3704 *Inorg. Chem.* **1987**, *26*, 3704–3708

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Characterization of the Perhydroxytitanyl(2+) Ion in Acidic Aqueous Solution. Products and Kinetics of Its Decomposition

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Received May 8, 1987

Peroxotitanium(IV) is shown to have the composition $Ti(O_2)^{2+}$. The stability constant $K_{H_2O_2} = (8.7 \pm 1.4) \times 10^3$ M^{-1}, determined at 25 °C and $I = 1.0$ ($NaClO_4$), agrees with the literature value and is acid-independent. The oxidation of $Ti(O_2)^{2+}$ by Ce^{IV} produces the title complex, $TiO(HO_2^{\bullet})^{2+}$, which was characterized via its decomposition kinetics. TiO^{2+} and $HO_2^{\bullet}$ are formed reversibly in an acid-catalyzed ($\Delta H_{1,H}^{\ddagger} = 81 \pm 8$ kJ mol^{-1}, $\Delta S_{1,H}^{\ddagger} = 7.6 \pm 3.3$ J mol^{-1} K^{-1}) and a spontaneous associative ($\Delta H_{1,o}^{\ddagger} = 62 \pm 5$ kJ mol^{-1}, $\Delta S_{1,o}^{\ddagger} = -68 \pm 18$ J mol^{-1} K^{-1}) substitution process. In a second, fast step, $HO_2^{\bullet}$ and $TiO(HO_2^{\bullet})^{2+}$ are transformed irreversibly into $Ti(O_2)^{2+}$, O_2, and H_2O. The charge of $TiO(HO_2^{\bullet})^{2+}$, was determined from the ionic strength dependence of its acid-catalyzed decay. This is the first example of a thermodynamic, kinetic, and structural characterization of a complex of $HO_2^{\bullet}$ with a transition-metal aqua ion in solution. Molecular oxygen does not react with aquatitanium(III) at all, but it oxidizes hydroxotitanium(III) at the rate $k_3 = 4.25 \pm 0.13$ M^{-1} s^{-1} (25 °C, $I = 1.0$, LiCl). The transition state arising from this reaction is different from and higher in energy than those formed via the decomposition of $TiO(HO_2^{\bullet})^{2+}$.

Introduction

Currently, the peroxotitanium(IV) complex is usually formulated as $Ti(O_2)^{2+}$, although its composition has not been established.[1] On the basis of recently available knowledge[2,3] that titanium(IV) exists as TiO^{2+} in acidic solution, the present study shows by spectrophotometric measurements and ion-exchange chromatography that the formulation $Ti(O_2)^{2+}$ is correct.

Recently, Thompson[4] reported the generation of a superoxotitanium(IV) complex (which was not characterized) via oxidation of $Ti(O_2)^{2+}$ by Ce^{IV}. The lifetime of this species was found to be pH-dependent and to be on the order of seconds.[4] It increases slightly with increasing pH.[4]

EPR spectra of superoxo complexes of Ce^{III}, Ti^{IV}, Zr^{IV}, Hf^{IV}, Th^{IV}, V^{V}, Nb^{V}, Mo^{VI}, and U^{VI} have been reported[5,6] some time ago, but their structures or compositions still remain unknown. Furthermore, the decomposition mechanism has not been studied so far. Therefore, we investigated the decomposition kinetics of the superoxotitanium(IV) complex. This allowed us to identify this species as perhydroxytitanyl(2+) and to derive its detailed mechanism of decomposition. This study offers complete thermodynamic, kinetic, and structural information on a complex of a metal aqua (oxo) ion with the perhydroxyl radical.

Surprisingly, we found that the oxidation of aqueous titanium(III) by molecular oxygen proceeds via the outer-sphere pathway, producing initially superoxide anions. Oxygen addition to titanium(III) does not occur.

