alkyne (k *ca.* 2×10^6 dm^3 mol^{-1} s^{-1}: see ref. 12).

Rearrangement reactions at higher pH. Our interpretation of the trends observed in Figure 3 is that base-catalysed rearrangement of the first-formed vinyl radical is responsible for the formation of $^{\bullet}CH(CO_2^-)C(O)CO_2^-$ (**2**), and that the other radicals detected are derived from secondary reactions of (**2**): in particular we believe that reduction of (**2**) by Ti^{III} (a reaction which is well-established for keto-conjugated radicals)[5] leads to



Scheme 2.

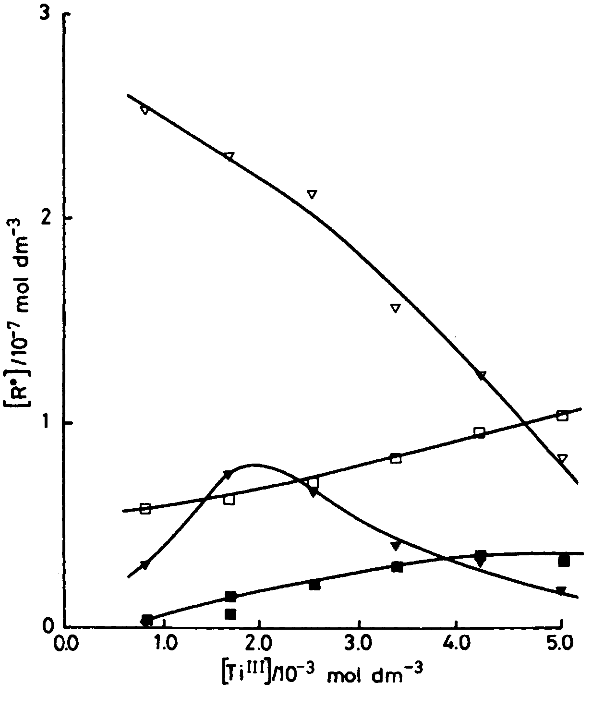


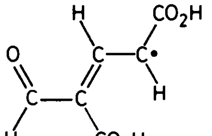
Figure 4. Variation with [Ti^{III}–EDTA] of the steady-state concentrations of radicals **(2)** (▼,▽) and **(5)** (■,□) at both pH 4 (▼,■) and pH 8 (▽,□); [butynedioic acid]$_0$ 0.0167, [H_2O_2]$_0$ 0.0167, [Ti^{III}]$_0$ = [EDTA]$_0$ 0.001 67 mol dm^{-3}.

the production of oxalacetic acid, in its enolate form, and which undergoes further reaction (see Scheme 2).

Since the observed rearrangement of **(1)** into **(2)** occurs at pH *ca.* 3 [*i.e.* close to the pK_a value expected for the carboxylate groups in **(1)**] we suggest that ionization of one of the latter groups is involved (*NB* a parallel, rapid rearrangement has been reported[13] for the unsubstituted analogue $HOCH{=}CH^{\bullet}$, but this only occurs above pH *ca.* 9). Scheme 2 indicates a process whereby intramolecular proton transfer, followed by protonation at carbon, could bring about the required transformation; the detailed structure of the intermediate and the relative importance of canonical structures are unclear at this stage (carbene anion-radical character may be important) but precedents for *C*-protonation of electron-rich vinyl and phenyl radicals have been established (see ref. 8 and references therein).

In support of the suggestion that radicals **(5)** and **(6)** result from addition to the enol **(12)** formed by reduction of **(2)** by Ti^{III}, we showed that in experiments at both pH 4 and 8 (with [H_2O_2]$_0$ *ca.* 10^{-2} mol dm^{-3} and with a number of ligands, namely EDTA, HEDTA, and NTA, as well as tartrate and citrate) signals from secondary radicals [and especially **(5)**] built up at the expense of **(2)** as [Ti^{III}]$_0$ was increased (see Figure 4). Kinetic simulations of detailed observations of the variation with [Ti^{III}–EDTA] of [**(2)**] and [**(5)**], using a procedure described previously,[8] lead to estimates of the rate constant for reduction of **(2)** (see Scheme 2) of *ca.* 10^8 dm^3 mol^{-1} s^{-1} and 5×10^8 dm^3 mol^{-1} s^{-1} at pH 4 and 8 respectively* (*NB* the rate constant for reduction of $^{\bullet}CH_2CHO$ by Ti^{III}–EDTA has been estimated[5] as 6×10^7 dm^3 mol^{-1} s^{-1}).

