Formation of $Ti(O_2)(edta)^{2-}$ by the Addition of Molecular Oxygen to $Ti(edta)(H_2O)^-$; $edta^{4-}$ = ethylenediaminetetra-acetate

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Summary The peroxo Ti^{IV} complex, $Ti(O_2)(edta)^{2-}$, is formed by the substitution of O_2 on the labile Ti^{III} complex, $Ti(edta)(H_2O)^-$, followed by two sequential one-electron reductions forming the co-ordinated peroxo ligand, the analogous reaction with H_2O_2 in stoicheiometric amounts produces only $TiO(edta)^{2-}$, $edta^{4-}$ = ethylenediaminetetra-acetate

THE formation of dioxygen, superoxo, and peroxo adducts of transition metal complexes has received widespread attention owing to the relevance of this chemistry to oxygen transport and catalytic activation as in the haem O_2 carriers, oxygenases, and hydroxylases[1] The reactions of Ti^{III} complexes with H_2O_2 and O_2 have been studied for several years[2] The formation of the well-characterized peroxo Ti^{IV} complex, $Ti(O_2)(edta)^{2-}$, is a sensitive indicator for the analytical determination of either Ti^{IV} or H_2O_2[3] Although other peroxo Ti^{IV} complexes are easily prepared from the corresponding Ti^{IV} series and H_2O_2, no simple peroxo mononuclear adduct has been prepared by the direct addition of O_2 to a Ti^{III} complex with the exception of the very recent report of the addition of O_2 to Ti(F)(TPP) [TPP^{2-} = tetraphenylporphyrin dianion] in dichloromethane or benzene[4] Marchon, *et al* found the $Ti(O_2)$-(TPP)/$Ti(F)_2$(TPP) system to be reversible by evacuation of O_2, the existence of the superoxo intermediate, Ti(F)-(O_2)(TPP) during formation of the peroxo product was suggested[4] We report here the first observation of the addition of O_2 to a classical Ti^{III} complex, $Ti(edta)(H_2O)^-$ resulting in a co-ordinated peroxo ligand We have observed the similar 50:50 product mixture of the peroxo complex, $Ti(O_2)(edta)^{2-}$, and the titanyl complex TiO-$(edta)^{2-}$ as detected by the appearance of the charge transfer maximum for $Ti(O_2)(edta)^{2-}$ at 364 nm (ϵ = 1 24 × 10^3 l mol^{-1} cm^{-1}) in aqueous solution (equations 1 and 2) The yield of $Ti(O_2)(edta)^{2-}$ was *ca* 44% and depended upon

$$k = 1{\cdot}2 \times 10^4\ \mathrm{l\ mol^{-1}\ s^{-1}}$$

$$Ti(edta)(H_2O)^- + O_2 \rightleftharpoons Ti(O_2)(edta)^- + H_2O \qquad (1)$$

$$Ti(edta)(H_2O)^- + Ti(O_2)(edta)^- + 2H_2O \xrightarrow{\text{fast}} 2H_3O^+ + TiO(edta)^{2-} + Ti(O_2)(edta)^{2-} \qquad (2)$$

the conditions of mixing In these experiments [Ti(edta)-$(H_2O)^-$] was varied over the range (2·19—9 75) × 10^{-4} M [O_2] was varied by combining appropriate ratios of O_2-saturated and N_2-purged buffer solutions prior to mixing with N_2-purged $Ti(edta)(H_2O)^-$ solutions The decrease from the theoretical yield of 50% $Ti(O_2)$ $(edta)^{2-}$ was shown to be due to the slower, competitive reduction of co-ordinated peroxo ligand by unreacted $Ti(edta)(H_2O)^-$ (equation 3) This feature was confirmed by a stopped-flow experiment at 400 nm in which $Ti(edta)(H_2O)^-$ in an excess rapidly bleached the colour of the $Ti(O_2)(edta)^{2-}$ prepared by addition of a stoicheiometric quantity of H_2O_2 to $TiO(edta)^{2-}$ (equation 4) The addition of H_2O_2 to $TiO(edta)^{2-}$ was followed independently at pH = 4 57 by stopped-flow methods (k = 53 l mol^{-1} s^{-1}) † A second-order rate for the limiting reaction step of equation (3) was

$$2Ti(edta)(H_2O)^- + Ti(O_2)(edta)^{2-} + H_2O \xrightarrow{k\,=\,79\ 5\ \mathrm{l\ mol^{\ 1}\ s^{\ 1}}} 3TiO(edta)^{2-} + 2H_3O^+ \qquad (3)$$

