Electron Spin Resonance Detection of Free Radicals in the Reaction of Titanium(III) Tartrate Complexes with Oxygen in Aqueous Alkaline Solution

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Summary Radical anions of tartaric and glycolic acids are observed by e.s.r. spectroscopy when oxygen-saturated water reacts with aqueous tartrate complexes of titanium(III) at pH 12. While detailed investigations of titanium(III) reduction have been reported recently,1 activation of molecular oxygen by Ti" has not been extensively studied as a model for the generation of peroxide intermediates in
biological systems, or in the chemistry of dioxygen metal complexes. Using a rapid-flow system, we have observed steady-state e.s.r. signals 50 ms after mixing oxygenated water with an alkaline solution of titanium(III) chloride that had been complexed with excess of potassium tartrate. Two sets of doublets in intensity ratio 2:1 dominated the spectrum. The more intense was the tartrate radical anion (1) \( \text{[ Tartrate] }^+ \) g 0.0042 resulting from hydrogen abstraction and ionization (equation 1). The second doublet was the glycate dianion (2) \( \text{[ Glycate] }^{--} \) g 0.0044. When excess of sodium glycate was added

\[
\text{[Tartrate] }^+ \rightarrow \text{[Glycate]}^{--} + \text{[Tartrate]}^{--}
\]

(equation 1)

The spectrum of the former, accounted for >80% of the signal intensity. Fragmentation of (1), 'q-cleavages,' represents one possible route to glycate-derived radicals (equation 2):

\[
\text{[Tartrate]}^{--} \rightarrow \text{[Glycate]}^{--} + \text{[Tartrate]}^{--}
\]

(equation 2)

At pH 11–13 using 0.13 M tartrate, e.s.r. spectra were observed in the concentration range 0.002–0.005 M Ti(III). The colourless effluent obtained by mixing a 0.005 M Ti(III) solution with oxygen-saturated water at 22°C was ascorbised and tested for hydrogen peroxide as the orange persytanium(IV) complex \( \text{[Persyt]}^{+} \) g 0.30 at pH 0.8, 0.13 M tartrate. A yield of 69% based on 2:1 \( \text{[Ti(III)]} : \text{[Tartrate]}^{--} \)

† Note however that oxidation of potassium tartrate by the titanium(III)-ethylenebis(ethylenediamine)oxacetic acid complex and \( \text{H}_2\text{O}_2 \) in a three-stream experiment gave (1) as 85% of the tartrate-derived signal at pH 10.5–12.5 (efficient).


\[ \text{Ti}^{III} + \text{O}_2 \rightarrow \text{Ti}^{IV} + (\text{O}^-) \rightarrow \text{Ti}^{IV} + (\text{O}^{2-}) \]

(equation 3)

\[ \text{HOO}^- + \text{Ti}^{III} \rightarrow \text{HO}^+ + \text{Ti}^{IV} + \text{O}_2 \]

(equation 4)

Addition of organic substrate to either the titanium or oxygen streams changed the e.s.r. spectrum. When a persistent negatively charged radical could be formed its spectrum appeared together with signals from (1) and (2). Lactic and malic acids gave \( \text{MeC(O)CH(O)CO}_2^- \) and \( \text{CH}_2\text{C(O)CH(O)CO}_2^- \) [lit. \( \text{MeC(O)CH(O)CO}_2^- \) g 2.0042]. Nitrilotriacetic acid gave the abstraction radical \( \text{[TiC(CN)\text{CH}_2\text{CO}_2]}^{--} \) having the literature parameters. Other efficient hydrogen donors such as triethanolamine, ethylenediamine, and propan-2-ol gave weak background resonances together with a reduced-intensity tartrate spectrum. Radical ion (2) gave the dominant signal, and two further doublets had appeared: \( \text{[Glycate]}^{--} \) g 0.01 and \( \text{[Tartrate]}^{--} \) g 2.0041. Both the shift to higher field and the asymmetric character of the latter doublet suggest a metal ion complex of radical (1). The authors acknowledge support by the National Research Council of Canada and the University of Victoria.

(Received, 26th July 1977; Com. 769.)