(*b*) *Reactions of propynoic acid.* Reaction of $^{\bullet}OH$ (from Ti^{III}–H_2O_2) and propynoic acid at low pH (typically with [alkyne] 10^{-2} mol dm^{-3}) led to the detection solely of radicals **(13)** and **(14)** (with parameters as noted previously)[1] which are believed to be formed *via* addition of first-formed radicals $HOCH{=}C(CO_2H)^{\bullet}$ and $HOC(CO_2H){=}CH^{\bullet}$ to the parent compound, followed by a 1,5-shift. At higher pH (*ca.* 4) these signals were replaced by spectra attributed to the ionized forms of these radicals. These radicals were also observed at very low concentrations of alkyne (down to *ca.* 3×10^{-3} mol dm^{-3}). Our failure to see radicals resulting from rearrangement either under acidic or basic conditions (contrast butynedioic acid) suggests that addition to the alkyne is now much faster than the alternative processes described earlier (presumably as a result of reduced steric effects and charge repulsion).



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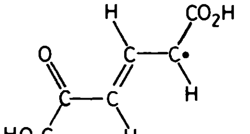

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Reaction of $^{\bullet}$OH *with Tartaric and Oxalacetic Acids.*—The detection of radicals **(5)** and **(6)** in the reaction between $^{\bullet}OH$ and $HO_2CC{\equiv}CCO_2H$ in the presence of Ti^{III} (but not Fe^{II}) is consistent with the formation of the enol **(12)** *via* reduction of the carbonyl-conjugated radical **(2)** (see Scheme 2), followed by addition of $^{\bullet}OH$ to either end of the alkenic double bond

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* The following rate constants were employed: k 2.7×10^3 dm^3 mol^{-1} s^{-1} for the reaction between Ti^{III}–EDTA and H_2O_2 under these conditions,[7] k 2.6×10^9 dm^3 mol^{-1} s^{-1} for the reaction between $^{\bullet}OH$ and butynedioic acid (*cf.* ref. 14), and $2k_t$ 2×10^8 dm^3 mol^{-1} s^{-1} for the self- and cross-termination reactions of the di-negatively charged species **(2)** and **(5)** (see *e.g.* ref. 6).

Table 2. Variation with pH of tautomer concentrations (%) for oxalylacetic acid.[a]

pH	Keto (**15**)	Enol (**16**)	Hydrate (**17**)
1.30	13.3	6.2	80.5
ca. 2.90	*ca.* 66.0	*ca.* 6.5	*ca.* 27.5
6.70	87.3	7.2	5.5
6.89	87.4	7.4	5.2

[a] See ref. 15.

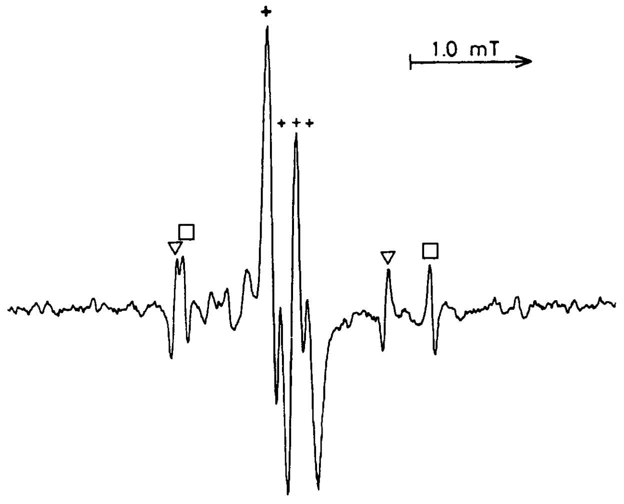


Figure 5. ESR spectra of radicals (**2**),▽, (**5**),□, and (**6**),+, detected in the reaction between ˙OH (from Ti^{III}–HEDTA and H_2O_2) and butynedioic acid, at pH 8.4 (with relatively low concentrations of H_2O_2, 0.003 mol dm^{-3}, $[Ti^{III}]_0$ = $[HEDTA]_0$ 0.003 mol dm^{-3}). The signal from ˙$CH(CO_2)C(O)CO_2^-$, [(**2**)▽] is detected in emission.