$$TiO(edta)^{2-} + H_2O_2 \xrightarrow{k\,=\,53\ 3\ \mathrm{l\ mol^{-1}\ s^{-1}}} Ti(O_2)(edta)^{2-} + H_2O \qquad (4)$$

found to be 79·5 l mol^{-1} s^{-1} compared to the second-order rate of formation of the peroxo complex (equation 1) of 1 2 × 10^4 l mol^{-1} s^{-1} (μ = 0 50 NaCl–$NaC_2H_3O_2$, T = 25 0 °C pH = 4 57) ‡ The water exchange value for $Ti(edta)(H_2O)^-$ has been estimated by Sykes to be *ca* 10^7 s^{-1}[5] Hence the oxidation of $Ti(edta)(H_2O)^-$ by O_2 appears to be substitution limited It is also of interest that the detectable product of the autoxidation of $Ti(H_2O)_6^{3+}$ is only TiO^{2+} while the autoxidation product of Ti(Hedta)(H_2O) is observed to be a binuclear $Ti^{III,IV}$ mixed oxidation state complex (pH > 4 0) The Ti(Hedta)(H_2O) system also forms the peroxo product $Ti(O_2)(Hedta)^-$ in 50% yield together with $TiO(Hedta)^-$ (pH = 2 5) These systems are the subject of separate reports[6]

It is striking that the reaction of $Ti(edta)(H_2O)^-$ with H_2O_2 does not form $Ti(O_2)(edta)^{2-}$ unless excess H_2O_2 beyond the 2 Ti^{III}. 1 H_2O_2 stoicheiometry is present This is consistent with a sequential one-electron reduction involving hydroxyl radical (equations 5, 6, 7) These

$$Ti(edta)(H_2O)^- + H_2O_2 \rightleftharpoons Ti(edta)(H_2O_2)^- + H_2O \qquad (5)$$

$$Ti(edta)(H_2O_2)^- + H_2O \longrightarrow TiO(edta)^{2-} + H_3O^+ + OH{\bullet} \qquad (6)$$

$$HO{\bullet} + Ti(edta)(H_2O)^- \longrightarrow TiO(edta)^{2-} + H_3O^+ \qquad (7)$$

steps are similar to the well-known method for generation of HO• during the continuous flow of $Ti(H_2O)_6{}^{3+}$ and H_2O_2 These reagents are often used in e s r experiments to promote H-atom abstraction from RH species to generate R• for observation $Ti(O_2)(edta)^{2-}$ is formed from excess of H_2O_2 and $TiO(edta)^{2-}$ as in equation (4) The fact that stoicheiometric oxidation of $Ti(edta)(H_2O)^-$ by H_2O_2 does

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† The substitution reaction shown in equation 4 is pH dependent, detailed studies are in progress The value reported for the second-order rate constant is in a virtually acid-independent range

‡ The second-order law holds for either O_2 or $Ti(edta)(H_2O)^-$ in excess with equivalent second-order rate constants measured in both cases, [O_2] was varied from (1—6) × 10^{-4} M and [Ti^{III}] from 1 17 × 10^{-4} to 5 10 × 10^{-3} M

not form a Ti^{IV}–peroxo complex while oxidation by O_2 yields *ca.* 50% of the $Ti(O_2)(edta)^{2-}$ complex may be understood in terms of the one-electron reduction products of H_2O_2 and O_2. These species are the $HO^-/HO\cdot$ pair and O_2^-. Formation of $HO\cdot$ generates a mobile species available to diffuse through solution until reduced by $Ti(edta)(H_2O)^-$. Formation of co-ordinated O_2^- in $Ti(O_2)(edta)^-$ results in a bound superoxo species which is rapidly reduced to the peroxo complex by an additional mole of $Ti(edta)(H_2O)^-$. The observations are nearly identical with those of Marchon's group on the Ti^{III} porphyrin system[4] except that the O_2 addition to $Ti(edta)(H_2O)^-$ forming $Ti(O_2)(edta)^{2-}$ in aqueous solution is not reversible on flushing with N_2. The nonreversibility of the $Ti(O_2)(edta)^{2-}$ complex is likely to be due to the difference in proton availability of the solvent and the high dielectric constant favouring ionic charge in water as compared to CH_2Cl_2 or C_6H_6 for the porphyrin case, the higher charge of the $edta^{4-}$ ligand *vs.* TPP^{2-} favouring Ti^{IV}, and the greater freedom of ligand reorganization to accommodate Ti^{IV} in the $edta^{4-}$ complex, as opposed to the more rigid TPP^{2-} which satisfies the co-ordination requirements of both Ti^{III} and Ti^{IV} more equally. The superoxo intermediate also has potential for homogeneous catalytic applications for incorporation of oxygen into other substrates.

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