The following nonzero orbital parameters exist for this symmetry:

$$J_{a_1} = -\frac{1}{2}\,\frac{1}{U}(e_{b_{1u}} - e_{a_g})^2 \qquad J_{a_2} = -\frac{1}{2}\,\frac{1}{U}(e_{a_u} - e_{b_{1g}})^2$$
$$J_{b_1} = -\frac{1}{2}\,\frac{1}{U}(e_{b_{3u}} - e_{b_{2g}})^2 \tag{12}$$

The ground-state J is related to the orbital parameters by

$$J = \frac{1}{9}(J_{a_1} + J_{a_2} + J_{b_1}) \tag{13}$$

For simplicity en was substituted by two NH_3 molecules for the extended Hückel calculations. The numerical result for $J_{b_1}/J_{a_1}/J_{a_2}$ was 1.0/3.5/6.2. It is interesting to note that the same order was found by a similar technique for the dimers $Cr_2O_{10}^{14-}$, which have dioxo instead of dihydroxo bridges.[3] The orbital parameters in ref 16 are given in the local octahedral coordinate system. They are related to the parameters in the symmetry-adapted C_{2v} system by

$$\begin{aligned} {}^1\!/\!_2(J_{a_2} + J_{b_1}) &= J_{yzyz} + J_{yzxz} \\ -(J_{a_2}J_{b_1})^{1/2} &= J_{yzyz} - J_{yzxz} \\ J_{a_1} &= J_{xyxy} \end{aligned} \tag{14}$$

The following experimental values were determined in ref 16: $J_{yzxz} = -145$ cm^{-1}, $J_{xyxy} = -5$ cm^{-1}, $J_{yzyz} = 33$ cm^{-1}, and $J_{yzxy} = 22$ cm^{-1}. The latter two parameters are ferromagnetic. They cannot be properly accounted for by the present model. The neglect of ferromagnetic contributions restricts the number of parameters to 3 in our present treatment. The additional parameter J_{yzxy}, which does not occur in the transformation (14), should have no antiferromagnetic contribution according to our model, in good agreement with the small ferromagnetic value found experimentally. J_{yzyz} is also ferromagnetic, and it is therefore not meaningful to use eq 14 to derive numerical values for J_{a_2} and J_{b_1}. The main experimental result is the dominant antiferromagnetic contribution of J_{yzxz}. This is in good correspondence with the calculated dominance of J_{a_2}. J_{a_1} is experimentally found to be very small, a result that the calculation does not predict. This may, at least partly, be due to our neglect of a ferromagnetic contribution. This is expected to be largest for J_{a_1}[3] and would lead to a partial compensation of the kinetic part of J_{a_1}. The overall agreement between experiment and extended Hückel calculation is semiquantitative. The experimental data indicate the presence of relatively large ferromagnetic contributions that the present model does not take into account.

Conclusions

Extended Hückel calculations are quite a useful tool for rationalizing and predicting "kinetic exchange" in a series of related dimeric complexes. Considerable care is necessary, however, because very small energy differences are involved. Furthermore, ferromagnetic exchange contributions are neglected. As a means for obtaining absolute values of exchange parameters, the procedure presented in this paper is not adequate. However, when one considers a trend in a series of related complexes, these problems may be relatively unimportant. By changing the anion in the series $Cr_2X_9^{3-}$, we obtained particularly pleasing agreement between experimental and calculated J ratios. The semiquantitative reproduction of the trend in the series $Ti_2Cl_9^{3-}$, $V_2Cl_9^{3-}$, $Cr_2Cl_9^{3-}$ results from, and therefore confirms, our method of relating exchange parameters to energy differences between MO's. The weaknesses of the extended Hückel technique become apparent in the comparison between the isoelectronic species $V_2Cl_9^{5-}$ and $Cr_2Cl_9^{3-}$. The calculated ratio of the exchange parameters is one order of magnitude too small. One of the major weaknesses of the extended Hückel treatment is the poor description of the transition-metal ion due to the very small number of basis functions centered at M. This deficiency of the technique is much more apparent in a situation where we exchange a trivalent against a divalent metal ion than within a series of complexes with the same metal ion and different ligands. In the same sense we can rationalize the good results obtained in our calculations of relative orbital contributions to the total J in a given complex.

The inability of this model to account for ferromagnetic contributions to the net exchange is probably its most severe weakness. In order to account for experimental orbital exchange parameters with a ferromagnetic sign as well as complexes with rather large ferromagnetic exchange parameters, a different approach is needed.

Registry No. $Cr_2Cl_9^{3-}$, 38855-73-1; $Cr_2Br_9^{3-}$, 45976-44-1; $Cr_2I_9^{3-}$, 99617-98-8; $Ti_2Cl_9^{3-}$, 45976-69-0; $V_2Cl_9^{3-}$, 45976-71-4; $V_2Cl_9^{5-}$, 99617-99-9; $[(en)_2Cr(OH)_2Cr(en)_2]^{4+}$, 47022-64-8.

