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Formation of Ti(O₂)(edta)²⁻ by Two Routes: Peroxo Displacement of Oxo in TiO(edta)²⁻ and Reduction of a Superoxo Transient, Ti(O₂)(edta)⁻

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The structural nature of TiO(edta)²⁻ in solution and the reaction of TiO(edta)²⁻ with H_2O_2 forming Ti(O₂)(edta)²⁻ have been investigated over the pH range of 2.0–5.2. The TiO(edta)²⁻ complex exists as an equilibrium mixture of at least six isomeric and protolytic forms which vary in whether a water molecule is attached or whether the edta ligand occupies five coordination positions at Ti(IV). Pendant carboxylate groups of the edta ligand may be ionic or protonated to varying degrees throughout the pH range of 2.0–5.2. Two distinctly different primary coordination spheres in terms of spectral properties and reactivities toward H_2O_2 are observed for TiO(edta)²⁻ solutions in this pH range. These are the aquated forms (A), $TiO(edtaH_n)(H_2O)^{n-2}$, having two coordinated carboxylates and two ethylenediamine nitrogens of the edta ligand and one coordinated water molecule, and the fully chelated (B) forms, $TiO(edtaH_n)^{n-2}$, with three carboxylates and two ethylenediamine nitrogens of edta attached to Ti(IV). The distribution of A and B forms obeys a conditional equilibrium involving 1.18 ± 0.02 hydrogen ions with a conditional acid dissociation constant, K, equal to $(3.73 \pm 0.07) \times 10^{-4}$ M⁻¹ (25.0 °C, μ = 0.50 NaCl). The displacement of the oxo ligand by peroxo is first order in [H_2O_2] and [TiO(edta)²⁻]; the observed rate constants have been resolved with the A forms having an $[H_3O^+]^{1.0}$ dependence with $k_A = (5.25 \pm 0.25) \times 10^6$ M⁻² s⁻¹ and the B forms having only an acid independent path, k_B = 49 ± 5 M⁻¹ s⁻¹ at 25.0 °C. Activation parameters are found to be the following: A path, $\Delta H^{\ddagger}$ = 4.8 ± 0.9 kcal/mol, $\Delta S^{\ddagger}$ = −22 ± 3 eu; B path, $\Delta H^{\ddagger}$ = 5.7 ± 0.5 kcal/mol, $\Delta S^{\ddagger}$ = −31 ± 2 eu. The mechanism is interpreted to be the associative displacement of oxo by peroxo in which the available pendant functional groups assist the reorganization of the Ti(IV) coordination sphere. Comparisons are made to the analogous studies of Tanaka et al. on the associative displacement of oxo by peroxo in the dioxo V(V) complexes of the edta family of ligands. The preassociation constant of H_2O_2 with TiO(edta)²⁻ is ≤1 M⁻¹ (at least 25-fold smaller than the V(V) analogue). TiO(edta)²⁻ converts to the peroxo complex ~1.2 × 10⁴ times faster than the V(V) case, attributed to lesser reorganization with a single oxo group on Ti(IV). The formation of Ti(O₂)(edta)²⁻ by the reaction of O_2 with Ti(edta)(H₂O)⁻ has been examined. Substitution and intramolecular electron transfer occur by an H_3O^+-independent path with k_{O_2} = (1.02 ± 0.04) × 10⁴ M⁻¹ s⁻¹, $\Delta H^{\ddagger}$ = 8.1 ± 0.7 kcal/mol, $\Delta S^{\ddagger}$ = −13.2 ± 2.4 eu at 25.0 °C, and μ = 0.50. The superoxo transient, Ti(O₂)(edta)⁻, is rapidly scavenged by Ti(edta)(H₂O)⁻ with a second-order constant of ≥10⁶ M⁻¹ s⁻¹. This process is presumably outer-sphere. The resultant peroxo complex, Ti(O₂)(edta)²⁻, may be reduced by Ti(edta)(H₂O)⁻ in an H_3O^+-independent manner (k = 75 ± 5 M⁻¹ s⁻¹ at 25.0 °C, $\Delta H^{\ddagger}$ = 7.2 ± 0.5 kcal/mol, $\Delta S^{\ddagger}$ = −26 ± 2 eu). Elimination of HO· from Ti(O₂)(edta)³⁻ is rapid in contrast to the longer-lived $(NH_3)(en)_2Co(\mu-O_2H)Cr(H_2O)_5^{4+}$ species. Comparisons are made for the reduction of O_2^- and O_2^{2-} coordinated by Co(III) and Ti(IV) by one-electron reductants and the affinities of the O_2^{3-} or O_2H^{2-} radical toward these centers.

Introduction

Dioxygen, superoxo, and peroxo complexes of transition-metal centers have received widespread attention owing to the relevance of this chemistry of oxygen transport and catalytic activation as in the biological O_2 carriers oxygenases, peroxidases, and hydroxylases.[1] The peroxo complex of Ti(IV), Ti(O₂)(edta)²⁻,[2a] has been used as an analytical method for either Ti(IV) or H_2O_2.[2b,c] We recently communicated some early results in which Ti(O₂)(edta)²⁻ was shown to be generated by the coordination of O_2 with the Ti(III) complex Ti(edta)(H₂O)⁻.[3] This present report gives additional details on the redox processes which occur to form Ti(O₂)(edta)²⁻ through a superoxo intermediate, Ti(O₂)(edta)⁻. The results implicate a rate-limiting intramolecular electron-transfer step that converts the Tiᴵᴵᴵ–O_2 complex into the Tiᴵⱽ–O_2^- complex.[8] The superoxo complex is then rapidly reduced to the peroxo species.

The peroxo complex may also be generated by the substitution reaction of H_2O_2 with various species present in a solution of *TiO(edta)²⁻* over the pH range of 2.0–5.2. Recently Tanaka et al. have described the associative addition of H_2O_2 to the Vⱽ–edta family of complexes including the edta⁴⁻, edda²⁻, and dmedda²⁻ cases,[4] the nta³⁻ complex,[5] and mida²⁻ complex.[6] The associative nature of the formation of the vanadyl peroxo species VO(O₂)L from the dioxo complex VO₂L, is implicated by rather large, negative entropies of activation and by the hydrogen ion dependencies for these systems.[4] Both V(V) and Ti(IV) are d⁰ electronic configurations. However the Ti(IV) complexes contain only one oxo ligand while the V(V) species exist as both α-cis and β-cis isomers.[7] The VO₂(edta)²⁻ complex is known to have the α-cis structure with both oxo ligands trans to the nitrogen of the ethylenediamine backbone of the edta⁴⁻ ligand.[8] VO(O₂)(edta)²⁻ appears to have a seven-coordinate structure with an axial vanadyl oxygen and the peroxo ligand in the five-coordinate plane, trans to a nitrogen donor.[4] It is of interest to determine what effect a single oxo ligand instead of two oxo groups at the d⁰ coordination center would impart to the mechanistic aspects of the oxo to peroxo substitution process. The absence of a spectral chromophore for d–d transitions has prevented substantive knowledge of what species are present in solutions of *TiO(edta)²⁻* in the pH range of 2.0–5.2.[9]

(1) (a) F. Basolo, B. M. Hoffman, and J. A. Ibers, *Acc. Chem. Res.*, **8**, 384 (1975). (b) J. P. Collman, *ibid.*, **10**, 265 (1976). (c) E. I., Ochiai, "Bioinorganic Chemistry", Allyn and Bacon, Boston, 1977.
(2) (a) Throughout this manuscript there exists the need to describe the composite nature of chemical reactivities of species which may exist in protolytic and structural equilibria with varying pH. We have introduced the notation of italizing the formula of the simplest species to indicate the sum total of all species which may be present. For example *Ti(O₂)(edta)²⁻* refers to Ti(O₂)(edta)²⁻, Ti(O₂)(edtaH)⁻, and any other protonated species or aquated forms which may be present under the conditions mentioned in the discussion; unitalicized species refers to an exact chemical entity as given by the formula shown. Ligand abbreviations: edta⁴⁻ = ethylenediaminetetraacetate, nta³⁻ = nitrilotriacetate, edda²⁻ = ethylenediamine-*N,N'*-diacetate, dmedda²⁻ = *N,N'*-dimethylethylenediamine-*N,N'*-diacetate. (b) J. Muhlebach, K. Muller, and G. Schwartzenbach, *Inorg. Chem.*, **9**, 2381 (1970). (c) G. Schwatzenbach and H. Flaschka, "Complexometric Titrations", Methuen, London, 1969, p 200.
(3) F. J. Kristine and R. E. Shepherd, *J. Chem. Soc., Chem. Commun.*, 1000 (1980).
(4) S. Funahashi, T. Midorikawa, and M. Tanaka, *Inorg. Chem.*, **19**, 91 (1980).
(5) S. Funahashi, D. Haraguchi, and M. Tanaka, *Inorg. Chem.*, **16**, 1349 (1977).
(6) S. Funahashi, Y. Ito, and M. Tanaka, *J. Coord. Chem.*, **3**, 125 (1973).
(7) L. W. Amos and D. T. Sawyer, *Inorg. Chem.*, **11**, 2692 (1972).
(8) (a) W. R. Scheidt, C. Tsai, and J. L. Hoard, *J. Am. Chem. Soc.*, **93**, 3807 (1971). (b) W. R. Scheidt, R. Countryman, and J. L. Hoard, *ibid.*, **93**, 3878 (1971).

Titration studies and the kinetic behavior on addition of H_2O_2 to $TiO(edta)^{2-}$ have allowed the identification of several species which exist at equilibrium in these solutions. The oxo displacement reaction by H_2O_2 for $TiO(edta)^{2-}$ is again observed to be associative in nature with intrinsically H_3O^+-independent and -dependent pathways, similar to those proposed for the $VO_2(edta)^{3-}/H_2O_2$ system. However the unassisted pathway for $TiO(edta)^{2-}$ is at least 490 times more efficient than that for $VO_2(edta)^{3-}$. Also coordinationally labile species such as $TiO(edtaH)(H_2O)^-$ are found to play a major kinetic role. This feature is in contrast to the V(V) system where aquated forms are thought to be unimportant relative to the direct associative displacement of the oxo group by H_2O_2.

