

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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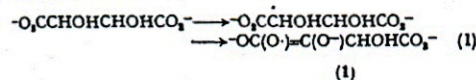
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Summary Radical anions of tartaric and glycolic acids are observed by e.s.r. spectroscopy when oxygen-saturated water reacts with aqueous tartrate complexes of titanium(III) at pH 12.

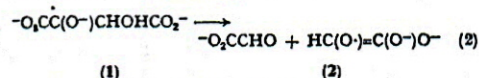
WHILE detailed investigations of titanium(III) reduction have been reported recently,¹ activation of molecular oxygen by Ti^{3+} has not been extensively studied as a model for the generation of peroxide intermediates in

biological systems,³ or in the chemistry of dioxygen metal complexes.³

Using a rapid-flow system,⁴ 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) [$a_{\text{CH}}(1)$ 0.266 mT, g 2.0042] resulting from hydrogen abstraction and ionization (equation 1). The second doublet was the glycolate dianion (2) [$a_{\text{H}}(1)$ 1.43 mT, g 2.0044].^{5,6} When excess of sodium glycolate was added

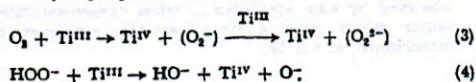


to the titanium(III) (tartrate) solution, (2) accounted for >90% of the signal intensity. Fragmentation of (1), 'α-cleavage,' represents one possible route to glycolate-derived radicals (equation 2).[†]



At pH 11–13 using 0.13 M tartrate, e.s.r. spectra were observed in the concentration range 0.02–0.002 M Ti^{III} . The colourless effluent obtained by mixing a 0.002 M Ti^{III} solution with oxygen-saturated water at 22 °C was acidified and tested for hydrogen peroxide as the orange peroxy-titanium(IV) complex (λ_{max} 405, ϵ 830 at pH 0.8, 0.13 M tartrate). A yield of 68% based on 2:1 [Ti^{III}]: $[\text{O}_2]$

stoichiometry suggests involvement of intermediate peroxide in the radical ion generation. In agreement, at pH 12 nearly identical e.s.r. spectra were obtained on mixing 5 mM titanium(III) (tartrate) with either oxygenated water or a low concentration of hydrogen peroxide (5 mM). Three consecutive electron transfers to oxygen can provide an oxidizing agent very similar in reactivity to the metal ion-hydrogen peroxide system (equations 3 and 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 $\text{MeC}(\text{O}^-)=\text{C}(\text{O}^-)\text{O}^-$,^{6,7} and $^-\text{O}_2\text{CCH}_2\text{C}(\text{O}^-)=\text{O}^-$ [$a(\text{CH}_2)$ 0.829 mT, g 2.0042]. Nitrotri-acetic acid gave the abstraction radical $^-\text{O}_2\text{C}\dot{\text{C}}\text{HN}(\text{CH}_2\text{CO}_2^-)_2$ having the literature parameters.⁷ 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; [$a_{\text{H}}(1)$ 0.49 mT, g 2.0041 and $a_{\text{H}}(1)$ 0.21 mT, g 2.0039]. Both the shift to higher field and the asymmetric character of the latter doublet suggest a metal ion complex of radical (1).⁸

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[†] Note however that oxidation of potassium tartrate by the titanium(III)-ethylenediaminetetra-acetic acid complex and H_2O_2 in a three-stream experiment gave (1) as 95% of the tartrate-derived signal at pH 10.5–12.5 (effluent).

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