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Reduction of Peroxotitanium(IV) by Sulfur(IV), Iron(II), and Titanium(III) in Acidic Solution

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The net reduction of peroxotitanium(IV) by sulfur(IV) in acidic solution proceeds by a rate-determining dissociation of peroxide from TiO_2^{2+} followed by the rapid reaction of H_2O_2 and HSO_3^-. The absence of a detectable direct reaction between TiO_2^{2+} and either SO_2 or HSO_3^- is consistent with the previously proposed electrophilic nature of the peroxide moiety when coordinated to a d^0 transition-metal ion. The reduction of TiO_2^{2+} with excess iron(II) or titanium(III) was shown to proceed by both a direct reaction and reduction of H_2O_2 formed by dissociation of the peroxo complex. The rate expressions for the direct reactions are respectively $-d[TiO_2^{2+}]/dt = (k_a + k_b/[H^+])[TiO_2^{2+}][Fe(II)]$ and $(k_c/[H^+])[TiO_2^{2+}][Ti(III)]$. Values of $k_a = 1.1 \pm 0.1$ M^{-1} s^{-1} and $k_b = 0.16 \pm 0.01$ s^{-1} at 17 °C and $k_c = 11.1 \pm 0.4$ s^{-1} at 25 °C were determined at $I = 1.0$ M ($LiClO_4$). These rate constants are smaller than those reported previously for the corresponding reductions of H_2O_2. The results do not allow an assignment of an inner- or outer-sphere mechanism for the direct reactions. The reduced reactivity of the peroxide moiety in TiO_2^{2+} relative to H_2O_2 in our systems is contrasted with its enhanced reactivity observed in other studies.

Introduction

The reduction of hydrogen peroxide in acidic solution has been studied extensively. A one-electron transfer with concomitant formation of the hydroxyl radical is usually inferred for transition-metal ions.[1] On the other hand, a nonradical mechanism involving nucleophilic displacement on peroxide has been proposed

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(1) Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1983**, *22*, 779.

for a number of nucleophiles comprised of main-group elements.[2] Oxygen atom transfer from peroxide to the substrate has been demonstrated in several cases.

It is of interest to examine how these reduction processes and the attendant rates may be modified when the peroxide unit is complexed to a metal ion. Few such studies with inorganic species have been reported.[3] In contrast, there is considerable interest in the role of metal ion catalysts in the transfer of peroxidic oxygen to organic substrates.[4] We report here a kinetic study of the reduction of peroxotitanium(IV), TiO_2^{2+}, by sulfur(IV) and the transition metal ions iron(II) and titanium(III). The corresponding reactions with hydrogen peroxide have been investigated previously.[5-7] Peroxotitanium(IV) is readily formed according to eq 1. The formation constant[8] is 8.7×10^3 M^{-1} and the formation

$$TiO^{2+} + H_2O_2 \rightleftarrows TiO_2^{2+} + H_2O \qquad (1)$$

rate constant is 164 M^{-1} s^{-1} in 1.0 M $HClO_4$ at 25 °C.[8a,9] The ratio $[TiO_2^{2+}]/[H_2O_2]$ is easily maintained at large values by the use of excess TiO^{2+} although the possibility of reduction of the free H_2O_2 by the reducing agent must be considered. Titanium(IV) is not reduced by the reagents we have selected.

Experimental Section

Reagents. Solutions of $TiO(ClO_4)_2$ and $TiO(CF_3SO_3)_2$ were prepared by the method described previously.[8a] Fresh solutions of Na_2SO_3 in water were prepared for each set of experiments. Iron(II) solutions were made by the dissolution of reagent grade iron wire in perchloric acid and were stored under nitrogen. Traces of iron(III) were reduced by use of amalgamated zinc for the experiments monitored in the ultraviolet region. Solutions of titanium(III) were prepared from TiO^{2+} in triflic acid, CF_3SO_3H, by reduction with amalgamated zinc in an inert atmosphere. Hydrogen peroxide (Fisher, Certified, 30%, "stabilizer free") was used as supplied. Lithium perchlorate was prepared by neutralizing Li_2CO_3 with $HClO_4$ followed by three recrystallizations.

All other chemicals were of reagent grade and were used without further purification. Deionized water was distilled before use, first from acid dichromate and then from alkaline permanganate.

Analytical Procedures. Solutions of TiO^{2+}, H_2O_2, Ce(IV), and sulfur(IV) were analyzed by methods described previously.[8a] Iron(II) was determined by titration with permanganate that had been standardized against arsenious oxide. Titanium(III) was assayed by reaction with excess cerium(IV) followed by iodometric titration of the excess oxidant. TiO_2^{2+} was assayed spectrophotometrically at its 410-nm absorption maximum.

Table I. Kinetic Results for the Peroxotitanium(IV)–Sulfur(IV) System[a]

T, °C	$[HClO_4]$, M	$10^3[S(IV)]_0$, M	$10^2k_{SO_2}$, s^{-1} [b]
25.0	1.0	0.894	2.1
25.0	1.0	1.79	1.7
25.0	1.0	3.58	1.8
25.0	1.0	7.16	1.9
25.0	1.0	14.3	1.9
25.0[c]	1.0	3.58	1.7
25.0[d]	1.0	3.58	1.8
25.0	0.52	3.58	1.6
25.0	0.23	3.58	1.5
25.0	0.13	3.58	1.5
25.0[e]	0.13	3.58	1.9
17.0	1.0	3.58	0.61
17.0	1.0	7.16	0.64
10.0	1.0	3.58	0.24
10.0	1.0	7.16	0.23
4.0	1.0	3.58	0.094
4.0	1.0	7.16	0.099

[a] Unless otherwise indicated, $[TiO_2^{2+}]_0 = (4.33\text{–}4.43) \times 10^{-4}$ M, $[TiO^{2+}]_0 = 3.47 \times 10^{-3}$ M, and ionic strength = 1.0 M ($LiClO_4$). [b] Determined as the slope of plots of $-\ln(A - A_\infty)$ vs. t. [c] $[TiO_2^{2+}]_0 = 2.17 \times 10^{-4}$ M. [d] $[TiO^{2+}]_0 = 1.50 \times 10^{-3}$ M. [e] Ionic strength = 0.13 M.