The species present in a solution of $TiO(edta)^{2-}$ and the reaction pathways of these species are in marked contrast to Ti^{IV}/nta system. Wieghardt et al. have recently isolated the tetrameric complex $Cs_4([TiO(nta)]_4) \cdot 6H_2O.^{29}$ The cyclic Ti^{IV}–nta tetramer is the reactive entity with H_2O_2 in the pH range of 3.5–2.0 while aquated species such as $Ti(nta)(H_2O)_2^+$ appear to be reactive in the pH range of 0–1.5. By contrast $TiO(edta)^{2-}$ appears to be reactive via solution monomers throughout the accessible pH range of 2.0–5.2. At pH 2.0 the reactivity of $TiO(edta)^{2-}$ is 10^2 more rapid than Ti^{IV}/nta system (proposed to be dimeric by Weighardt et al. at pH 2.0)[29] and 5×10^2 faster at pH 1.5 where both $TiO(edta)^{2-}$ and $Ti(nta)(H_2O)_2^+$ are proposed to be monomeric. These differences further emphasize the changes in mechanisms that may be imparted to transition-metal centers by controlling the number of labile ligand sites and nature of solution isomers available for chemical reactivity.

The redox reactivities of transition-metal complexes containing coordinated superoxo and peroxo ligands are important as models for oxygenases and hydroxylases. The behavior of $Ti(O_2)(edta)^-$ and $Ti(O_2)(edta)^{2-}$ toward reduction by $Ti(edta)(H_2O)^-$ is discussed. Hydroxyl radical is found to be involved in the reduction of the coordinated peroxo ligand just as hydroxyl radical is believed to be involved in the reaction of free H_2O_2 with $Ti(edta)(H_2O)^-.^3$

Experimental Section

Preparation of Ti(III) and Ti(IV) Solutions. Stock solutions of Ti^{3+} (aq) (~ 0.5 M) were prepared by dissolving a weighed sample of $TiCl_3$ (Alfa) in 0.60 M HCl. Insoluble materials were removed by filtration, and the total titanium was converted to Ti(III) by the reduction of residual Ti(IV) over Zn/Hg under an inert atmosphere for at least 3 h. Analysis of $Ti(H_2O)_6^{3+}$ was made spectrally at 502 nm (ϵ 3.97 M^{-1} cm^{-1}).[10] These solutions were stored under N_2 until a noticeable absorbance change was noted at $\lambda = 300$ nm (ϵ for Ti(IV) 24.9 M^{-1} cm^{-1}; a ϵ for Ti(III) ~ 1 M^{-1} cm^{-1}).[10]

Stock solutions of TiO^{2+}(aq) were prepared by dropwise addition of H_2O_2 to a portion of the stock Ti(III) solution (prior to Zn/Hg reduction) until the purple color of the $Ti(H_2O)_6^{3+}$ was barely noticeable by eye. The remaining Ti(III) was then oxidized by bubbling the solution with O_2. Ti(IV) content was determined spectrally by conversion to the peroxide complex according to the procedure of Sykes (ϵ_{408} 717 ± 2 M^{-1} cm^{-1}, $[H_2O_2] = 0.15$ M, $[H_2SO_4] = 1.8$ M).[10] The Ti(IV) solutions were refrigerated to slow any hydrolysis and were kept for weeks without any change in titre or appearance of TiO_2.

The edta complexes were prepared by mixing measured aliquots of the stock metal ion solutions and 0.100 M Na_2H_2edta. The stoichiometry of edta:Ti(III) of 2:1 was maintained to assure chelation of both Ti(III) and Zn^{2+}(aq). The Ti(III) solutions were used immediately in order to prevent loss of Ti(III) titre due to air or solvent oxidation. An additional 10% of free Na_2H_2edta was maintained in the solutions in order to suppress dissociation of Ti(IV) particularly in the acid region (pH ~ 2).

Air-sensitive solutions were handled by standard procedures with the use of gas-tight, preflushed syringes and platinum needles. These

solutions were saturated with N_2 or Ar gas which had been scrubbed through Cr(II) solutions prior to Ti(III) addition.

H_2O_2 and O_2 Solutions. The H_2O_2 titre of a stock solution (~ 1 M) was determined by titration with primary standard $Ce(NH_4)_2$-$(SO_4)_3$ in 0.5 M H_2SO_4. O_2 solutions of varying concentration were prepared by mixing aliquots of oxygen saturated solutions with Ar or N_2 saturated solutions. With the use of appropriate dilution factors and tabulated values of $[O_2]$ in oxygen saturated solutions,[11] the $[O_2]$ was calculated for any particular experiment.

UV–Visible Spectra. Spectra were obtained on a Varian-Cary 118C spectrophotometer with a thermostated sample compartment. The cells were purged with N_2 or Ar gas before solution for the air-sensitive systems and sealed by rubber septa.

pH-Dependent Equilibria of $TiO(edta)^{2-}$ Species. A spectrophotometric titration of an aqueous solution of $TiO(edtaH_2) \cdot H_2O$ at $\mu = 0.5$ (NaCl) was monitored at $\lambda = 252$ nm. Based on the equilibrium in eq 2, the expression in eq 3 was derived to treat the data in a linear fashion by least-squares analysis using appropriate programs with a DEC-1103 computer. A_0 is the limiting absorbance at low pH when only species A are present and A_f is the limiting absorbance at high pH when only species B are present. The titrant, HCl, was added with a Gilmont microburet.

Stoichiometry of the Reacton of $Ti(edta)(H_2O)^- + O_2$. Solutions of known concentrations of Ti(III) and O_2 were mixed by syringe techniques in an inert atmosphere. The absorbance of this final mixture was determined at $\lambda = 363$ nm to determine the initial amount of $TiO_2(edta)^{2-}$ produced (ϵ (1.24 ± 0.07) $\times$ 10^3 M^{-1} cm^{-1}). H_2O_2 was then added to the solution to determine the total titanium content by total conversion to the Ti^{IV}–peroxo complex.

Kinetic Measurements. Data were collected on a Durrum (Dionex) D-110 stopped-flow spectrophotometer. All reactions discussed were followed at λ 363 nm where the $TiO_2(edta)^{2-}$ complex absorbs (ϵ (1.24 ± 0.07) $\times$ 10^3 M^{-1} cm^{-1}). Data analysis was carried out in an on-line fashion with a DEC-1103 interfaced computer using appropriate first-order kinetic programs on floppy magnetic disks. Temperature control was determined as ±0.1 °C.

For the formation reaction of $TiO_2(edta)^{2-}$ from $TiO(edta)^{2-}$ and H_2O_2, the pH range of 2–5.2 was covered by using these buffers: acetate (0.1 M)/HCl (pH 5.2–3.75); formate (0.1 M)/HCl (pH 3.5–2.75); HCl/NaCl (pH 2.50–2.0). Ionic strength was maintained at $\mu = 0.5$ (NaCl).

The rate of reduction of $TiO_2(edta)^{2-}$ by limiting amounts of $Ti(edta)(H_2O)^-$ was studied by monitoring the decrease in absorbance at $\lambda = 363$ nm on the Varian-Cary 118C spectrophotometer. The data were obtained from the absorbance curves as a function of time and analyzed by using first-order kinetic programs with a DEC-1103 computer.

Preparation of $TiO(edtaH_2) \cdot H_2O$. Stoichiometric amounts (5.2 $\times$ 10^{-3} mol) of $Na_2edtaH_2 \cdot 2H_2O$ and a stock solution of Ti(IV) were added to 100 mL of water. Solid Na_2CO_3 was added in small amounts until pH ~ 5. The solution was allowed to stir for ~ 15 min at room temperature and then filtered to remove any insoluble materials. Concentrated HCl was added to the filtrate until pH ~ 1 was achieved. A white precipitate was immediately formed. The precipitate was washed with 0.3 M HCl and then ethanol, and allowed to air dry on a glass frit.

The formulation $TiO(edtaH_2) \cdot H_2O$ was based on a potentiometric titration of a sample of the solid with NaOH. This was verified by conversion of the complex to its peroxo form by addition of H_2O_2 and measuring the absorbance at $\lambda = 363$ nm. These results gave a molecular weight of the solid as 372 with an uncertainty of 10%.

Results and Discussion

$TiO(edtaH_2)(H_2O)$ Complex. The solid $TiO(edtaH_2)(H_2O)$ may be prepared by mixing stoichiometric amounts of aqueous TiO^{2+} and $Na_2edtaH_2 \cdot 2H_2O$ followed by adjustment of the pH to 1.5. The IR spectrum is shown in Figure 1. The presence of the titanium(IV)–oxygen bond is shown by the 950-cm^{-1} vibration. The carboxylate region shows three bands at 1705, 1675, and 1620 cm^{-1}. These carboxylate vibrations are attributed to two protonated carboxylates, one carboxylate group coordinated to Ti(IV) and the other carboxylate of the

(9) J. Podlahova and J. Podlaka, *J. Inorg. Nucl. Chem.*, **28**, 2267 (1966).
(10) J. D. Ellis and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 537 (1973).

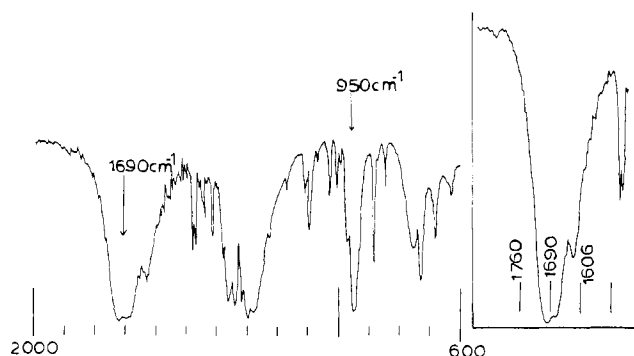(11) John A. Dean, Ed., "Langes Handbook of Chemistry", McGraw-Hill, New York, 1972, p 10-7.