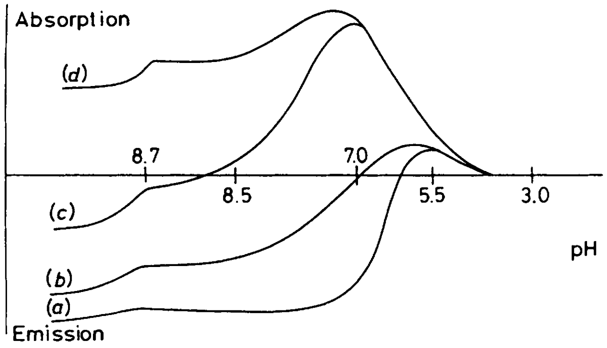
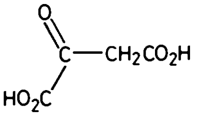


Figure 6. Variation of the intensity of the low-field line in the ESR spectrum of (**2**) as a function of pH, for different $[H_2O_2]_0$ (in experiments with $[Ti^{III}]_0$ 0.003 and [butynedioic acid]$_0$ 0.0083 mol dm^{-3}). $[H_2O_2]_0$ (*a*) 0.003 mol dm^{-3}; (*b*) 0.009 mol dm^{-3}; (*c*) 0.018 mol dm^{-3}; (*d*) 0.027 mol dm^{-3}.

(analogous rapid reductions of carbonyl-conjugated radicals by Ti^{III} have been established[5]). The assignment of these radicals was confirmed *via* their separate generation from other substrates.

Reaction of tartaric acid with ˙OH at all pH values gave only radical (**6**) (and its ionized counterparts: see Table 1). On the other hand, reaction of oxalylacetic acid gave radicals (**5**), (**6**), and (**2**) in ratios which were found to depend not only on the pH at observation, but also on the pH of the oxalylacetic acid solution prior to mixing. We attribute these observations to the occurrence (and pH dependence) of three tautomeric forms of this substrate, [keto (**15**), enol (**16**), and hydrate (**17**), for which the equilibrium proportions, as a function of pH, are given in Table 2].[15]



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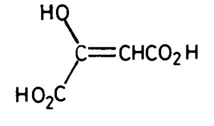

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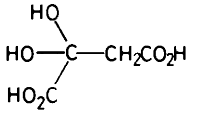

(17)

In experiments at pH *ca.* 1 in which the substrate stream was acidified prior to flowing, the observation of signals from (**6**) (major), (**5**) (in significant concentration) and (**2**) (minor) is attributed to three separate reactions of ˙OH: these are, respectively, addition to the enol form (**16**) (present at only *ca.* 6% but likely to be the most reactive form), hydrogen abstraction from the hydrated form (**17**) (present at *ca.* 80% under these circumstances), and, finally, hydrogen abstraction from the minor component, the keto form [to give (**2**) directly]. In accord with this, in experiments in which the final pH was *ca.* 1 but in which the substrate solution had pH *ca.* 7 prior to mixing, a significantly increased concentration of (**2**) [and correspondingly reduced concentration of (**5**)] was observed: this is consistent with the proposed mechanism and the observation that the keto form (**15**), as precursor to (**2**), is the predominant form of oxalylacetic acid at this pH. [Interconversion of (**15**), (**16**), and (**17**) would not be expected to be significant in the time between mixing and observation (*ca.* 0.03 s) under these conditions (see *e.g.* ref. 16)].

At pH 4, and in the presence of complexing ligands (*e.g.* EDTA and NTA), signals from (**5**) and (**6**), but not (**2**) were observed in addition to a singlet (*g* 2.004 95, see above). The disappearance of (**2**) is entirely consistent, as noted earlier, with the rapid reduction of this keto-substituted radical by Ti^{III} [reaction (3)], the rate of which is evidently dramatically increased in the presence of EDTA and other ligands.

Observation of Chemically Induced Dynamic Electron Polarization (CIDEP) with Butynedioic Acid.—As noted above, in experiments with relatively high concentrations of H_2O_2 (*ca.* 10^{-2} mol dm^{-3}) at pH 8, reaction of HO˙ (from Ti^{III}) with butynedioic acid gave signals from the carbonyl-conjugated radical (**2**) and, in particular (**5**), the former decreasing with increase in $[Ti^{III}]_0$ (see *e.g.* Figure 4): this behaviour was characteristic of the range of ligands explored.