Stoichiometric Determinations. The reduction of H_2O_2 by excess SO_2 (and/or HSO_3^-), Fe^{2+}, and Ti^{3+} has been shown previously[5-7] to be in accord with eq 2–4.

$$H_2O_2 + SO_2 \rightarrow HSO_4^- + H^+ \qquad (2)$$

$$2H^+ + H_2O_2 + 2Fe^{2+} \rightarrow 2Fe^{3+} + 2H_2O \qquad (3)$$

$$H_2O_2 + 2Ti^{3+} \rightarrow 2TiO^{2+} + 2H^+ \qquad (4)$$

The stoichiometric ratio $\Delta[TiO_2^{2+}]/[S(IV)]_0 = 0.99 \pm 0.02$ was determined spectrophotometrically by use of excess $[TiO_2^{2+}]$ in cells tightly stoppered to prevent loss of gaseous SO_2. The 2:1 stoichiometry for the reaction of excess Fe^{2+} with TiO_2^{2+} was confirmed by measuring the [Fe(III)] formed at 280 and 265 nm. The stoichiometric ratio $\Delta[Ti^{3+}]/[TiO_2^{2+}]_0 = 1.92 \pm 0.02$ was determined for the reaction of excess Ti^{3+} with TiO_2^{2+} in 1 M triflic acid. The excess Ti^{3+} was added to the solution of TiO_2^{2+} (containing initial concentrations $[H_2O_2] = 4.00 \times 10^{-4}$ M and $[TiO^{2+}] = 1.96 \times 10^{-3}$ M) under N_2. After complete reaction the excess Ti^{3+} was determined by addition of excess Ce(IV) followed by back-titration of the remaining oxidant.

Kinetic Procedures. The TiO_2^{2+}–S(IV) reaction was monitored at the 410-nm absorption maximum of TiO_2^{2+}, a wavelength where the other reagents are essentially transparent. The reactions were initiated by addition of a fresh solution of Na_2SO_3 in water to a spectrophotometer cell containing the other desired reagents. The cell was nearly full and was tightly stoppered to prevent loss of gaseous SO_2.

The TiO_2^{2+}–Fe(II) and H_2O_2–Fe(II) reactions were initiated by addition of Fe^{2+} to a spectrophotometer cell containing the other desired reagents. The peroxotitanium(IV) reaction was monitored either at 410 nm or by the appearance (largely) of Fe(III) at 280 and 265 nm.

The TiO_2^{2+}–Ti(III) reaction was monitored at 410 nm and was initiated by addition of Ti^{3+} under a nitrogen atmosphere. Triflic acid was used exclusively. Constant ionic strength was maintained with lithium perchlorate in the hydrogen ion dependence studies; the rate of reduction of ClO_4^- by Ti^{3+} was negligible relative to the reduction of TiO_2^{2+}.[10]

A Zeiss PMQII spectrometer equipped with a temperature-controlled (±0.1 °C) and rapid-mixing (~1 s) sample compartment was used. Fifteen to thirty optical density–time data pairs were analyzed for each experiment.

Results

Reaction Stoichiometries. The stoichiometries were determined with excess peroxotitanium(IV) for the SO_2 system and with excess reductant for the Fe^{2+} and Ti^{3+} reactions. The details are sum-

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(2) (a) Edwards, J. O. In "Inorganic Reaction Mechanisms"; Benjamin: New York, 1964. (b) Edwards, J. O. In "Peroxide Reaction Mechanisms"; Edwards, J. O., Ed.; Interscience: New York, 1962; pp 67–106.

(3) (a) Secco, F. *Inorg. Chem.* **1980**, *19*, 2722. (b) Wong, C.; Endicott, J. F. *Inorg. Chem.* **1981**, *20*, 2233. (c) McClendon, G.; Martell, A. E. *Inorg. Chem.* **1976**, *15*, 2662. But see: Al-Shatti, W.; Ferrer, M.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1980**, 2533. (d) Kristine, F. J.; Shepherd, R. E.; Siddiqui, S. *Inorg. Chem.* **1981**, *20*, 2571. (e) Hyde, M. R.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1974**, 1550. (f) Edwards, J. O.; Yang, C.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1974**, 1561. (g) Thompson, R. C. *Inorg. Chem.* **1985**, *24*, 3542. (h) McClendon, G.; Martell, A. E. *Coord. Chem. Rev.* **1976**, *19*, 1.

(4) (a) Chong, A. O.; Sharpless, K. B. *J. Org. Chem.* **1977**, *42*, 1587. (b) Mimoun, H.; Postel, M.; Casablanca, F.; Fischer, J.; Mitschler, A. *Inorg. Chem.* **1982**, *21*, 1303. (c) Mimoun, H.; Saussine, L.; Daire, E.; Postel, M.; Fischer, J.; Weiss, R. *J. Am. Chem. Soc.* **1983**, *105*, 3101. (d) Chaumette, P.; Mimoun, H.; Saussine, L.; Fischer, J.; Mitschler, A. *J. Organomet. Chem.* **1983**, *250*, 291. (e) Mimoun, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 734. (f) Sheldon, R. A.; Kochi, J. K. In "Metal-Catalyzed Oxidations of Organic Compounds"; Academic Press: New York, 1981; pp 48–97. (g) Sharpless, K. B.; Woodard, S. S.; Finn, M. G. *Pure Appl. Chem.* **1983**, *55*, 1823. (h) Mimoun, H. *Isr. J. Chem.* **1983**, *23*, 451. (i) Bach, R. D.; Wolber, G. J.; Coddens, B. A. *J. Am. Chem. Soc.* **1984**, *106*, 6098.

(5) (a) Hoffman, M. R.; Edwards, J. O. *J. Phys. Chem.* **1975**, *79*, 2096. (b) McArdle, J. V.; Hoffman, M. R. *J. Phys. Chem.* **1983**, *87*, 5425.