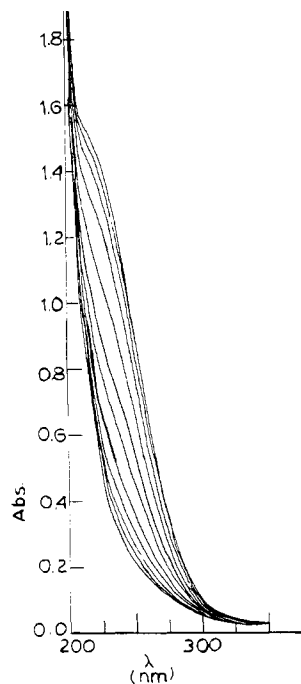**Figure 1.** Infrared spectrum of TiO(edtaH$_2$)(H$_2$O) in KBr.

Figure 2. Charge-transfer region in the spectrum of *TiO(edta)*$^{2-}$ from pH 5.0 to 2.0. Ascending curves: pH 5.00, 4.00, 3.75, 3.49, 3.21, 2.99 2.75, 2.50, 2.30, 2.16, and 2.00.

edtaH$_2$$^{2-}$ ligand free or coordinated. Analogous vanadyl complexes have a V=O stretch at ca. 1000 cm^{-1} unless a trans-ligand donor lowers the V=O vibrational frequency.[12] A strong donor shifts the V=O stretch up to 50 cm^{-1}. The presence of the Ti=O vibration at 950 cm^{-1} suggests the oxo ligand is trans to a nitrogen donor of the ethylenediamine backbone of edtaH$_2$$^{2-}$. Weighardt et al. found no Ti=O stretch in the region of 900–1050 cm^{-1} for complexes formulated as [TiO(dipic)(OH$_2$)]·3H$_2$O, [TiO(ida)(OH$_2$)]·2H$_2$O, Cs[TiO(nta)]·1.5H$_2$O, or Cs$_4$([TiO(nta)]$_4$)·6H$_2$O.[29] These workers point out that true titanyl moieties are rarely found in solution or in the solid state.[29] In this regard, the TiO-(edtaH$_2$)(H$_2$O) complex is quite interesting. The known preference of V(V) complexes of the edta family of ligands for a oxo-trans-N structure also suggests the likelihood of an oxo-trans-N structure for TiO(edtaH$_2$)(H$_2$O).[8] The presence of a coordinated H$_2$O is consistent with the effective molecular weight of TiO(edtaH$_2$)(H$_2$O) as determined by acid–base titration and by the conversion of the complex into the peroxo complex Ti(O$_2$)(edta)$^{2-}$ in solution. The presence of the "partially coordinated" carboxylate vibration at 1620 cm^{-1} also implies a possible vacant site for H$_2$O.
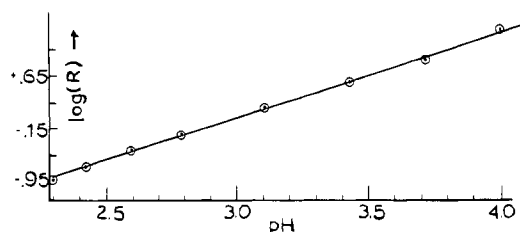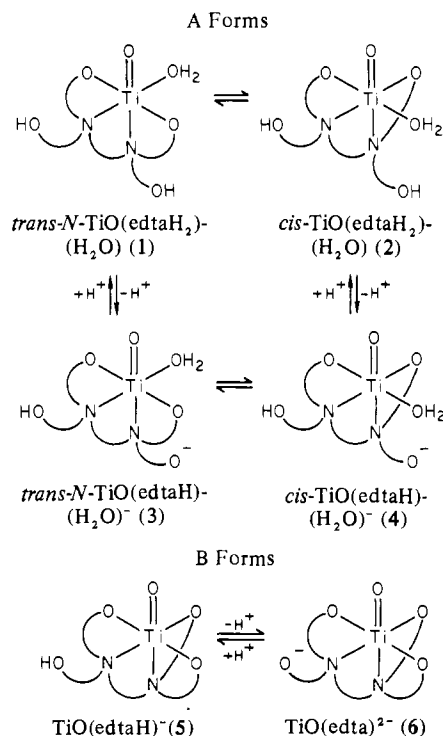
(12) K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds", Wiley, New York, 1976, p 253.

Figure 3. Hydrogen ion dependence of the charge-transfer spectrum of *TiO(edta)*$^{2-}$. log R = log [($A_0 - A_{obsd}$)/($A_{obsd} - A_f$)], as described in the text for eq 3.

TiO(edta)$^{2-}$ Species. A titration of stoichiometric amounts of aqueous TiO^{2+} and Na$_2$edtaH$_2$ detects two titratable protons as anticipated by eq 1. Beyond 2 equiv of NaOH, an addition

$$TiO(edtaH_2)(H_2O) + 2OH^- \rightleftharpoons$$
$$2H_2O + TiO(edta)(H_2O)^{2-} \quad (1)$$
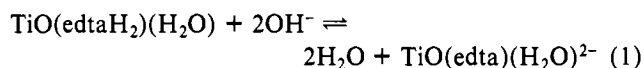
of NaOH to TiO(edta)$^{2-}$ produces a sudden pH jump followed by a slower decrease, suggestive of a polymerization reaction above pH 6. Also the Ti(III) complex used as a reagent in several studies is reported to have a pK_a of a coordinated water molecule at 8.64 ± 0.01,[9] which further complicates the issue of what species are available in Ti(IV) and Ti(III) edta solutions above pH 6. Therefore no studies of the solution species of *TiO(edta)*$^{2-}$ were carried out above pH 6. Solutions of *TiO(edta)*$^{2-}$ below pH 5 exhibit a charge-transfer band in the range of 300–200 nm. The band is bathochromically shifted with decreasing pH until a limiting spectrum is obtained at ca. pH 2 (see Figure 2). The red shift in the Ti=O ligand-to-metal charge-transfer band with increasing [H$_3$O$^+$] suggests a decrease in negative charge near the Ti(IV) center. A breakage of the Ti^{IV}–carboxylate bond with protonation of the *TiO(edta)*$^{2-}$ complex is the consistent explanation. This H$_3$O$^+$-promoted process equilibrates two spectrally distinct forms: A and B. The spectral forms, A and B, are themselves mixtures of isomeric solution structures and protolytic forms in which pendant carboxylate groups may be protonated or not. Consider the aquated forms, A, and chelated forms, B, shown. The pK_a's of the pendant carboxylate functionalities
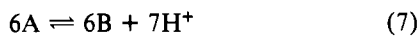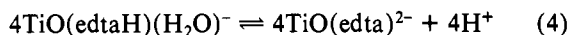
A Forms

trans-N-TiO(edtaH$_2$)-(H$_2$O) (1)   *cis*-TiO(edtaH$_2$)-(H$_2$O) (2)

trans-N-TiO(edtaH)-(H$_2$O)$^-$ (3)   *cis*-TiO(edtaH)-(H$_2$O)$^-$ (4)

B Forms

TiO(edtaH)$^-$(5)   TiO(edta)$^{2-}$ (6)

in these structures are likely to be very close in magnitude. The overall conditional equilibria in which N protons are released in equilibrating the aquated (A) and chelated (B) forms is governed by the conditional equilibrium constant, K, in eq 2. The distribution of species obeys eq 3 as shown by

$$A \xrightleftharpoons{K} B + N(H_3O^+) \tag{2}$$
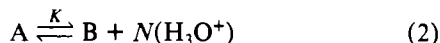
$$\log [(A_0 - A_{obsd})/(A_{obsd} - A_f)] = \log K + N(pH) \tag{3}$$

Figure 3 for data at 252 nm. A_f refers to the limiting absorbance at high pH (ca. 5), A_0 refers to the limiting absorbance at low pH (ca. 2), and A_{obsd} is the absorbance at intermediate pH values. The left-hand side of eq 3 defines the $\log ([B]/[A])$. Therefore eq 3 correctly describes the conditional equilibrium defined by eq 2. The value of N for eq 2 was determined to be 1.18 ± 0.02 from the slope of Figure 3. The numerical value of $K = (3.73 \pm 0.07) \times 10^{-4}$ was evaluated from a plot of $(A_0 - A_{obsd})/(A_{obsd} - A_f)$ vs. $[H_3O^+]^{1.18}$.

On the basis of analytical data for $TiO(edtaH_2)(H_2O)$, the IR spectrum of this salt, and the bathochromic shift in TiO-$(edta)^{2-}$ solutions as the pH is adjusted from 5 to 2, we conclude that species **1-6** are the minimum set of solution species that exist throughout the pH range. The IR evidence also supports the existence of H_2O coordinated either trans to nitrogen or cis to nitrogen, e.g., isomers **1** and **2**. The IR data of other M(edta) complexes generally infer that trans to nitrogen coordination is weaker. For the two ionic carboxylate groups, when water is trans to nitrogen in **1**, the carboxylates are trans with vibrations at 1675 cm^{-1} while the "cis" water orientation of **2** places a carboxylate trans to nitrogen with a lower vibration of 1620 cm^{-1}. On the basis of the intensity of the IR bands, isomer **2** with carboxylate trans to nitrogen is 37.5% abundant while the trans-N-water isomer (**1**) would be 62.5% abundant in the solid $TiO(edtaH_2)(H_2O)$. It is important to suggest how the fractional dependence on H_3O^+ is compatible with equilibrating the aquated and chelated structures. No unique combination of equations is suggested for $N = 1.18 \pm 0.02$. However, an illustrative case is shown by the sum of eq 4-6. The net reaction (eq 7) equilibrates

$$4TiO(edtaH)(H_2O)^- \rightleftharpoons 4TiO(edta)^{2-} + 4H^+ \tag{4}$$

$$TiO(edtaH_2)(H_2O) \rightleftharpoons TiO(edta)^{2-} + 2H^+ \tag{5}$$

$$TiO(edtaH_2)(H_2O) \rightleftharpoons TiO(edtaH)^- + H^+ \tag{6}$$

$$6A \rightleftharpoons 6B + 7H^+ \tag{7}$$

six species of the A form with six species of the B form, releasing seven hydrogen ions. On a per mole of $TiO(edta)^{2-}$ complex, the value of $N = 1.17$ is obtained for eq 7. In this manner it is readily seen how a fractional hydrogen ion dependence may arise from the coupling of closely related pK_a's and different structural types for Ti^{IV}/edta solutions.