Experimental Section

Materials. $TiOSO_4 \cdot 2H_2O$ was obtained from Dr. D. Urwin (British Tioxide UK Limited) and purified according to the literature.[7] $TiO(ClO_4)_2$, $TiO(CF_3SO_3)_2$, and $TiOCl_2$ (0.1 M) in 1 M solutions of the corresponding acid were prepared by dissolving $TiOSO_4 \cdot 2H_2O$ in 2 M acid and adding slowly a stoichiometric amount of the corresponding Ba^{2+} salt dissolved in water. The solutions were filtered through Millipore membrane filters (0.1 μM) and stored in the freezer. Titanium(IV) was analyzed spectrophotometrically as peroxotitanium.[8] Ti^{3+} was prepared by reduction of a $TiOX_2$ (X = Cl, CF_3SO_3) solution (0.1 M) with amalgamated zinc.

Physical Measurements. Spectrophotometric measurements were performed on a Hewlett-Packard 8450 A instrument thermostated to 25 °C. A High Tech SFA-11 rapid-mixing device was used to measure the superoxotitanium(IV) decomposition.

Stability Constant of Peroxotitanium. The parameters ϵ_{412} and $K_{H_2O_2}$ were calculated by a least-squares fit assuming that the following equations hold:

$$D_{412} = \epsilon_{412}[Ti(O_2)^{2+}]$$

$$K_{H_2O_2} = [Ti(O_2)^{2+}]/([TiO^{2+}][H_2O_2])$$

$$[Ti^{IV}]_{tot} = [TiO^{2+}] + [Ti(O_2)^{2+}]$$

$$[H_2O_2]_{tot} = [H_2O_2] + [Ti(O_2)^{2+}]$$

The function $\sum_i (D_{obsd,i} - D_{calcd,i})^2$ was minimized.

Kinetics. (a) Decomposition of Perhydroxytitanyl(2+). Solutions containing Ti^{IV} and H_2O_2 at a given $[H^+]$ and ionic strength were reacted with solutions of $(NH_4)_2Ce^{IV}(NO_3)_6$ at the same $[H^+]$ and ionic strength by using the SFA-11 instrument. Re-formation of $Ti(O_2)^{2+}$ was monitored at 410 nm.[4] The first-order rate constants k_I = (slope)/2 were obtained by least-squares fits of ln $(D_\infty - D)$ vs $-t$ using the weight $w = (D_\infty - D)^2$.

(b) Oxidation of Ti^{3+} by Molecular Oxygen. A solution of 0.1 M TiO^{2+} and 1 M H^+ was deoxygenated by purified N_2 (Cr^{2+}) and reduced over amalgamated Zn overnight, leading to a solution of 0.1 M Ti^{3+} and 0.8 M H^+. The anion was Cl^- or $CF_3SO_3^-$. This solution was prepared freshly every day. Five milliliters of reactant solution was prepared as follows: 2.5–4.5 mL of a solution containing H^+ and Li^+ was saturated with O_2 at ~1 atm and ~25 °C. The reaction was started by adding quickly 0.5–2.5 mL of Ti^{3+} solution and transferring the mixture into a serum-capped 1-cm quartz cell. Care was taken to remove any bubbles from the reaction solution in the cell in order to avoid perturbations of the reaction by O_2 supply from a bubble. All the solutions were handled with gastight syringes. Spectral scans over the range λ = 260–600 nm showed that for every Ti^{3+} consumed one TiO^{2+} was formed. Usually, the reaction was monitored at 270 nm, but runs at 502 nm in a 10-cm cell produced the same rates.

Results and Discussion

Structure of Peroxotitanium(IV). In general, peroxotitanium(IV) is believed to exist as $Ti(O_2)^{2+}$ in acid solution (pH ≤1) although $Ti(O_2)OH^+$ has been postulated on the basis of electrochemical measurements,[9] also. To our knowledge, the composition of peroxotitanium(IV) has not been proven so far.