(6) Po, H. N.; Sutin, N. *Inorg. Chem.* **1968**, *7*, 261.

(7) Samuni, A.; Meisel, D.; Czapski, G. *J. Chem. Soc., Dalton Trans.* **1972**, 1273.

(8) (a) Thompson, R. C. *Inorg. Chem.* **1984**, *23*, 1794. There is still some debate concerning the formulation of titanium(IV) and its peroxo complex in acidic solution. See also: (b) Ellis, J. D.; Thompson, A. K.; Sykes, A. G. *Inorg. Chem.* **1976**, *15*, 3172. (c) Muhlebach, J.; Muller, K.; Schwarzenbach, G. *Inorg. Chem.* **1970**, *9*, 2381. (d) Veber, M.; Csanyi, L. J. *Acta Phys. Chem.* **1977**, *23*, 297. (e) Ciavatta, L.; Ferri, D.; Riccio, G. *Polyhedron* **1985**, *4* (1), 15.

(9) Orhanovic, M.; Wilkins, R. G. *J. Am. Chem. Soc.* **1967**, *89*, 278.

(10) (a) Cope, V. W.; Miller, R. G.; Fraser, R. T. M. *J. Chem. Soc. A* **1967**, 301. (b) Duke, F. R.; Quinney, P. D. *J. Am. Chem. Soc.* **1954**, *76*, 3800.

Table II. Kinetic Results for the Reduction of TiO_2^{2+} and H_2O_2 by Fe^{2+}

T, °C	λ, nm	$[HClO_4]$, M[a]	$10^3 \times$ initial concn, M TiO^{2+}	 TiO_2^{2+} [b]	 Fe^{2+}	k_{obsd},[c] $M^{-1}\ s^{-1}$	k_1,[d] $M^{-1}\ s^{-1}$
25.0	410	1.0	3.63	0.240	4.96	3.1_1	2.4
25.0	280	1.0	3.63	0.240	4.96	3.1_3	2.4
17.0	410	1.0	13.7	0.383	11.3	1.4_3	1.3
17.0	410	1.0	3.53	0.395	2.35	1.8_0	1.3
17.0	410	1.0	3.48	0.390	4.65	1.8_5	1.4
17.0	410	1.0	1.57	0.386	2.35	2.1_4	1.2
17.0	410	1.0	0.800	0.369	2.35	2.6_0	1.2
17.0	410	0.73	3.48	0.390	4.65	1.6_9	1.2
17.0	410	0.52	3.48	0.390	4.65	1.8_4	1.4
17.0	410	0.26	3.48	0.390	4.65	2.0_3	1.6
17.0	410	0.108	3.48	0.390	4.65	3.0_8	2.7
17.0	410	0.069	1.56	0.381	4.65	3.9_1	3.2
10.0	410	1.0	3.44	0.388	6.90	0.94_0	0.78
10.0	410	1.0	3.37	0.380	11.3	0.91_1	0.79

T, °C	λ, nm	$[HClO_4]$, M[a]	$10^4[H_2O_2]_0$, M	$10^4[Fe^{2+}]_0$, M	k'_{obsd}, $M^{-1}\ s^{-1}$ [e]
25.0	265	1.0	0.672	7.25	$53._2$
17.0	280	1.0	1.39	6.75	$33._1$
17.0	265	1.0	0.672	6.80	$34._6$
10.0	280	1.0	1.39	6.75	$22._9$
10.0	265	1.0	0.672	6.80	$23._3$
10.0	280	0.13	1.39	6.75	$22._0$
10.0	265	0.13	0.692	6.80	$22._8$

[a] Ionic strength was maintained at 1.0 M with $LiClO_4$. [b] With the exception of the seventh experiment, greater than 96% of the total peroxide is initially complexed as TiO_2^{2+}. [c] Calculated from the slope of a plot of ln $([Fe^{2+}]/[TiO_2^{2+}])$ vs. t, where k_{obsd} = slope/$([Fe^{2+}]_0 - 2[TiO_2^{2+}]_0)$. [d] Calculated by means of eq 11. [e] Calculated from the slope of a plot of ln $([Fe^{2+}]/[H_2O_2])]$ vs. t, where k'_{obsd} = slope/$([Fe^{2+}]_0 - 2[H_2O_2]_0)$.

marized in the Experimental Section. The results are consistent with eq 5–7 and indicate that the overall reactions are analogous to the corresponding reductions of hydrogen peroxide.

$$H_2O + TiO_2^{2+} + SO_2 \rightarrow TiO^{2+} + HSO_4^- + H^+ \qquad (5)$$

$$2H^+ + TiO_2^{2+} + 2Fe^{2+} \rightarrow TiO^{2+} + 2Fe^{3+} + H_2O \qquad (6)$$

$$H_2O + TiO_2^{2+} + 2Ti^{3+} \rightarrow 3TiO^{2+} + 2H^+ \qquad (7)$$

Kinetic Studies. The kinetics of the reduction of peroxotitanium(IV) by sulfur(IV) were monitored at the TiO_2^{2+} absorption maximum at 410 nm. Plots of $-\ln (A - A_\infty)$ vs. time were linear to 95% of complete reaction. The experimental conditions and slopes of the kinetic plots, k_{SO_2}, are summarized in Table I. The data are consistent with the rate expression given in eq 8.

$$-d[TiO_2^{2+}]/dt = k_{SO_2}[TiO_2^{2+}] \qquad (8)$$

The values of the rate parameter k_{SO_2} are independent of the excess sulfur(IV) concentration and decrease only slightly with decreasing hydrogen ion concentration over the range 0.13–1.0 M at an ionic strength of 1.0 M. Values of the activation parameters $\Delta H^* = 22.4 \pm 0.1$ kcal/mol and $\Delta S^* = 8.8 \pm 0.4$ cal/(deg mol) were determined from the temperature dependence of k_{SO_2}.