A reviewer has pointed out that Karadokov and Nenona[30] have previously studied equilibrium 2. These workers had no additional experimental evidence for the presence of isomeric and protolytic structure as shown for A and B forms. Therefore Karadakov and Nenona have fit their data for eq 2 with $N = 1$, yielding a pK_a value of 2.78 ± 0.02.[30] Our value for the effective pK_a of equilibrium 2 is 3.43 ± 0.01. A careful examination of Karadokov and Nenona's data reveals that the determined value of N was 1.14 rather than 1.00. This compares favorably with our experimental value of $1.18 \pm .02$. In the pH range of 2.0-5.0 if N is forced to 1.00, the value found for the pK_a will become 2.80 from our data. Therefore both data sets are in close agreement; however, we have applied the refinements required by the presence of multiple solution species in extracting the values of $N = 1.18 \pm 0.02$ and pK_a = 3.43 ± 0.01. The quoted error estimate of ± 0.02 on N

reflects the least-squares fit to the evaluated values of log $[(A_0 - A_{obsd})/(A_{obsd} - A_f)]$. If extreme estimates are used for the error in log $[(A_0 - A_{obsd})/(A_{obsd} - A_f)]$, an uncertainty in N of ± 0.10 is found. It might be argued that $N = 1.18 \pm 0.10$ is sufficiently close to 1.00 to warrant the assignment of a single acid dissociation equilibrium to eq 2. However, kinetic and IR data support the presence of multiple species. We have chosen to accept the mean value of the slope as a meaningful estimate of the number of hydrogen ions released per mole of Ti(IV).

Ti(O$_2$)(edta)$^{2-}$ Complex. Addition of H_2O_2 to a solution of $TiO(edta)^{2-}$ quantitatively generates the known peroxo complex.[2] Therefore the formation constant of the peroxo complex is very large. One intense band at $\lambda_{max} = 363$ nm (ϵ $(1.24 \pm 0.07) \times 10^3$ M^{-1} cm^{-1}) is observed for the peroxo complex. The amount of peroxo complex does not increase with $[H_2O_2]$ above a 1:1 $TiO(edta)^{2-}$:H_2O_2 ratio. Therefore as with peroxo vanadyl complexes,[4] the reverse reaction of eq

$$TiO(edta)^{2-} + H_2O_2 \rightleftharpoons Ti(O_2)(edta)^{2-} + H_2O \tag{8}$$
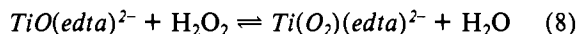
8 may be neglected for kinetic interpretations since the formation constant is very large over the entire pH range of 2.0-5.2 studied here. The number of protons involved in the titanyl complex has been omitted. The species on the left-hand side of eq 8 represents all species of A and B forms present in solution. The spectrum of the product is independent of pH from 1.5 to 6.5. Other Ti(IV) and V(V) peroxo complex adopt the "side-on" peroxo coordination. The most likely structure of the peroxo product is shown by **7** in which the pendant carboxylate group is either protontated or ionized.

7
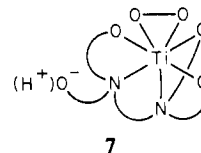
Addition of H_2O_2 to a solution of $TiO(edta)^{2-}$ induces a release of protons in the pH range below 4.5 while no change occurs above 4.5. The displacement of the oxo ligand by H_2O_2, releasing H_2O, would cause no pH change. The proton release observed for acidic solutions, in which **1-4** are favored, is accounted by the ring-closed structure in **7**. At the higher pH values where species **5** and **6** of $TiO(edta)^{2-}$ are predominant, no deprotonation on ring closure is required. In addition, the pendant carboxylate of peroxo complexes are usually less basic than the corresponding oxo complex. The pK_a of $VO_2(edtaH_2)$ is 3.45 while that of $VO(O_2)(edtaH_2)$ is 2.63. Since no pH drop occurs upon addition of H_2O_2 to $TiO(edta)^{2-}$ solutions with pH ca. 5, one can infer that species **6**, $TiO(edta)^{2-}$, is the only major species of the titanyl complex near pH 5.

The reaction of $TiO(edta)^{2-}$ with H_2O_2 was studied over the pH range of 2.0-5.2. Below pH 2.0 the measured rates were very large, and accurate values were difficult to measure. In the range of pH 2.0-5.2, the rate law followed eq 9 for the

$$d[Ti(O_2)(edta)^{2-}]/dt = k_{obsd}[H_2O_2][Ti^{IV}] \tag{9}$$
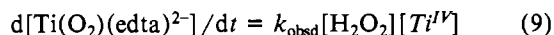
formation of the peroxo complex. The rate is pseudo-first order in Ti(IV) with H_2O_2 in a 10-200-fold excess as shown in Figure 4 under conditions of pH 4.60, $T = 25.0$ °C, and $\mu = 0.50$ (acetate/NaCl). The measured slope gives $k_{obsd} = 53.3 \pm 3.1$ M^{-1} s^{-1} with a virtually zero-valued intercept term of 0.03 ± 0.12 s^{-1}. The pH dependence of k_{obsd} was followed from 2.00 to 5.20 as shown by the plot of log k_{obsd} vs. pH in Figure 5. Tabular data are also presented in Table I. Two linear regions are observed. At pH >4.5 no dependence on H_3O^+ is observed. Below pH 4.5 a slope of -1.00 is determined. If there are two species in protolytic equilibrium with different chemical reactivities for a substrate (H_2O_2 in this case), the
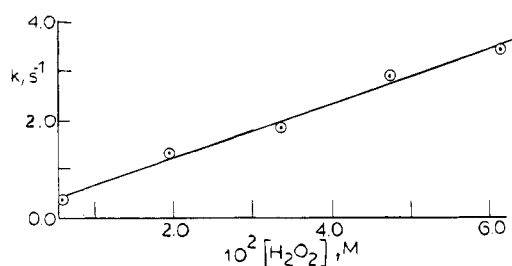
Figure 4. Dependence of the oxo displacement reaction on $TiO(edta)^{2-}$ by H_2O_2: $[TiO(edta)^{2-}] = 3.47 \times 10^{-4}$ M; pH 4.60; $T = 25.0$ °C; $\mu = 0.50$ (0.40 M NaCl/0.10 M NaC₂H₃O₂).
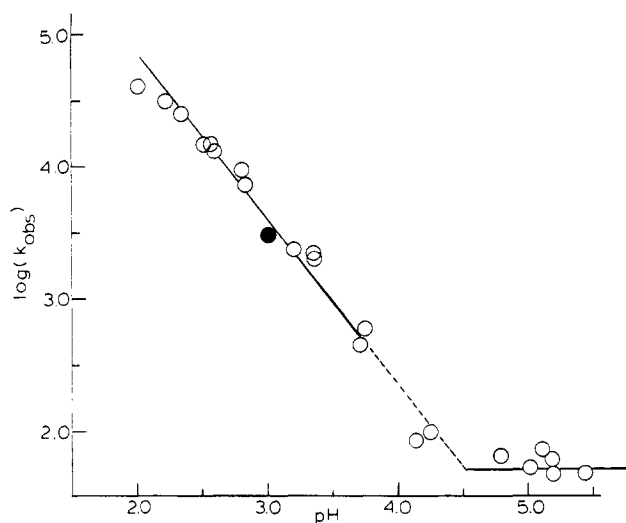

Figure 5. Dependence of the second-order rate constant for oxo displacement by H_2O_2 on $TiO(edta)^{2-}$; conditions are specified in Table I and the text.

form of the observed rate constant for forms A and B is given by the general eq 10.[13] The rate constants k_A' and k_B' may

$$k_{obsd} = (k_A'[H^+]^N + k_B'K)/([H^+]^N + K) \qquad (10)$$

have their own intrinsic dependence on $[H_3O^+]$ in addition to the $[H_3O^+]$ dependence due to the overall equilibria involving A and B. Other forms for k_{obsd} related to eq 10 may be obtained. The slope of -1.00 for the data below pH 4.5 in Figure 5 suggests eq 11 as the proper mathematical form of

$$k_{obsd} = (k_A[H^+]^M + k_BK)/([H^+]^N + K) \qquad (11)$$

k_{obsd}, assuming that all aquated or A forms of $Ti(ed-taH_n)(H_2O)^{n-2}$ have equivalent rate constants, k_A, and all ring-closed forms B have similar constants, k_B. When the $[H^+]$ is sufficiently large such that $[H^+]^N > K$ and $k_A[H^+]^M > k_BK$, a linear dependence for the k_{obsd} vs. $[H^+]^{(M-N)}$ should be obtained. The slope of -1.00 in Figure 5, below pH 4.0, shows that the intrinsic $[H_3O^+]$ dependence of the k_A path is first order in H_3O^+. A least-squares fit to the data below pH 4.0 determined that $k_A = (5.25 \pm 0.25) \times 10^6$ while the data above pH 4.0 sets $k_B = 49 \pm 5$ M⁻¹ s⁻¹.

A reviewer questioned whether the dissociation of the edta ligand from $TiO(edta)^{2-}$ might cause errors in the measurements of the rate of substitution of H_2O_2 on $TiO(edta)^{2-}$. Measurements for Table I were carried out in the presence of a 10% excess of edta ligand to prevent dissociation of Ti(IV) causing a side-reaction pathway. Because of the legitimate concern expressed by the reviewer, the effect of excess edta

(13) R. G. Wilkins, "The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes", Allyn and Bacon, Boston, 1974, pp 43–45.

