Polarisation Effects in the E.S.R. Spectra of Radicals Formed by the Hydroxyl Radical Attack on the Anions of Acetylenedicarboxylic Acid and Benzene-1,3,5-tricarboxylic Acid[1]

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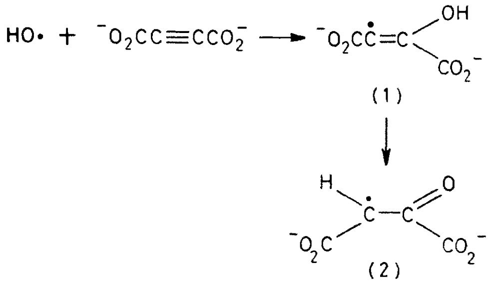
Summary Novel polarisation effects in the radicals $^-O_2C\dot{C}HCOCO_2^-$ and a cyclohexadienyl adduct from benzene-1,3,5-tricarboxylate (the radicals are produced by the reaction of the hydroxyl radical generated from the Ti^{III}–H_2O_2 couple) gave e.s.r. signals which are wholly in emission and are observed above pH *ca.* 8; the significant pair reaction responsible evidently involves electron transfer from Ti^{III} to the radicals concerned.

RECENT work by several groups has established a firm basis for the interpretation of polarisation effects in e.s.r. spectra (chemically-induced dynamic electron polarisation, CIDEP) (refs. 2 and 3 and references therein). Of the major processes which can lead to polarisation, namely the triplet mechanism (TM) and the radical-pair mechanism (RPM), it is the latter which is normally responsible for polarisation in radicals produced in steady-state thermal processes. The basis of the RPM is the formation of radical pair units (F-pairs) from which products are formed by the reaction of singlet units, leaving an excess of triplet units which, on separation, may give polarised radicals (though the total polarisation remains zero). In the absence of hyperfine splittings in the spectra of the two radicals concerned, polarisation only occurs when the g_{average} values differ, but this is not a necessary requirement when the spectra of either or both of the radicals are split by hyperfine interactions. Almost invariably, CIDEP signals comprising hyperfine multiplets have their low-field components in emission and their high-field components in enhanced absorption (E–A); an example of this type of effect, detected in Ti^{III}–H_2O_2 systems, is provided by the spectra of radicals formed by the hydrogen-atom abstraction reactions of •OH with some alkanoate anions in the presence of a large excess of hydrogen peroxide.[4]

We report here two novel examples of polarisation detected using the Ti^{III}–H_2O_2 system, the substrates being acetylenedicarboxylic acid and benzene-1,3,5-tricarboxylic acid (trimesic acid). In the reaction of the former our observations relate to the radical (**2**) [with a(1H) 1·77 mT, g 2·0045] which is thought[5,6] to be formed *via* (**1**) in a base-catalysed rearrangement [equation (1)]. In a series of



(1)

reactions of •OH with acetylenedicarboxylic acid (RH), we employed a 3-way mixing chamber (with mixing time *ca.* 60 ms) and the initial concentrations of Ti^{III} and the disodium salt of ethylenediaminetetra-acetic acid (EDTA) (in one stream), H_2O_2, and RH, were 0·003, 0·003, 0·01, and 0·02 mol dm^{-3}, respectively; the pH was adjusted by the addition of NH_3 to the first stream. As the pH was raised the signal from (**2**) first appeared, in absorption (A-A), at pH *ca.* 4; as the pH was raised above *ca.* 7·5, both lines became detectable in emission (E–E) (see the Figure). This polarisation, which was not observed by Neta and

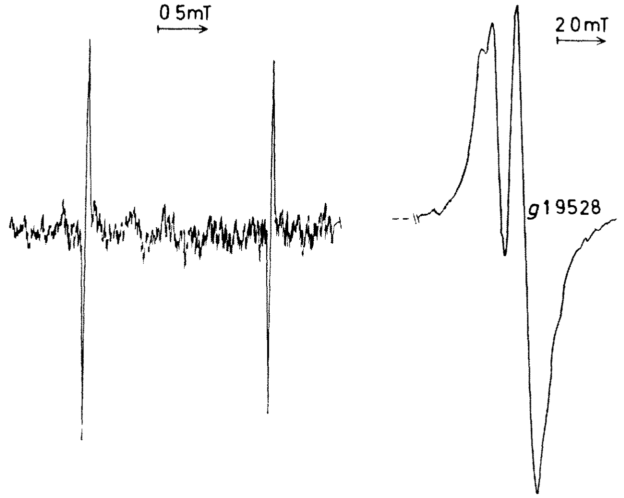
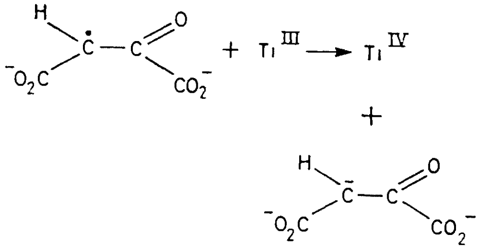