The kinetics of the reduction of TiO_2^{2+} by excess Fe^{2+} were monitored by following the disappearance of TiO_2^{2+} at 410 nm or (largely) the appearance of Fe(III) at 280 and 265 nm. The kinetics of the H_2O_2–Fe^{2+} reaction were briefly reinvestigated by monitoring the formation of Fe(III). Plots of ln $([Fe^{2+}]/[TiO_2^{2+}])$ and ln $([Fe^{2+}]/[H_2O_2])$ vs. time, respectively, were linear for at least 80% of total reaction. These results are in accord with rate expressions 9 and 10, respectively.

$$-d[TiO_2^{2+}]/dt = \tfrac{1}{2}d[Fe(III)]/dt = k_{obsd}[TiO_2^{2+}][Fe^{2+}] \qquad (9)$$

$$-d[H_2O_2]/dt = \tfrac{1}{2}d[Fe(III)]/dt = k'_{obsd}[H_2O_2][Fe^{2+}] \qquad (10)$$

The experimental results are summarized in Table II. Our values of k'_{obsd} for the H_2O_2–Fe^{2+} reaction are in good agreement with those previously reported.[6] Values of the activation parameters $\Delta H^* = 8.8 \pm 0.2$ kcal/mol and $\Delta S^* = -21 \pm 1$ cal/(deg mol) were determined from the temperature dependence of k'_{obsd}.

The values of k_{obsd} for the TiO_2^{2+}–Fe^{2+} reaction increase with a decrease in the excess $[TiO_2^{2+}]$ and to a lesser extent with a decrease in the excess $[Fe^{2+}]$. These metal ion dependencies are satisfactorily correlated by eq 11. This expression is derived from

$$k_{obsd} = k_1 + k_2k_4/(k_3[TiO^{2+}]_{av} + k_4[Fe^{2+}]_{av}) \qquad (11)$$

the reaction scheme shown in eq 12–15 if the steady-state approximation is made for the free, uncomplexed $[H_2O_2]$ and the concentration of the hydroxyl radical. Water and hydrogen ions

$$H^+ + TiO_2^{2+} + Fe^{2+} \rightarrow TiO^{2+} + Fe^{3+} + \cdot OH \quad k_1 \qquad (12)$$

$$H_2O + TiO_2^{2+} \rightleftarrows TiO^{2+} + H_2O_2 \quad k_2, k_3 \qquad (13)$$

$$H^+ + H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + \cdot OH + H_2O \quad k_4 \qquad (14)$$

$$H^+ + \cdot OH + Fe^{2+} \rightarrow Fe^{3+} + H_2O \quad \text{fast} \qquad (15)$$

are included only for material balance and have no kinetic implications. Values of k_2 and k_3 were estimated from data previously reported.[8a] Appropriate values of k_4 were taken from the k'_{obsd} values in Table II. Reaction 15 is known to be very rapid ($k > 10^8\ M^{-1}\ s^{-1}$)[11] and provides the sole "sink" for the hydroxyl radicals under our experimental conditions.[20] The average values of the excess titanium(IV), $[TiO^{2+}]_{av}$, and the excess iron(II), $[Fe^{2+}]_{av}$, concentrations for the individual experiments were taken as $[Ti(IV)]_{tot} - [H_2O_2]_{tot\ init}/2$ and $[Fe^{2+}]_{init} - [H_2O_2]_{tot\ init}$, respectively.

The resulting values of k_1 as calculated in this manner are listed in the last column of Table II. A pathway inversely dependent on the $[H^+]$ was detected at 17 °C, where $k_1 = 1.1 \pm 0.1\ M^{-1}\ s^{-1} + (0.16 \pm 0.01\ s^{-1})/[H^+]$. The activation parameters $\Delta H^* = 11.9 \pm 0.6$ kcal/mol and $\Delta S^* = -17 \pm 2$ cal/(deg mol) were determined from the temperature dependence of k_1 in 1.0 M $HClO_4$ (where the acid-independent path is predominant).

The kinetics of the TiO_2^{2+}–Ti^{3+} reaction were monitored at 410 nm. Plots of ln $([Ti^{3+}]/[TiO_2^{2+}])$ vs. time were linear for at least 80% of total reaction, in accordance with the rate expression

$$-d[TiO_2^{2+}]/dt = k_{Ti}[TiO_2^{2+}][Ti^{3+}] \qquad (16)$$

The experimental conditions and kinetic results are summarized in Table III. The values of the rate parameter k_{Ti} are seen to increase with decreasing excess of either $[TiO^{2+}]$ or $[Ti^{3+}]_0$ and with decreasing $[H^+]$ at a constant ionic strength of 1.1 M. The metal ion dependencies are satisfactorily correlated by eq 17. This

$$k_{Ti} = k_5 + k_2k_6/(k_3[TiO^{2+}]_{av} + k_6[Ti^{3+}]_{av}) \qquad (17)$$

expression is identical in form with eq 11 and may be derived from the reaction scheme given in eq 18–21 in the same manner as for the iron(II) system.