Table I. Displacement of Oxo by H_2O_2 on $TiO(edta)^{2-}$ at $\mu = 0.50$ (NaCl/acetate)

T, °C	pH[a]	$10^{-3}k_{obsd}/[H_2O_2]$
25.0	2.03[b]	37.2
	2.04[b]	28.2
	2.09[b]	29.6
	2.23[b]	30.6
	2.34[b]	25.3
	2.55[b]	15.5
	2.58[b]	17.9
	2.63	14.4
	2.88	7.11
	3.00	2.87
	3.31	2.39
	3.34	1.98
	3.36	2.64
	3.71	0.466
	3.74	0.648
	4.16	0.0893
	4.27	0.0995
	4.51	0.0641
	4.76	0.0538
	5.00[c]	0.0486
	5.20	0.0490
30.8	5.00	0.0538
25.3	5.00	0.0486
19.7	5.00	0.0376
15.0	5.00	0.0300
9.8	5.00	0.0247
33.0	5.28	0.0531
30.0	5.28	0.0489
27.0	5.28	0.0414
23.0	5.28	0.0381
21.5	5.28	0.0366
19.2	5.28	0.0338
33.2	2.28	37.4
24.0	2.28	29.4
19.0	2.28	25.2
25.0	2.28	30.6
31.1	2.00	53.7
22.8	2.00	44.5
15.4	2.00	32.2
10.5	2.00	26.3

[a] Unless otherwise noted, $[TiO(edta)^{2-}]_i = 1.70 \times 10^{-4}$ M, $[H_2O_2]_i = 3.94 \times 10^{-3}$ M, $\mu = 0.50$ (0.40 M NaCl/0.10 M NaC₂H₃O₂), and $T = 25.0$ °C. [b] $\mu = 0.50$ (NaCl + HCl). [c] $[H_2O_2]_i = 5.74 \times 10^{-3}$ M.

on the measured rate at pH 3.00 was carefully studied. In one set of experiments 5.0%, 10.0%, 50.0%, and 100.0% excess of edta was added such that a 5.0% excess originated from the $TiO(edta)^{2-}$ stopped-flow barrel and the remainder was contributed from the H_2O_2 reagent. In another set of experiments, 5.0%, 10.0%, 50.0%, and 100.0% excess edta was present from the $TiO(edta)^{2-}$ solution alone. The rate constants were the same within ±3.5% for all measurements, independent of the mixing procedure or the time allowed for equilibration with the $TiO(edta)^{2-}$ reagent. The mean value of all these studies is shown as the solid point in Figure 5. Therefore the concern that dissociation provides an important competitive substitution pathway for H_2O_2 is eliminated.

A more troublesome problem appears to be related to the preparation of the stock Ti(IV) solution as TiO^{2+}. Although the method of preparation of TiO^{2+} was repeated in the same manner as described in the experimental section, a small amount of polymeric Ti(IV) may be present. Values measured for k_{obsd} on aged solutions of $TiO(edta)^{2-}$ stored at pH 1.7 showed an increase in rate constant of about 10% and the value of A_∞ was too high. We assume that for stock solutions stored in the acidic region and quickly readjusted to higher pH values for rate studies suffer the dissociation problems suggested by the reviewer. Therefore solutions of TiO(edta)²⁻ should be prepared and stored above pH 2.

Table II. Hydrogen Ion Dependencies and Activation Parameters for Oxo Displacement by H_2O_2 on Ti(IV) and V(V) Complexes[a,b]

reacting species	k_0	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$k_1[H_3O^+]$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
TiO(edta)$^{2-}$	49 ± 5	5.7 ± 0.9	-33 ± 2			
TiO(edtaH)(H$_2$O)$^-$				$(5.25 \pm 0.25) \times 10^6$	4.8 ± 0.9	-22 ± 3
VO$_2$(edta)$^{3-}$	$\leqslant 0.1$			1.5×10^6	11.2 ± 1.0	6.9 ± 2
VO$_2$(edtaH)$^{2-}$				4.6×10^5	8.6 ± 1.9	-4 ± 2
VO$_2$(nta)$^{2-}$	7.4	9.3 ± 0.2	-23 ± 2	1.86 ± 10^4	9.3 ± 0.2	-8 ± 2

[a] Ti(IV) data, this work; V(V) data, ref 4 and 5. [b] Units: k_0 given in M^{-1} s^{-1}; $k_1[H_3O^+]$ in M^{-2} s^{-1}; $\Delta H^{\ddagger}$ in kcal/mol; $\Delta S^{\ddagger}$ in eu.

Scheme I
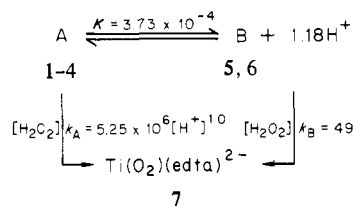
The temperature dependence of eq 8 was studied under limiting conditions at pH 5.0 and 5.28, where **6** predominates and at pH 2.0 and 2.28 where **1–4** contribute. The activation parameters evaluated by the Eyring treatment of log (k/T) vs. $1/T$ gave $\Delta H^{\ddagger} = 5.7 \pm 0.5$ kcal/mol and $\Delta S^{\ddagger} = -33 \pm 2$ eu at pH 5.0 for the k_B path. At pH = 2.0 the effective activation parameters are $\Delta H^{\ddagger}$ 4.8 ± 0.9 kcal/mol and $\Delta S^{\ddagger}$ $= -22 \pm 3$ eu. The data are presented in Table I. Values given for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are the average of two independent temperature studies found on independently prepared samples of *TiO(edta)$^{2-}$* prepared from TiCl$_3$.

Mechanism of Formation of Ti(O$_2$)(edta)$^{2-}$. In keeping with the data described above, Scheme I appropriately describes the substitution of H_2O_2 to provide pathways that convert oxo to peroxo Ti^{IV}-edta species. H_2O_2 assumes an outer-sphere position by rapid diffusion to a face near the oxo ligand of **5** or **6**. A slow reorganization step obtains in which proton transfer from H_2O_2 to the oxo group occurs with some reorganization of the coordinated carboxylates to form **7**. The reorganization may involve partial Ti^{IV}–carboxylate rupture. The large negative activation entropy of -33 eu for **6** supports this view. The barrier for species **1–4** is lower in magnitude by about 10 eu although the value for $\Delta H^{\ddagger}$ is similar for all species, **1–6**. A rapid substitution of H_2O_2 for the coordination water molecule is reasonable for **1–4**. Therefore the primary advantage of the aquated forms **1–4** appears to be availability of the pendant functional groups to adjust more readily to the needs of Ti(IV) coordination, concerted with proton transfer, than is available for the more structured reactant for either **5** or **6**. For the k_A path, the H_2O_2 is further removed from the oxo ligand by coordination at the water position than when H_2O_2 interacts through a facial position cis to oxo in the k_B path. An interaction with an external proton source that helps activate the rupture of the oxo ligand–Ti^{IV} bond accounts for the first-order dependence of the k_A path for **1–4**. A first-order dependence on H_3O^+ has been observed for the VO$_2$-(edta)$^{2-}$/H_2O_2 system.[4]. Since the advantage of the k_A path over the k_B path appears mostly in the entropy of activation term, it is also of interest to note that rupture of metal carboxylate bonds generally cost about 10–12 eu.[4] This value is conveniently close to the observed difference in entropy barriers for **1–4** vs. **5** and **6** forms.

Comparisons with VO$_2$L/H$_2$O$_2$ Systems. The studies of Tanaka et. al. on *VO$_2$(edta)$^{3-}$* and *VO$_2$(nta)$^{2-}$* reactions with H_2O_2 provide several interesting comparisons with the *TiO-(edta)$^{2-}$* data. Pathways involving k_0 and $k_1[H_3O^+]$ are observed, depending on the metal center and extent of ligand protonation, with activation parameters as shown in Table II. The k_0 or acid-independent path for TiO(edta)$^{2-}$:VO$_2$-

(nta)$^{2-}$:VO$_2$(edta)$^{3-}$ are in the relative ratio of ca. 490:74:1. Protonation of the oxo ligand as the origin of the $k_1[H_3O^+]$ pathway is proposed for all V(V) peroxo displacement of oxo reactions.[4] The observed rate constants for the k_1 paths are within a factor of 10 for Ti(IV) and V(V) reactions. In the V(V) cases $\Delta S^{\ddagger}$ is modestly small (even positive for VO$_2$-(edta)$^{3-}$) which is attributed by Tanaka to oxo protonation.[4] The first-order proton-dependent path has a lower $\Delta S^{\ddagger}$ barrier of ~ 11 eu relative to the k_0 path for Ti(IV) complexes. With V(V) complexes the first-order proton assistance lowers $\Delta S^{\ddagger}$ by 15 eu. Therefore, the effect of proton assistance on the entropy of activation is comparable for either Ti(IV) or V(V) while the values of $\Delta H^{\ddagger}$ remain virtually unchanged as shown by TiO(edta)$^{2-}$ (5.7 $\pm$ 0.5 kcal/mol) and TiO(edtaH)$^-$ (4.8 $\pm$ 0.9 kcal/mol) and by VO$_2$(nta)$^{2-}$ with $\Delta H^{\ddagger} = 9.3 \pm 0.2$ for both k_0 and $k_1[H_3O^+]$ paths.[5]

For V(V) complexes including VO$_2$(edta)$^{3-}$, VO$_2$(edda)$^-$, and VO$_2$(dmedda)$^-$, k_{obsd} saturates in [H$_2$O$_2$], indicative of a preequilibrium association with constants of 25 ± 10, 20 ± 10, and 300 ± 100 M^{-1}, respectively.[4] The range of [H$_2$O$_2$] required to establish saturation effects for V(V) complexes was up to 0.30 M in H_2O_2. No saturation is observed for the *TiO(edta)$^{2-}$* case with [H$_2$O$_2$] as high as 0.07 M in our study. Curvature is detected over the range of 0–0.07 M [H$_2$O$_2$] for the *VO$_2$(edta)$^{3-}$* case. This implies that the association constant of H_2O_2 for *TiO(edta)$^{2-}$* is much less than the 25 ± 10 M^{-1} value for *VO$_2$(edta)$^{2-}$*. The strict linearity shown in Figure 4 implies $K_{as} \leq 1$ M^{-1}. The difference in affinities of *TiO-(edta)$^{2-}$* compared to *VO$_2$(edta)$^{3-}$*, may be due to the effect of two oxo groups in the *VO$_2$(edta)$^{3-}$*, presenting a large effective area open to solvent molecules and H_2O_2 on the "facial" positions than for the Ti(IV) complex **6**. Assuming a similar mechanism such that the second-order rate constant equals $K_{as}k$ in both the V(V) and Ti(IV) cases, the first-order step, k, is favored by $\sim 1.2 \times 10^4$ for the Ti(IV) center which more than compensates for a smaller value of K_{as}. This may be attributed to the greater ease in reorganizing a single oxo group for Ti(IV) vs. two for V(V).