FIGURE E s r spectra of the radical (**2**) (in emission) and Ti$^{\mathrm{III}}$ complexes (in absorption) obtained from the reaction between $^-\mathrm{O_2CC\ CCO_2^-}$ and •OH (generated from Ti$^{\mathrm{III}}$–EDTA and hydrogen peroxide) at pH 8 6

Fessenden in a related study (in which •OH was generated radiolytically[5]) and which is not detected for other radicals characterized[6] in this system, appears to be the first example in which a multiplet exhibits *only* E features for a radical in which the RPM operates

To explain these results we either require the presence of another paramagnetic species whose g-value corresponds to a resonance which falls outside the lines from the radical (**2**) (see, *e g*, ref 2) or we must postulate that polarisation is acquired by radical (**1**) prior to rearrangement [if radical (**1**) could become polarised in emission then both components of the doublet from (**2**) would similarly appear in emission] However, the latter explanation is improbable since no emission signals from (**1**) were detected, and, since [(**2**)] > [(**1**)], we would expect the rearranged radicals to be more susceptible than the precursor to polarisation by the RPM mechanism (this should, in any case, give the normal E-A behaviour, which was not observed) Further, such a mechanism is not applicable to our results for trimesic acid (see below)

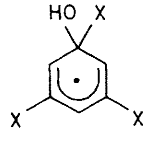
We believe instead that radical (**2**) itself becomes polarised and that the species responsible for this is a Ti$^{\mathrm{III}}$ complex A general mechanism could involve electron transfer from certain Ti$^{\mathrm{III}}$ complexes in solution [equation (2)] (*cf* e s r evidence[7] for the ready reduction of carbonyl-conjugated radicals by Ti$^{\mathrm{III}}$–EDTA complexes) Provided that the electron can only be transferred into the semi-occupied orbital, only the singlet pairs should be destroyed and the separated radicals (**2**) should be polarised



(2)

The effective Ti$^{\mathrm{III}}$ complexes must be good electron donors *and* must be sufficiently asymmetric to prevent rapid electron relaxation The observation that Ti$^{\mathrm{III}}$ e s r signals become detectable and grow in the pH range for which emission effects are also detected (Figure, see also ref 8) adds support to this interpretation, as do the findings that an increase in [Ti$^{\mathrm{III}}$] leads to an earlier onset of emission as the pH is raised and to emission signals of enhanced intensity at a given pH † In contrast, no emission effects were detected when (**2**) was generated from the $\mathrm{Fe^{II}}$–$\mathrm{H_2O_2}$ system for which otherwise comparable results were obtained Although Fe$^{\mathrm{II}}$ would be expected to be as effective a reductant as Ti$^{\mathrm{III}}$ (see ref 7 for a comparison of their rates of reduction of carbonyl-conjugated radicals), no polarisation effects would have been anticipated since Fe$^{\mathrm{II}}$ and Fe$^{\mathrm{III}}$ form complexes with EDTA which have high-spin configurations and a very rapid spin relaxation

Finally, we have also observed that the reaction of •OH (generated as above) with trimesic acid gives the adducts (**3**,X = $\mathrm{CO_2H\ CO_2^-}$) and (**4**,X = $\mathrm{CO_2H,CO_2^-}$) At low pH both adducts are detected in absorption However, as the pH is raised by the addition of carbonate ion the signal from (**4**,X = $\mathrm{CO_2^-}$) appears in emission at pH > 8, whereas that from (**3**,X = $\mathrm{CO_2^-}$) remains in absorption We suggest that the adduct (**4**,X = $\mathrm{CO_2^-}$) is likewise able to accept an electron from a Ti$^{\mathrm{III}}$ complex whose concentration grows in this pH range



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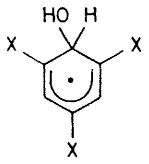

(4)

These results are, as far as we are aware, the first examples in which the electron transfer from a transition-metal complex to an organic radical has been responsible for polarisation

We thank Dr K A McLauchlan for helpful discussions

(*Received*, 30*th June* 1980; *Com* 710)

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† Since the high-field (m_I $+\frac{1}{2}$) component of the doublet from (**2**) is closer to the absorption of the Ti$^{\mathrm{III}}$ complex than is the $-\frac{1}{2}$ component it should be less strongly polarised as is, indeed, observed

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