$$H_2O + TiO_2^{2+} + Ti^{3+} \rightarrow 2TiO^{2+} + \cdot OH + H^+ \quad k_5 \qquad (18)$$

$$H_2O + TiO_2^{2+} \rightleftarrows TiO^{2+} + H_2O_2 \quad k_2, k_3 \qquad (19)$$

$$H_2O_2 + Ti^{3+} \rightarrow TiO^{2+} + \cdot OH + H^+ \quad k_6 \qquad (20)$$

$$\cdot OH + Ti^{3+} \rightarrow TiO^{2+} + H^+ \quad \text{fast} \qquad (21)$$

Values of k_6 at 25 °C are available;[12] values at 17 and 10 °C were estimated by assuming an activation energy of 6 kcal/mol. Reaction 21 is known to be very rapid ($k = 3 \times 10^9\ M^{-1}\ s^{-1}$ at 25 °C).[7] The average values of the excess titanium(IV), $[TiO^{2+}]_{av}$, and the excess titanium(III), $[Ti^{3+}]_{av}$, concentrations for the individual experiments were taken as $[Ti(IV)]_{tot\ init} + [H_2O_2]_{tot\ init}/2$ and $[Ti(III)]_{init} - [H_2O_2]_{tot\ init}$, respectively.

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(11) Ross, A. E.; Neta, P. *Natl. Stand. Ref. Data Ser.* (*U.S., Natl. Bur. Stand.*) **1979**, *NSRDS-NBS 65.*

(12) As noted by Espenson,[1] the values of the rate constants for the H_2O_2–Ti(III) reaction given in ref 7 are too low by a factor of 2 due to a computational error.

Table III. Kinetic Results for the Reduction of TiO_2^{2+} by Ti^{3+}

T, °C	$[H^+]$, M[a]	10^3 × initial concn, M TiO^{2+}	 TiO_2^{2+}[b]	 Ti(III)	k_{Ti},[c] M^{-1} s^{-1}	k_5,[d] M^{-1} s^{-1}	$k_5[H^+]$, s^{-1}
25.0	9.61	9.61	0.389	2.49	14.$_0$	10.$_4$	11.$_3$
25.0	1.05	6.61	0.385	2.49	15.$_0$	10.$_6$	11.$_1$
25.0	1.04	2.13	0.369	2.49	16.$_7$	10.$_2$	10.$_6$
25.0	1.02	0.905	0.345	2.49	17.$_6$	10.$_1$	10.$_3$
25.0	0.764	9.61	0.389	2.45	18.$_2$	14.$_6$	11.$_2$
25.0	0.438	9.61	0.389	2.45	29.$_6$	26.$_0$	11.$_4$
25.0	0.281	9.61	0.389	2.45	46.$_9$	43.$_2$	12.$_1$
							av 11.$_1$ ± 0.$_4$
17.0	1.11	9.31	0.377	4.16	5.8$_5$	4.$_7$	5.$_2$
17.0	1.09	9.61	0.389	2.45	6.8$_2$	5.$_3$	5.$_8$
17.0	1.08	9.80	0.395	1.56	6.8$_2$	5.$_0$	5.$_4$
17.0	0.764	9.61	0.389	2.45	8.4$_4$	7.$_0$	5.$_3$
17.0	0.438	9.61	0.389	2.45	14.$_6$	13	5.$_7$
17.0	0.259	9.61	0.389	2.45	22.$_3$	21	5.$_4$
							av 5.$_5$ ± 0.$_2$
10.0	1.09	9.61	0.389	2.50	2.6$_4$	2.$_0$	2.$_2$
10.0	0.764	9.61	0.389	2.50	3.7$_7$	3.$_2$	2.$_4$
10.0	0.438	9.61	0.389	2.50	6.5$_4$	5.$_9$	2.$_6$
10.0	0.270	9.61	0.389	2.50	9.7$_7$	9.$_1$	2.$_5$
							av 2.$_4$ ± 0.$_1$

[a] Trifluoromethanesulfonic acid was used. Ionic strength was maintained at 1.1 M with $LiClO_4$. [b] With the exception of the third and fourth experiments, >98% of the total peroxide is initially complexed as TiO_2^{2+}. [c] Calculated from the slope of a plot of ln $([Ti(III)]/[TiO_2^{2+}])$ vs. t, where $k_{Ti} = \text{slope}/([Ti(III)]_0 - 2[TiO_2^{2+}]_0)$. [d] Calculated by means of eq 14.

The resulting values of k_5 are listed in the next to last column of Table III. Under our experimental conditions the rate parameter k_5 is inversely dependent on $[H^+]$, as may be seen from the values of $k_5[H^+]$ in the last column of Table III. Activation parameters for this pathway are $\Delta H^* = 16._5 \pm 1._2$ kcal/mol and $\Delta S^* = 2 \pm 4$ cal/(deg mol).

Discussion

The rate-limiting step in the sulfur(IV) system appears to be loss of peroxide from peroxotitanium(IV):

$$TiO_2^{2+} + H_2O \rightarrow H_2O_2 + TiO^{2+} \quad k_2 \qquad (22)$$

$$H_2O_2 + HSO_3^- \rightarrow HSO_4^- + H_2O \quad k_{23} \qquad (23)$$

The values of k_{SO_2} listed in Table I are within experimental error identical with those determined previously for k_2.[8a] The reduction of free H_2O_2 by HSO_3^- is very rapid ($k_{23} = 2.4 \times 10^6$ M^{-1} s^{-1} at 15 °C and $[H^+] = 1.0$ M).[5b] The $[HSO_3^-]$ ranged from 2 to 12% of the total [S(IV)] over our experimental conditions.[5b,13]