Reaction of O$_2$ and Ti(edta)(H$_2$O)$^-$. The UV–Visible spectrum of the Ti(III) complex Ti(edta)(H$_2$O)$^-$ is unchanged in the pH range of 2.0–7.5. The complex is thought to be six-coordinated as shown by **8**. The pK$_a$ of the pendant
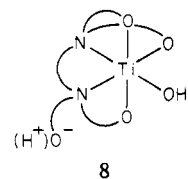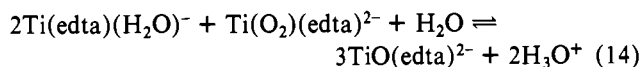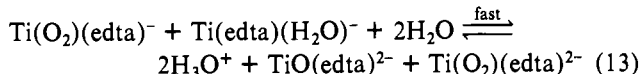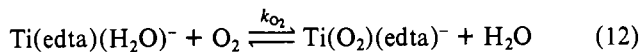

8

carboxylate is reported to be 2.02 while the pK$_a$ of the coordinated water molecule is 8.64.[9] When N$_2$-purged solutions containing **8** are mixed with buffers saturated with various concentrations of O$_2$ with [Ti^{III}]$_i$/[O$_2$] ≤ 2.0, between 40 and 50% of Ti(O$_2$)(edta)$^{2-}$ is produced. The amount of the peroxo complex, as analyzed by its maximum at 364 nm, is virtually independent of pH. As shown in Table III, the amount of *TiO(edta)$^{2-}$* is greatest if [Ti^{III}]$_i$/[O$_2$] < 1.0. In the presence of a 10-fold excess of Ti(III), no peroxo product is detectable.

Table III. Percent $Ti(O_2)(edta)^{2-}$ Formed under Various $Ti^{III}:O_2$ Ratios^a

pH	$10^3 \times$ $[O_2]$, M	$10^4 \times$ $[Ti^{III}]$, M	% $[Ti(O_2)$- $(edta)^{2-}]$ found	$[Ti^{III}]/$ $[O_2]$
5.03	1.1	1.88	50	0.17
4.50	1.1	1.89	50	0.17
3.90	1.1	2.02	48	0.18
3.45	1.1	2.03	48	0.18
4.55	1.1	2.19	45	0.19
4.55	1.0	6.45	45	0.65
4.52	0.60	4.44	42	0.74
4.55	0.80	1.24	41	1.6
4.55	0.33	5.94	40	1.8

^{a} $\mu = 0.50$ (0.40 M NaCl/0.10 M NaC₂H₃O₂), $T = 25.0$ °C.
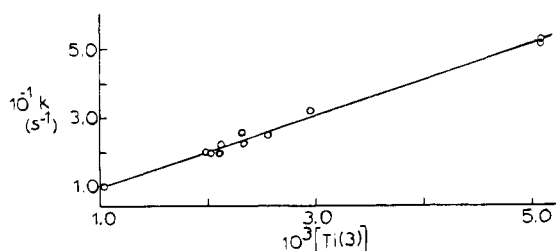
Figure 6. Rate of formation of $Ti(O_2)(edta)^{2-}$ by the O_2/Ti-(edta)(H₂O)⁻ reaction; conditions are specified in Table IV.

These results are consistent with the sequential reactions 12–14. When the abundance of the Ti(III) pool is small

$$Ti(edta)(H_2O)^- + O_2 \overset{k_{O_2}}{\rightleftharpoons} Ti(O_2)(edta)^- + H_2O \quad (12)$$

$$Ti(O_2)(edta)^- + Ti(edta)(H_2O)^- + 2H_2O \overset{fast}{\rightleftharpoons}$$
$$2H_3O^+ + TiO(edta)^{2-} + Ti(O_2)(edta)^{2-} \quad (13)$$

$$2Ti(edta)(H_2O)^- + Ti(O_2)(edta)^{2-} + H_2O \rightleftharpoons$$
$$3TiO(edta)^{2-} + 2H_3O^+ \quad (14)$$

relative to O_2, the reduction of the coordinated peroxo complex $Ti(O_2)(edta)^{2-}$ to water and $TiO(edta)^{2-}$ is retarded and the stoichiometry approaches the theoretical 50.0% value according to eq 12 and 13. The reactions responsible for reduction of $Ti(O_2)(edta)^{2-}$ are slow enough that both the generation of $Ti(O_2)(edta)^{2-}$ from O_2 and $Ti(edta)(H_2O)^-$ and the reduction of the peroxo product may be studied separately at 363 nm. The appearance of $Ti(O_2)(edta)^{2-}$ obeys eq 15 under pseudo-first-order conditions in $Ti(edta)(H_2O)^-$. The constant, k_{O_2},

$$d[Ti(O_2)(edta)^{2-}]/dt = k_{O_2}[Ti(edta)(H_2O)^-][O_2] \quad (15)$$

is independent of $[H_3O^+]$ as shown by the conformity of all data in the pH range of 4.0–5.3 to a single linear relationship in $[Ti(edta)(H_2O)^-]$. These data are shown in Figure 6 (see also Table IV). At 25.0 °C and $\mu = 0.50$ (NaCl/CH₃COOH/CH₃CO₂⁻), the value of k_{O_2} is $(1.02 \pm 0.04) \times 10^4$ M⁻¹ s⁻¹. The temperature dependence of k_{O_2} was examined between 15.0 and 31.6 °C. Activation parameters of $\Delta H^{\ddagger} = 8.1 \pm 0.7$ kcal/mol and $\Delta S^{\ddagger} = -13.2 \pm 2.4$ eu were measured at pH 5.0. Data are shown in Table V.

Mechanism of Redox Generation of Ti(O₂)(edta)²⁻. The measured rate constant for the generation of $Ti(O_2)(edta)^{2-}$ by the addition of O_2 to $Ti(edta)(H_2O)^-$ is 200 times faster than the substitution of peroxo for oxo on $TiO(edta)^{2-}$ at pH 5.0. Therefore an outer-sphere reduction of O_2 to H_2O_2 followed by substitution on a generated Ti(IV) species is not a possible mechanism for the $O_2/Ti(edta)(H_2O)^-$ route forming $Ti(O_2)(edta)^{2-}$. The inner-sphere sequence in which the addition step of eq 12 is rate limiting accounts for the rate law. The water-exchange rate of $Ti(H_2O)_6^{3+}$ has been evaluated

Table IV. Rate of Formation of $Ti(O_2)(edta)^{2-}$ via the $O_2/Ti(edta)(H_2O)^-$ Redox Pathway^a

pH	$10^4[O_2]$, M	$10^3[Ti^{III}]$, M	k_{obsd} s⁻¹
4.60	6.0^b	0.117	7.3
4.60	3.0	2.94	31.6
4.60	2.0	5.10	51.6
4.60	2.0	2.04	19.6
4.60	1.0	5.10	50.3
4.60	1.0	2.55	24.5
4.60	1.0	1.02	9.83
5.30	1.1	2.31	25.6
4.60	1.1	2.33	22.3
4.90	1.1	2.11	19.5
4.50	1.1	2.13	19.7
4.00	1.1	2.13	21.9

^{a} $\mu = 0.50$, $T = 25.1$ °C. ^{b} O_2 in excess; all other runs, Ti^{III} in excess. Note $k_{O_2} = 1.22 \times 10^4$ M⁻¹ s⁻¹ calculated for run b.

Table V. Temperature Dependence of the $O_2/Ti(edta)(H_2O)^-$ Formation of $Ti(O_2)(edta)^{2-}$ at pH 5.0^a

T, °C	$10^3 k_{O_2}$	T, °C	$10^3 k_{O_2}$
31.6	12.4	19.7	6.86
25.2	9.91	15.0	5.59

^{a} $\mu = 0.50$ (0.40 M NaCl/0.10 M NaC₂H₃O₂); $[O_2] = 1.10 \times 10^{-4}$ M; $[Ti^{III}] = 2.29 \times 10^{-3}$ M.

with use of ¹⁷O NMR to occur with $k_{ex} = 7 \times 10^4$ s⁻¹ at 25 °C and with activation parameters of $\Delta H^{\ddagger} = 6.2$ kcal/mol and $\Delta S^{\ddagger} = -15$ eu.[14] It has been suggested that water exchange on $Ti(edta)(H_2O)^-$ is accelerated to $>10^7$ s⁻¹.[15] The effect is due to labilization of metal centers having pendant carboxylate functionalities with t_{2g} levels of lower occupancy than 6.[16] Uncharged small molecules such as pyridine and O_2 generally have outer-sphere association constants between 0.1 and 0.01 M⁻¹. A substitution limited process to form the superoxo species should occur with a rate constant between 10^6 and 10^5 M⁻¹ s⁻¹ if $k_{ex} \sim 10^7$ s⁻¹. Since the reaction step that limits the appearance of $Ti(O_2)(edta)^{2-}$ is first order in $Ti(edta)(H_2O)^-$, the intermediate superoxo complex $Ti(O_2)(edta)^-$ must be rapidly scavenged by $Ti(edta)(H_2O)^-$ even in the presence of O_2. Note that the yield of $Ti(O_2)(edta)^{2-}$ is maximum in Table III with $[Ti(III)]:[O_2] = 0.17$. The value of $k_{O_2} = 1.02 \times 10^4$ M⁻¹ s⁻¹ is a factor of 10 lower than predicted for a substitution-limited rate for forming the $Ti(O_2)(edta)^-$ intermediate. This result suggests that the rate-limiting step measured by k_{O_2} reflects the intramolecular electron-transfer process with converts the $Ti^{III}-O_2$ adduct into the $Ti^{IV}-O_2^-$ intermediate.[18] If this view is correct for the rate-determining step, the activation entropy reflects the reorganization cost for orbitals on Ti(III) and O_2 in the adduct. This assumes that the loss of entropy for binding O_2 is com-

