

Detection of Paramagnetic Intermediates in the Reaction of Aqueous Titanium(III) Complexes with Dioxygen

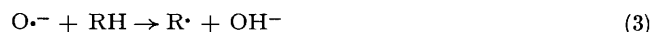
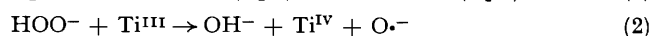
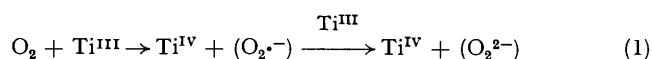
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Summary At pH 7–9, the e.s.r. signal observed during reaction of aqueous titanium(III) tartrate complex with dioxygen is a singlet, $g = 2.0134$, assigned as the superoxide complex.

ACTIVATION of oxygen in haem model systems and in some oxidase enzymes involves electron transfer from a reducing metal ion, ultimately converting oxygen into water.¹ Since the nature of the intermediate complexes of dioxygen, superoxide, and peroxide with the transition metal play a central role in these natural processes, it is important to consider model systems involving other one-electron reductants such as titanium(III). The overall process for such Fenton-like systems can involve attack on organic

substrates (co-ordinating ligands) as shown schematically in equations (1)–(3). We have previously reported the

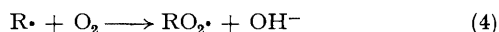


observation of radical ions (*e.g.* R^{\cdot}) when oxygen reacts with titanium(III) tartrate complexes at pH 12 using e.s.r. detection in a rapid flow system.² Recently, using stopped flow spectrophotometry, rapid formation of a discrete peroxo titanium(IV) complex was observed on mixing $[\text{Ti}(\text{edta})(\text{H}_2\text{O})]^-$ with dioxygen at pH 4.57³ (H_4edta = ethylenediaminetetra-acetic acid).

We now report that 1×10^{-3} M titanium(III) chloride complexed with an excess of tartaric acid (0.1 M) at pH 7.0 reacts with oxygenated water (*ca* 1.0×10^{-3} M) in a rapid-flow e.s.r. system² to exhibit a relatively narrow singlet $\Delta H_{pp} = 0.16$ mT, 20–50 ms after mixing. A *g*-value of 2.0134 ± 0.0002 is determined relative to the tartrate ketyl trianion $^{-}O_2C\dot{C}(O^{-})CHOHCO_2^{-}$, *g* = 2.0042 with $a_{\text{CHOH}}(1) = 0.266$ mT. The latter species can be generated under virtually identical spectrometer conditions by allowing the titanium(III) solution to react with basic 0.0125 M hydrogen peroxide solution instead of oxygenated water in a consecutive experiment. The same mixing cell-cavity configuration is maintained throughout the sequence.

When the initial titanium(III) tartrate solution is adjusted to pH 9.0–9.5, a less intense second singlet appears at *g* = 2.0145. Its intensity is sharply increased when metal ion solutions are deliberately partially hydrolysed, indicating probable dimeric complexes containing superoxide ligands. The first singlet is still 3 times more intense at pH 9.0.

In order to assign the signal at *g* = 2.0134 to a titanium(III) dioxygen complex, it is necessary to eliminate possible peroxy radicals ROO• that would arise through capture of the ketyl in a full 'Fenton' sequence, equation (4)



During our initial work² we measured peroxide yields for the reaction of 2×10^{-3} M titanium(III) tartrate with 1×10^{-3} M

oxygenated water over the pH range 8–12, obtaining a conversion of oxygen into peroxide of 75% at pH 9.0. In these experiments we acidified after mixing and assayed the peroxy titanium(IV) complex at pH 0.8 (λ_{max} 405 nm, ϵ 830). In agreement with Kristine and Shepherd³ we observed promptly the yellow peroxy titanium(IV) tartrate complex (λ_{max} 348 nm) at pH 8–10.5. Clearly, in the light of these studies on two electron reduction it is kinetically unlikely that the *g* = 2.0134 signal is due to an alkyl-peroxy species. Such peroxy radicals, in any event, normally give broad signals at g_{iso} values of 2.0150–2.0165.⁴

In further experiments we have allowed titanium(III) to form a complex with sodium gluconate at pH 7.0–9.0, observing an analogous singlet at *g* = 2.0128 on reaction with 1 equiv. of oxygen. Now the *g* value is relative to the gluconate 2-ketyl radical $(HOCH_2)(CHOH)_3\dot{C}(O^{-})CO_2^{-}$, *g* = 2.0042, $a_{\text{CHOH}}(1) = 0.66$ mT.⁵ Attempts to generate the Ti(edta)O₂⁻ species by flowing aqueous dioxygen against 1 mM Ti(edta)H₂O⁻ gave no signal over the pH range 4–9. Comparison of the observed *g* values (2.0134, 2.0128) with approximate g_{av} values derived from data on anisotropic superoxide complexes in the solid state⁶ lends support to the assignment of the signals to titanium(III) dioxygen complexes.

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