A noteworthy feature is that we see no indication of a direct reaction between TiO_2^{2+} and either HSO_3^- or SO_2, even though the ratio $[TiO_2^{2+}]/[H_2O_2]$ is quite large in our experiments (typically 27 prior to addition of S(IV) and $\sim 10^4$ during the reaction on the basis of a steady-state analysis). Peroxotitanium(IV) was also found to be unreactive toward chlorine, and the reaction was proposed to proceed solely by oxidation of traces of free hydrogen peroxide.[8a] A common feature in both of these nonradical reactions is the requirement of the formation of a precursor peroxo complex prior to electron transfer: O_2SOOH^- with sulfur(IV)[5] and ClOOH with chlorine.[14] Peroxotitanium(IV) is apparently unable to form these precursor peroxo complexes and as a result is quite unreactive relative to hydrogen peroxide in both systems. The peroxo complex of zirconium(IV) was also found to be unreactive toward sulfur(IV), although in this case the comparison is complicated by the tetrameric structure of peroxozirconium(IV).[3g]

On the other hand, a variety of peroxo complexes of later transition metal ions have been shown to be quite reactive toward SO_2, although under experimental conditions rather different from those we have employed. Examples include several group 8 metals,[15] some metalloporphyrins,[16] and both monomeric[17] and dicobalt(III)[3f] species. In several cases sulfato complexes were detected as a result of the facile uptake of SO_2. Many of these peroxo complexes have the η^2 (triangular) geometry, as does TiO_2^{2+} in all likelihood. It has been noted that formally the peroxide moiety behaves as a nucleophile in the group 8 complexes but as an electrophile in the d^0 complexes.[18] Our observation that TiO_2^{2+} is quite unreactive toward HSO_3^- and SO_2 is consistent with this proposal. The facile reaction of H_2O_2 and HSO_3^- has been viewed as involving nucleophilic substitution by H_2O_2 on HSO_3^-.[5] However, the electrophilic nature of the peroxide moiety in TiO_2^{2+} can apparently be modified by the presence of other ligands in the coordination sphere of the metal. A titanium(IV) porphyrin peroxo complex has recently been shown to be reactive toward SO_2.[16]

The reaction schemes we have proposed for both the iron(II) and titanium(III) systems involve competition between a direct reduction of peroxotitanium(IV) and reduction of hydrogen peroxide formed by dissociation of the peroxo complex. Qualitatively, the rate constants for the direct reactions are considerably smaller, and these pathways were detected only by the use of excess concentrations of both the reductant and free titanium(IV). Quantitative rate comparisons between the TiO_2^{2+} and H_2O_2 paths are complicated by the increased importance of an inverse-$[H^+]$ dependence for the direct reactions. The rate constant (k_4) for the iron(II)–H_2O_2 reaction is independent[6] of $[H^+]$, whereas k_1 for the iron(II)–TiO_2^{2+} is equal to $1._1$ M^{-1} s^{-1} + 0.1_6 $s^{-1}/[H^+]$ at 17 °C. At 25 °C, k_6 for the titanium(III)–H_2O_2 system is approximately[7] equal to 500 M^{-1} s^{-1} + 42 $s^{-1}/[H^+]$, whereas k_5 for the titanium(III)–TiO_2^{2+} system is equal to 11 $s^{-1}/[H^+]$. That titanium(III) is able to utilize an inverse-$[H^+]$ path in the reduction of H_2O_2 whereas iron(II) is not as consistent with the greater tendency of Ti^{3+} to undergo hydrolysis.[19] The inverse-$[H^+]$ terms detected for both reductants in the direct reactions with TiO_2^{2+} serve to lower the relatively high charge on the activated complexes. The enhanced reactivity of titanium(III) over that of

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(13) Deveze, D.; Rumpf, P. *C. R. Hebd. Seances Acad. Sci.* **1964**, *258*, 6135.

(14) (a) Connick, R. E. *J. Am. Chem. Soc.* **1947**, *69*, 1509. (b) Held, A. M.; Halko, D. J.; Hurst, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 5732.

(15) Valentine, J. S. *Chem. Rev.* **1973**, *73*, 233.

(16) Miksztal, A. R.; Valentine, J. S. *Inorg. Chem.* **1984**, *23*, 3548.

(17) Ohishi, T.; Kashiwabara, K.; Fujita, J. *Chem. Lett.* **1984**, 1917.

(18) (a) Regen, S. L.; Whitesides, G. M. *J. Organomet. Chem.* **1973**, *59*, 293. (b) Norman, J. G. *Inorg. Chem.* **1977**, *16*, 1328.

(19) (a) Brunschwig, B. S.; Sutin, N. *Inorg. Chem.* **1979**, *15*, 1934. (b) Birk, J. P. *Inorg. Chem.* **1975**, *14*, 1724. (c) Ram, M. S.; Martin, A. H.; Gould, E. S. *Inorg. Chem.* **1983**, *22*, 1103.

(20) A reviewer suggested that the ferryl ion, FeO^{2+}, may be formed as an intermediate in reaction 12 rather than the hydroxyl radical. While our results do not allow a distinction to be made between these possibilities, there is little doubt that hydroxyl radicals are formed in reaction 14. See: Koppenol, W. H.; Liebman, J. I. *J. Phys. Chem.* **1984**, *88*, 99.

iron(II) toward both H_2O_2 and TiO_2^{2+} probably reflects the greater reducing strength of titanium(III).

The greater reactivity of H_2O_2 relative to TiO_2^{2+} persists even when allowance is made for the role of the hydrogen ion. Electrostatic effects could account for some of the difference. If the TiO_2^{2+} reactions are inner sphere, as the H_2O_2 reactions almost certainly are, then the reduced "nucleophilic" character of the peroxide moiety in TiO_2^{2+} may be important. Inner-sphere reductions of H_2O_2 by transition-metal ions are in general much more rapid than their outer-sphere counterparts.[1] Unfortunately, our results do not allow us to make a distinction between inner-sphere and outer-sphere mechanisms for the reduction of TiO_2^{2+} by either iron(II) or titanium(III).