(14) H. Diebler, *Z. Phys. Chem.*, **68**, 64 (1969). (b) A. Chmelnik and D. Fiat, *J. Chem. Phys.*, **51**, 4238 (1969).
(15) G. A. K. Thompson and A. G. Sykes, *Inorg. Chem.*, **18**, 2024 (1979).
(16) (a) Reference 15. (b) J. Guardalabene, S. Gulnac, N. Keder, and R. E. Shepherd, *Inorg. Chem.*, **18**, 22 (1979). (c) T. Matsubara and C. Creutz, *J. Am. Chem. Soc.*, **100**, 6255 (1978). (d) N. Oyama and F. C. Anson, *ibid.*, **101**, 1634 (1979).
(17) (a) F. J. Kristine and R. E. Shepherd, presented at the American Chemical Society/Chemical Society of Japan Congress, Honolulu, Hawaii, April 1979. (b) F. J. Kristine and R. E. Shepherd and R. E. Shepherd, submitted for publication in *Inorg. Chem.*
(18) The ambiguities in the assignment of $M^{n+}-O_2$ vs. $M^{n+1}-O_2^-$ formalisms have recently been discussed by Drago in detail (R. Drago, *Inorg. Chem.*, **18**, 1408 (1979)). Our discussion adopts the useful nomenclature which describes the chemical reactive intermediate at Ti^{IV}-(edta)(O₂⁻), being scavenged by a second mole of $Ti^{III}(edta)(H_2O)^-$. These assignments, assuming an authentic superoxo character to the transient, are certainly in concert with the relative rates of reduction of the intermediate species and the peroxo complex $Ti(O_2)(edta)^{2-}$ by $Ti(edta)(H_2O)^-$ and the known chemistry for the reduction of μ-superoxo and μ-peroxo complexes of Co(III) as reported in ref 20–26.

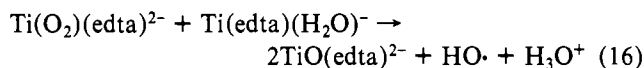**Table VI.** Reduction of Ti(O$_2$)(edta)$^{2-}$ in the Presence of Excess Ti(edta)(H$_2$O)$^{-a}$

T, °C	k, M^{-1} s^{-1}	T, °C	k, M^{-1} s^{-1}
34.7	115	19.4	58.0
29.6	101	14.8	50.0
24.4	74.6		

^{a} [Ti(O$_2$)(edta)$^{2-}$] = 1.32 × 10^{-4} M; [Ti(edta)(H$_2$O)$^-$] = 3.74 × 10^{-3} M; μ = 0.50 (0.40 M NaCl/0.10 NaC$_2$H$_3$O$_2$); pH 4.50.

pensated by the gain in entropy for the released water molecule in the addition step that occurs prior to rate-limiting intramolecular electron transfer. Support for the measured value of k_{O_2} as being related to electron transfer rather than the initial substitution rate for O$_2$ on Ti(edta)(H$_2$O)$^-$ is obtained from the rate of substitution at a faster rate approaching the 10^5 M^{-1} s^{-1} estimate made in the discussion above. A superoxo complex of Ti(IV) has been reported for the aquo system; a species TiO$_2$$^{3+}$ is detected by ESR in the Ti^{3+}/H$_2$O$_2$ reaction.[19]

Reduction of the Ti(O$_2$)(edta)$^{2-}$ Complex. The steps corresponding to the net reaction given in eq 14 have not been examined in great detail. However, several features have been observed that are of interest: (1) the peroxo complex is completely bleached in a pseudo-first-order decay with k = 75 ± 5 M^{-1} s^{-1} at 25.0 °C; (2) only a slight amount of Ti(III)—less than one-fifth required for stoichiometry of eq 14—will initiate the bleaching processes which occur by a first-order decay with $k \approx 3.5 \times 10^{-3}$ s^{-1}; (3) studies with Ti(III) in less than stoichiometric amounts are irreproducible, suggesting a chain of radical events that are terminated depending upon the presence of scavengers such as free ligand edtaH$_2$$^{2-}$ or O$_2$. From these results we infer that the first step in reduction of Ti(O$_2$)(edta)$^{2-}$ by Ti(edta)(H$_2$O) generates hydroxyl radical (eq 16). The

$$\text{Ti(O}_2\text{)(edta)}^{2-} + \text{Ti(edta)(H}_2\text{O)}^- \rightarrow$$
$$2\text{TiO(edta)}^{2-} + \text{HO·} + \text{H}_3\text{O}^+ \quad (16)$$

fate of HO· depends upon the amount of Ti(edta)(H$_2$O)$^-$ available in the system. With excess Ti(edta)(H$_2$O)$^-$ reaction 17 ensues rapidly.[3] However, if Ti(III) is consumed, HO· must

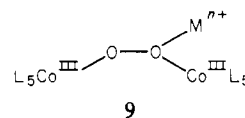$$\text{Ti(edta)(H}_2\text{O)}^- + \text{HO·} \rightarrow \text{TiO(edta)}^{2-} + \text{H}_3\text{O}^+ \quad (17)$$
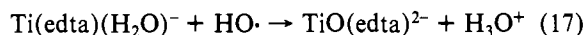
attack the edta complexes forming radical species, R·. A complicated sequence that promotes destruction of the peroxo complex must follow in which at least one step is very slow compared to the normal rates of radical reactions. Under the conditions of excess Ti(edta)(H$_2$O)$^-$, the second-order bleaching of 75 ± 5 M^{-1} s^{-1} is found. This rate constant may be assigned for eq 16 in which the initial reduction of Ti(O$_2$)(edta)$^{2-}$ is rate limiting. At pH 4.5 activation parameters of $\Delta H^{\ddagger}$ = 7.2 ± 0.5 kcal/mol and $\Delta S^{\ddagger}$ = -26 ± 2 eu were determined. These data are presented in Table VI. A study of $k_{\text{Ti(O}_2\text{)(edta)}^{2-}}$ for reaction 16 over the pH range of 3.5–5.0 revealed an independence of [H$_3$O$^+$] within experimental error of ±5% in the measured values. The activation parameters for step 16 reveal that $\Delta S^{\ddagger}$ = -26 ± 2 eu is quite close to the predicted $\Delta S^{\ddagger}$ of ~-20 eu based on the cost to bring 2- and 1- anions together in solution (-10 $Z_A Z_B$). The data are not sufficient to tell whether a peroxo bridge is established between Ti(IV) and Ti(III) in the activated complex or if the reaction is outer sphere in nature.

Reduction of Coordinated Superoxo and Peroxo Ligands. The rapid scavenging of the superoxo intermediate, Ti(O$_2$)-(edta)$^-$, by Ti(edta)(H$_2$O)$^-$ establishes a lower limit for the rate constant of ca. 10^6 M^{-1} s^{-1} at 25 °C. By contrast, the reduction of the peroxo ligand on Ti(O$_2$)(edta)$^{2-}$ occurs at 75 ± 5 M^{-1} s^{-1} with Ti(edta)(H$_2$O)$^-$. Most of the available

chemical literature concerning the reduction of coordinated superoxo and peroxo ligands has been carried out with use of substitution-inert Co(III) ammine and cyano complexes.[20–26] The reduction of μ-superoxo cobalt complexes is considered to be outer sphere in nature for labile metal ion reductants (Fe^{2+}, Cr^{2+}, V^{2+}, Eu^{2+})[25,22,21] and it is certainly outer sphere for the Co(bpy)$_3$$^{2+}$, Co(phen)$_3$$^{2+}$, Co(terpy)$_2$$^{2+}$ series.[20] The reduction of (NH$_3$)$_5$CoO$_2$Co(NH$_3$)$_5$$^{5+}$ by Cr^{2+}, V^{2+}, and Eu^{2+} are entropy controlled ($\Delta S^{\ddagger} \approx -43$ eu)[25] with second-order rate constants at 25 °C of 2.3 × 10^3 M^{-1} s^{-1} (Cr^{2+}), 9.4 × 10^4 M^{-1} s^{-1}, (V^{2+}), and 3 × 10^3 M^{-1} s^{-1} (Eu^{2+}).[25] With Fe^{2+} as a reductant, reduction of a superoxo complex to peroxo occurs at rates of ≥8 × 10^3 M^{-1} s^{-1} for (en)$_2$CoO$_2$(Co(en)$_2$$^{5+}$ and 430 ± 10 M^{-1} s^{-1} for (trien)Co(μ-O$_2$)Co(trien)$^{5+}$.[21] (NH$_3$)$_5$Co-(μ-O$_2$)Co(NH$_3$)$_5$$^{5+}$ is reduced by Co(terpy)$_2$$^{2+}$ and Co(bpy)$_3$$^{2+}$ at second-order rates of 6 × 10^3 and 3.8 × 10^2, respectively.[20] None of these rates are as fast as the lower limit established for the reduction of the superoxo intermediate, Ti(O$_2$)(edta)$^-$, by Ti(edta)(H$_2$O)$^-$. The lower limit (10^6 M^{-1} s^{-1}) for this process is borderline for a substitution-limited event on Ti-(edta)(H$_2$O)$^-$. Therefore the rapid scavenging process for Ti(O$_2$)(edta)$^-$ appears to be an outer-sphere electron-transfer process as in the cases of the μ-superoxo cobalt complex reductions. The rate advantage for Ti(edta)(H$_2$O)$^-$ as a reductant for a coordinated superoxo ligand reflects the much larger driving force imposed by the Ti^{III}(edta)$^-$ reagent ($E°$ $\approx$ 0.8 V)[27–29] relative to the weaker reductants (Fe^{2+}, V^{2+}, Cr^{2+}, Co(bpy)$_3$$^{2+}$, etc.). There is also an electrostatic advantage for building an outer-sphere activated complex for large monovalent anion pairs [Ti(O$_2$)(edta)$^-$/Ti(edta)(H$_2$O)$^-$] compared to the μ-superoxo cobalt complexes of 5+ charge with divalent reducing agents. The entropy barrier is likely to be lower in the monovalent anion pair case, in spite of a change in coordination structure upon converting Ti-(edta)(H$_2$O)$^-$ into TiO(edta)$^{2-}$. A reasonable estimate of the lower $\Delta S^{\ddagger}$ would be approximately 20 eu higher than the ~-40 eu value of (5+/2+) outer-sphere aggregates.[25] The charge advantage alone provides a kinetic factor of ~10^4 in favor of the higher rate of reduction of coordinated superoxo by Ti(edta)(H$_2$O)$^-$ relative to the μ-superoxo cobalt reductions. Therefore there are ample reasons for the ≥10^6 M^{-1} s^{-1} rate observed for Ti(edta)(H$_2$O)$^-$ in our studies.