The present results support the $Ti(O_2)^{2+}$ structure: Ti^{IV} is known[2,3] to exist as TiO^{2+} in acidic aqueous solutions. The UV-vis spectra measured at various $[H^+]$, $[Ti^{IV}]_{tot}$, and $[H_2O_2]_{tot}$ (Table I) are consistent with the presence of equilibrium 1, solely. The

$$TiO^{2+} + H_2O_2 \rightleftarrows Ti(O_2)^{2+} + H_2O \quad K_{H_2O_2} \qquad (1)$$

measured equilibrium constant $K_{H_2O_2} = (8.7 \pm 1.4) \times 10^3$ M^{-1}, which is in excellent agreement with the literature value,[4] was determined (Experimental Section) at 25 °C and I = 1.0 (Na-

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Table I. Absorption of $\mathrm{Ti^{IV}}$–$\mathrm{H_2O_2}$ Mixtures at λ = 412 nm, I = 1.0 ($\mathrm{NaClO_4}$), and 25 °C

$10^3[\mathrm{Ti^{IV}}]_{\mathrm{tot}}$, M	$[\mathrm{H_2O_2}]_{\mathrm{tot}}$, M	$[\mathrm{H^+}]$, M	D_{412} obsd	D_{412} calcd[a]
1.68	0.5	0.6	1.193	1.191
	0.01	0.6	1.169	1.175
	0.01	0.2	1.164	1.175
0.84	0.5	0.6	0.605	0.595
	0.005	0.6	0.583	0.580
	0.005	0.2	0.591	0.580
0.336	0.5	0.6	0.241	0.238
	0.004	0.6	0.232	0.231
	0.003	0.6	0.229	0.228
	0.002	0.6	0.223	0.223
	0.002	0.2	0.222	0.223
0.168	0.5	0.6	0.120	0.119
	0.004	0.6	0.121	0.116
	0.002	0.6	0.115	0.112
	0.0015	0.6	0.112	0.110
	0.0015	0.6	0.112	0.110
	0.001	0.6	0.103	0.105
	0.001	0.2	0.103	0.105

[a] See Experimental Section. $\epsilon_{412} = 709 \pm 2$ $\mathrm{M^{-1}\,cm^{-1}}$, and $K_{\mathrm{H_2O_2}} = (8.7 \pm 1.4) \times 10^3$ $\mathrm{M^{-1}}$.

$\mathrm{ClO_4}$). No systematic deviations (which would indicate additional equilibria and species) between calculated and observed optical densities became apparent (Table I).

In order to get a further proof for the $\mathrm{Ti(O_2)^{2+}}$ structure, its charge was verified by cation-exchange chromatography: ca. 5 mL of a solution containing 1.7 mM $\mathrm{TiO^{2+}}$, ca. 1 M $\mathrm{H_2O_2}$, and 0.2 M $\mathrm{HClO_4}$ was adsorbed on 200–400-mesh Dowex 50W-X2, $\mathrm{H^+}$ form, and eluted with 1 M $\mathrm{HClO_4}$/~1 M $\mathrm{H_2O_2}$. A single orange-yellow band with $\lambda_{\max}$ = 412 nm was eluted at a rate characteristic to 2+ ions.

Peroxide is bound to titanium(IV) through both the oxygen atoms (η^2 coordination) as in peroxotitanium complexes of known[10-13] crystal structures, since laser-flash photolysis (λ_{ex} = 353 nm) of $\mathrm{Ti(O_2)^{2+}}$ did not decompose detectable amounts of the peroxo complex. Usually, excitation into a charge-transfer band leads to homolytic cleavage of the corresponding bond and subsequent dissociation of the radicals, which is difficult, if the ligand is bidentate.

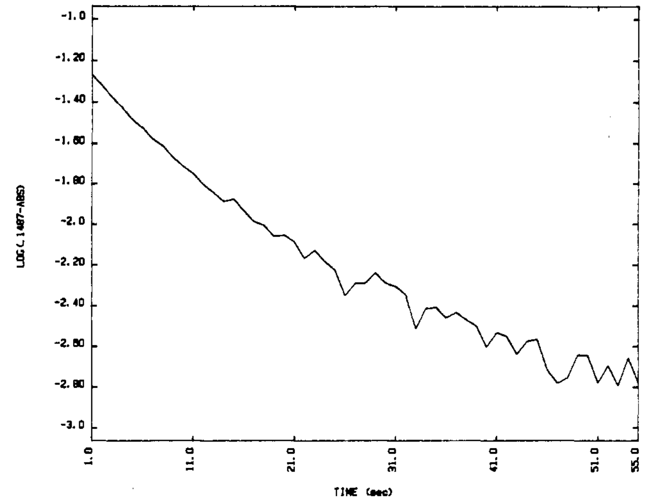

Figure 1. Curved first-order plot. Conditions correspond to those of the fourth entry in Table II.