However, in a series of experiments at considerably lower concentrations of hydrogen peroxide (0.003 mol dm^{-3}) in which $[Ti^{III}]_0$, the ligand, and pH were varied, we found certain conditions under which the signal from (**2**) was seen entirely in emission (see Figure 5 and ref. 3). The phenomenon appears to occur when relatively high concentrations of Ti^{III} are achieved in the ESR cavity (in part a consequence of low values of $[H_2O_2]$ used) in conjunction with pH values $\geqslant 6$ (see *e.g.* Figure 6): the phenomenon was also only observed when EDTA, HEDTA, or NTA was employed as a complexing agent (no emission was observed with tartrate or citrate as the ligand).

The observation of CIDEP effects only for those ligands studied (EDTA, HEDTA, and NTA) for which isotropic Ti^{III} spectra (*g ca.* 1.95) are detectable (under our conditions) and the fact that the appearance of these signals with increase in pH matches closely the appearance of emission in the spectrum from (**2**) provides strong support for the suggestion[3] that a radical-pair mechanism (RPM) [involving (**2**) and Ti^{III}] is responsible for the polarization observed.

The overall process leading to RPM can be envisaged as follows (see ref. 4). On initial encounter, electron-transfer occurs for S-pairs [*i.e.* (**2**)–Ti^{III} encounter-pairs with the unpaired electrons antiparallel], thus lowering the singlet population: in our example this corresponds to direct electron-transfer from Ti^{III} to (**2**), for which we have established that k is *ca.* 5×10^8 dm^3 mol^{-1} s^{-1} (to be effective the Ti^{III} complexes must also be sufficiently asymmetric to prevent rapid electron-relaxation, and hence possess an isotropic ESR signal). The remaining radicals separate, and $S \rightleftharpoons T_0$ mixing occurs as a result of hyperfine splitting or g-value interactions. On re-encounter, more S-pairs react and the separated radicals are polarized.

In almost all the cases in which RPM is known to cause CIDEP, the low-field lines are in emission (which accords well with the theory, since $J < 0$ and $|S>$ and $|T_0>$ states mix most effectively: Δg is usually small and hyperfine splittings lead to E/A polarization). In this case all hyperfine features for the organic radical are in emission (E) since Δg is much greater than the hyperfine splitting. Since the concentration of Ti^{III} (which gives the high-field signal) is far greater than that of the radical (**2**), the Ti^{III} spectrum is not greatly modified by this process and we have no method for estimating any enhanced absorption.

Experimental

ESR spectra were recorded on Bruker ESP 300 and Varian E-104 spectrometers each equipped with X-band microwave bridges and 100 kHz modulation. Hyperfine splittings and g-values were determined directly from the spectrometer's field scans, these having been calibrated with the signal from Fremy's salt [$a_N = 1.3091$ mT,[17] g 2.0055[18]]. Radical concentrations were determined by comparison with spectra obtained from standard solutions of vanadyl sulphate *via* double integration with the Bruker ESP 300. A mixing chamber was employed which allowed simultaneous mixing of three reagent streams *ca.* 30 ms before passage through the cavity of the spectrometer: the flow was maintained using a Watson–Marlow 502S peristaltic pump placed on the inlet tubing. pH Measurements were made using a Pye–Unicam PW9410 pH meter with the electrode inserted into the effluent stream. The three solutions typically contained (*i*) titanium(III) chloride (0.005 mol dm^{-3}), (*ii*) hydrogen peroxide (0.025 mol dm^{-3}), and (*iii*) the alkyne (0.02 mol dm^{-3}); pH was varied by the addition of sulphuric acid (18 mol dm^{-3}) or sodium hydroxide (10 mol dm^{-3}) to the first stream and all solutions were deoxygenated by a nitrogen purge both before and during use. At pH values greater than 2.5, a complexing agent (EDTA, NTA, *etc.*), was added to the titanium(III) stream.

In experiments to determine the variation with pH of CIDEP effects in the spectra from butynedioic acid (for different [H_2O_2]), a continuous titration system was employed. In this system, the vessel containing the substrate (in a solution initially such as to give a final pH of *ca.* 3) was connected to an identical reservoir which contained substrate (at the same concentration) of higher pH (adjusted with sodium hydroxide): when the flow commences, the pH of the substrate solution (and hence that of the final solution) steadily increases and the signal from the derived radical is continually monitored. Details are described elsewhere.[19] All chemicals employed were commercial samples used as supplied.

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