Reduction of coordinated peroxo ligands for the cobalt(III) ammine and cyano series is generally attributed to an inner-sphere reduction process.[24] However, the step that is frequently monitored is the inner-sphere reduction of a cobalt(III) site and not the reduction of the peroxo bridging ligand[21,24] via an intermediate such as **9**. An elegant study of Sykes[24] provides

9

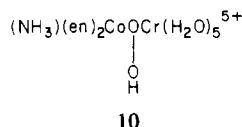a more meaningful comparison to the data obtained for the

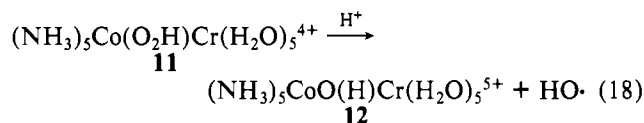(19) W. A. Armstrong, *Can. J. Chem.*, **47**, 3737, (1969).

(20) G. McLendon and W. F. Mooney, *Inorg. Chem.*, **19**, 12 (1980).
(21) G. McLendon and A. E. Martell, *Inorg. Chem.*, **15**, 2662 (1976).
(22) G. McLendon and A. E. Martell, *Coord. Chem. Rev.*, **19**, 1 (1976).
(23) A. G. Sykes, *Chem. Br.*, **10**, 170 (1974).
(24) M. R. Hyde and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1550 (1974).
(25) A. B. Hoffman and H. Taube, *Inorg. Chem.*, **7**, 1971 (1968).
(26) A. Sykes and J. Weil, *Prog. Inorg. Chem.*, **13**, 1 (1970).
(27) R. L. Pecsok and E. F. Maverick, *J. Am. Chem. Soc.*, **76**, 358 (1954); the value is quoted for pH ≃6.
(28) It is possible that addition of an electron to Ti(O$_2$)(edta)$^{2-}$ occurs with opening of the Ti^{IV}–peroxo chelate ring to achieve a end-on structure similar to the exo OH group of species **11**, ready to eliminate HO·.
(29) K. Weighardt, U. Quilitzsch, J. Weiss, and B. Nuber, *Inorg. Chem.*, **19**, 2514 (1980).
(30) B. Karadakov and P. Nenova, *J. Inorg. Nucl. Chem.*, **33**, 2541 (1971).

reduction of Ti(O$_2$)(edta)$^{2-}$ by Ti(edta)(H$_2$O)$^-$ in this work. Sykes has shown that species **10** is reduced by Cr^{2+} in an

$$(NH_3)(en)_2CoOCr(H_2O)_5^{5+}$$
$$|$$
$$O$$
$$H$$

10

outer-sphere step.[24] At 35 °C the scavenging of **10** by Cr^{2+} is rapid with a second-order rate constant of $\geq 10^2$ M^{-1} s^{-1}. An intermediate containing an O$_2$$^{3-}$ bridging ligand of bond order 0.5 is produced (**11**) which has the similar structure shown for **10** but a charge of 4+.[24,31] The intermediate **11** decays by a first-order process with $k \sim 2.1 \times 10^{-2}$ s^{-1}, forming the hydroxy bridged Co^{III}–Cr^{III} complex **12** with liberation of hydroxyl radical as shown in eq 18. In the presence of excess

$$(NH_3)_5Co(O_2H)Cr(H_2O)_5^{4+} \xrightarrow{H^+}$$
$$\mathbf{11}$$
$$(NH_3)_5CoO(H)Cr(H_2O)_5^{5+} + HO\cdot \quad (18)$$
$$\mathbf{12}$$

Cr^{2+}, the hydroxyl radical is rapidly scavenged, forming CrOH^{2+}. The steps in the Cr^{2+} reduction of **10** are very similar to the reduction of the peroxo ligand of Ti(O$_2$)(edta)$^{2-}$ by Ti(edta)(H$_2$O)$^-$. Step 16 is analogous to the rapid reduction of **10** forming **11**.[28] Indeed both rates are of the order of 10^2 M^{-1} s^{-1} although the titanium reaction (eq 16) has the same kinds of thermodynamic and electrostatic advantages as

mentioned for the reduction of the superoxo ligand of Ti-(O$_2$)(edta)$^-$. The O$_2$$^{3-}$ bridging group (protonated as HO$_2$$^{2-}$ in the Co^{III}/Cr^{III} system) appears to be much more stable since the ejection of hydroxyl radical is detectable in a separate step (eq 18) for Sykes' system while the Ti(IV) complex is much more rapidly reorganized to the final TiO(edta)$^{2-}$ product. The greater stability of **11** might be due to the effect of two withdrawing metal centers. In both cases an oxo ligand is left behind at the metal center which binds peroxo. In the reduction of **10**, the oxo ligand becomes protonated in species (**12**) under the highly acidic conditions required for the Cr^{2+} reagent, while for the Ti(IV) complex at pH ~ 5 of this study, the oxo ligand exists alone.

It is interesting that the actual reduction step forming either **11** or the Ti(IV) analogue Ti(O$_2$)(edta)$^{3-}$ occurs at nearly the same rate of $\sim 10^2$ M^{-1} s^{-1}. As mentioned above, the lability of Ti(edta)(H$_2$O)$^-$ prevents an unambiguous assignment of mechanism for reaction 16; however, the likely conclusion is that the reduction of the peroxo group is an outer-sphere event. The closeness in the rates for the highly dissimilar cases described here suggests that bond reorganization factors within the O$_2$$^{3-}$ of HO$_2$$^{2-}$ ligand,[31] and less on the attached metal centers, determine the rate of formation of this species. Once formed, however, the rate of ejection of hydroxyl radical is very sensitive to the charges and number of metal centers to which O$_2$$^{3-}$ or HO$_2$$^{2-}$ is attached.

(31) The first empty orbital of H$_2$O$_2$ or O$_2$$^{2-}$ has σ^* symmetry: cf. W. L. Jorgenson and L. Salen, "The Organic Chemists' Book of Orbitals", Academic Press, New York, 1973, p 112. The existence of O$_2$$^{3-}$ or O$_2$H^{2-} is only likely in the presence of strongly withdrawing groups such as transition-metal centers in high oxidation states.

Contribution from the Istituto di Chimica Analitica, University of Padova, the CNR Laboratorio di Polarografia ed Elettrochimica Preparativa, and the CNR Centro di Studi sulla Stabilità e Reattività dei Composti di Coordinazione, 35100 Padova, Italy

Influence of the Nature of Tricovalent Phosphorus Ligands on the Relative Stability of Nickel(II), Nickel(I), and Nickel(0). An Electroanalytical Approach Providing Thermodynamic and Structural Information

GINO BONTEMPELLI,* FRANCO MAGNO, GILBERTO SCHIAVON, and BENEDETTO CORAIN

The cathodic behavior of anhydrous nickel(II) perchlorate in the presence of a variety of tricovalent phosphorus ligands has been investigated in acetonitrile. A combination of electroanalytical and spectrophotometric measurements have made possible the synthesis and the characterization of various nickel(0), nickel(I), and nickel(II) complexes. The employed electroanalytical tools have also made it possible to demonstrate that phosphine ligands such as PPh$_3$, PEtPh$_2$, PEt$_2$Ph, PEt$_3$, and dppe stabilize the +1 oxidation state with respect to the 0 and +2 ones, while the phosphites P(OPh)$_3$ and P(OEt)$_3$ act in the opposite way. The complex [Ni^I(P(OEt)$_3$)$_4$]$^+$ can be, however, prepared and accumulated thanks to kinetic reasons. These techniques have allowed also information on the geometric configuration of the synthesized species to be obtained. Moreover, the reversible half-wave potentials relative to the redox processes Ni^0 $\rightleftarrows$ Ni^I + e$^-$ have made possible the ranking of the employed ligands in a thermodynamically well-grounded sequence of ligand properties relative to their ability to stabilize the lower oxidation states of nickel. In the case of P(OPh)$_3$, a bis(phosphite)nickel(0) complex has been clearly identified and synthesized.

Introduction

The +1 oxidation state in nickel complexes could be considered "rare" till about ten years ago.[1] In this last decade the family of nickel(I) complexes has grown a great deal, and

the occurrence of the +1 state in the reaction patterns of nickel organometallic species is now well recognized.[2,3] Not surprisingly, a significant number of authentic nickel(I) complexes has been prepared by electrochemical procedures in the last

(1) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 3rd ed.; Wiley-Interscience: New York, 1972.
(2) Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 6319–6332.
(3) Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 7547–7560.

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