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, $g = 2{\cdot}0134$, 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

$$O_2 + Ti^{III} \rightarrow Ti^{IV} + (O_2{\cdot}^-) \xrightarrow{Ti^{III}} Ti^{IV} + (O_2{}^{2-}) \quad (1)$$

$$HOO^- + Ti^{III} \rightarrow OH^- + Ti^{IV} + O{\cdot}^- \quad (2)$$

$$O{\cdot}^- + RH \rightarrow R{\cdot} + OH^- \quad (3)$$

observation of radical ions (*e.g.* R·) 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 $[Ti(edta)(H_2O)]^-$ with dioxygen at pH 4·57[3] (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.* $1·0 \times 10^{-3}$ M) in a rapid-flow e.s.r. system[2] 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_{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 peroxyl radicals ROO· that would arise through capture of the ketyl in a full 'Fenton' sequence, equation (4).

$$R\cdot + O_2 \longrightarrow RO_2\cdot + OH^- \qquad (4)$$

During our initial work[2] 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 peroxo titanium(IV) complex at pH 0·8 (λ_{max} 405 nm, ϵ 830). In agreement with Kristine and Shepherd[3] we observed promptly the yellow peroxo 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 alkylperoxyl species. Such peroxyl 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 $(HOCH_2)(CHOH)_3\dot{C}(O^-)CO_2^-$, $g = 2·0042$, $a_{CHOH}(1)$ 0·66 mT.[5] Attempts to generate the $Ti(edta)O_2^-$ species by flowing aqueous dioxygen against 1 mM $Ti(edta)H_2O^-$ 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 state[6] lends support to the assignment of the signals to titanium(III) dioxygen complexes.

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