In none of the three systems reported here is there a kinetic advantage imparted when the peroxide moiety is complexed to titanium(IV). That this is probably due to the nature of the reductants rather than a general effect may be inferred by consideration of the results obtained in other studies of d^0 metal ion peroxo complexes. Several of these metal ions, including titanium(IV), are effective catalysts in promoting the epoxidation of olefins by peroxides.[4] While the detailed mechanisms of these important reactions are debatable, there is a concensus[4] that the role of the metal ion is to organize the olefin and peroxide for reaction by coordination of both. A similar mechanism has been proposed for the reduction of peroxo complexes of vanadium(V) by iodide ion.[3a] Nucleophilic attack at the titanium(IV) center is unlikely for any of the reductants we have examined.

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Circularly Polarized Luminescence Studies of the Ternary Complexes Formed by Terbium(III) with Chiral Amino Polycarboxylates and Achiral Substrate Ligands

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Circularly polarized luminescence (CPL) spectroscopy has been used to study the ternary complexes formed by Tb(III) with chiral amino polycarboxylate (APC) and achiral carboxylate ligands. It was observed that when the steric requirements of the achiral carboxylate ligand were minor (e.g., small ligand bite), the Tb(III) chirality was essentially unchanged relative to that of the parent Tb(APC) complex. However, with certain bulky bidentate and tridentate ligands, the CPL spectra revealed that formation of the ternary complexes could perturb the amino polycarboxylate conformation. Above pH 10, the parent Tb(APC) compounds are known to exist as polynuclear species. The self-association process was found to take place in the ternary complexes when the substrate ligand bound too weakly to interfere with the process. When the substrate bound strongly with the Tb(APC) complex, the compounds remained monomeric at all pH values.

Introduction

Mixed-ligand lanthanide complexes containing an amino polycarboxylate (APC) ligand and other chelating species have recently been investigated since the Ln(APC) complexes appear to be useful as aqueous NMR shift reagents.[1-4] Peters and Kieboom have recently summarized the utility of lanthanide-induced shifts for study of molecular complexation in aqueous solutions.[5] Perhaps the greatest use of Ln(APC) complexes as aqueous shift reagents has been in the study of nucleotide conformation in aqueous solution.[6-8] The Eu(III) derivative of (*R*)-(−)-1,2-propanediaminetetraacetic acid ((*R*)-(−)-PDTA) has recently been shown to be an effective chiral shift reagent for the study of hydroxy, amino, and carboxylic acids in aqueous solutions.[9]

Studies of lanthanide ion chirality can be used to obtain useful information on these complexation processes. We have used circularly polarized luminescence (CPL) spectroscopy to study the complexation phenomena between Tb(APC) compounds and (*S*)-aspartic acid,[10] (*S*)-α-hydroxy carboxylic acids,[11] and (*R*,*R*)-tartaric acid.[12] At the onset, it was assumed that the nature of the achiral APC ligand would not affect the interaction of the Tb(III) ion and the chiral carboxylates. This assumption was not always found to be true;[12] hence, it has become clear that steric interactions may exist between the APC ligand and the additional carboxylate ligand.

These interactions among the ligands in the ternary complexes would be functions of the steric requirements of the various ligands. In the present work, the results of CPL investigations designed to study the steric interactions between APC and carboxylate ligands in Tb(III) complexes are reported. We have chosen to work with two chiral amino polycarboxylate ligands upon which CPL results have already been obtained for the simple binary complexes.[13] The amino polycarboxylate ligands used were (*R*)-(−)-PDTA and (*R*,*R*)-(−)-*trans*-1,2-cyclohexanediaminetetraacetic acid ((*R*,*R*)-(−)-CDTA). The mixed-ligand complexes of Tb((*R*)-(−)-PDTA), Tb(PDTA), and Tb((*R*,*R*)-(−)-CDTA), Tb(CDTA), were formed with a wide variety of achiral carboxylic acids, and the interaction phenomena were studied primarily by means of CPL spectroscopy.

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[†] Seton Hall University.

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(1) Elgavish, G. A.; Reuben, J. *J. Am. Chem.* **1976**, *98*, 4755.
(2) Reuben, J. *J. Am. Chem. Soc.* **1976**, *98*, 3726.
(3) Sherry, A. D.; Yang, P. P.; Morgan, L. O. *J. Am. Chem. Soc.* **1980**, *102*, 5755.
(4) Wenzel, T. J.; Ashley, M. E.; Sievers, R. E. *Anal. Chem.* **1982**, *54*, 615.
(5) Peters, J. A.; Kieboom, A. P. G. *Recl.: J. R. Neth. Chem. Soc.* **1983**, *102*, 381.
(6) Dobson, C. M.; Williams, R. J. P.; Xavier, A. V. *J. Chem. Soc., Dalton Trans.* **1974**, 1762.
(7) Geraldes, C. F. G. C.; Williams, R. J. P. *Eur. J. Biochem.* **1979**, *97*, 93.
(8) Sherry, A. D.; Stark, C. A.; Ascenso, J. R.; Geraldes, C. F. G. C. *J. Chem. Soc., Dalton Trans.* **1981**, 2078.
(9) Kabuto, K.; Sasaki, Y. *J. Chem. Soc., Chem. Commun.* **1984**, 316.
(10) Brittain, H. G. *Inorg. Chim. Acta* **1983**, *70*, 91.
(11) Ransom, M.; Brittain, H. G. *Inorg. Chem.* **1983**, *22*, 2494.
(12) Brittain, H. G.; Ransom, M. *Inorg. Chim. Acta* **1984**, *95*, 113.
(13) Brittain, H. G.; Pearson, K. H. *Inorg. Chem.* **1983**, *22*, 78.