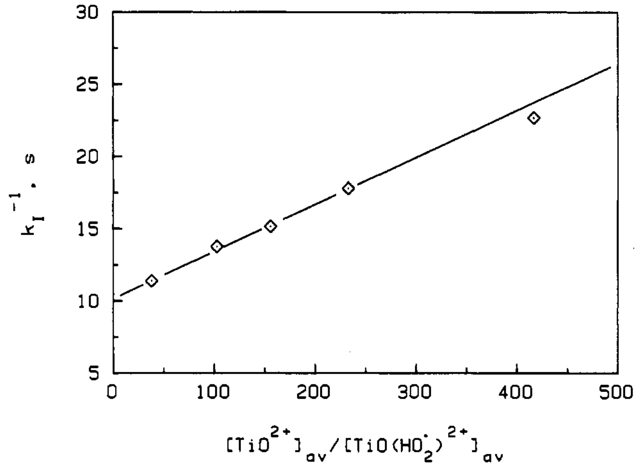

Figure 2. Plot of k_{I}^{-1} vs $[\mathrm{TiO^{2+}}]_{\mathrm{av}}/[\mathrm{TiO(HO_2^\bullet)^{2+}}]_{\mathrm{av}}$ (linearized expression of rate law II).

Table II. Dependence of the $\mathrm{TiO(HO_2^\bullet)^{2+}}$ Decay on Excess $\mathrm{TiO^{2+}}$ at 25 °C, 0.60 M $\mathrm{H^+}$, and I = 1.0 ($\mathrm{LiClO_4}$)[a]

$10^4[\mathrm{P}]_0$, M[b]	$10^2[\mathrm{TiO^{2+}}]_0$, M	$[\mathrm{TiO^{2+}}]_{\mathrm{av}}/[\mathrm{P}]_{\mathrm{av}}$[b]	10^2k_{I}, $\mathrm{s^{-1}}$ obsd[c]	10^2k_{I}, $\mathrm{s^{-1}}$ calcd[d]
2.50	0.47	38	8.78 ± 0.02 (7)	8.78
2.85	1.46	103	7.26 ± 0.18 (5)	7.40
2.85	2.21	156	6.60 ± 0.12 (5)	6.57
2.55	2.96	233	5.62 ± 0.07 (5)	5.64
1.42	2.96	417	4.41 ± 0.25 (5)	4.21

[a] $[\mathrm{H_2O_2}]_{\mathrm{tot}} = 3.5 \times 10^{-4}$ M. Quantitative conversion of $\mathrm{Ce^{IV}}$ to $\mathrm{TiO(HO_2^\bullet)^{2+}}$ was assumed. [b] P = $\mathrm{TiO(HO_2^\bullet)^{2+}}$. [c] Errors are standard deviations. Numbers of determinations are given in parentheses. [d] Calculated according to rate law II with $k_1 = (9.85 \pm 0.03) \times 10^{-2}$ $\mathrm{s^{-1}}$ and $k_{-1}/k_2 = (3.21 \pm 0.07) \times 10^{-3}$.

Structure and Mechanism of Decomposition of the Superoxotitanium(IV) Complex. The oxidation[4] of $\mathrm{Ti(O_2)^{2+}}$ by $\mathrm{Ce^{IV}}$ leads to a superoxotitanium(IV) complex that decomposes[4] with first-order kinetics by re-forming peroxotitanium(IV). The lifetime of the superoxo species was found[4] to increase with increasing pH. In analogy with the decomposition[14] of superoxocopper(II), it was proposed[4] that superoxotitanium(IV) decays via reductive elimination, forming $\mathrm{O_2}$ and titanium(III) according to reactions 2 and 3. The results obtained in this work are inconsistent with

$$\text{“}\mathrm{Ti(O_2)^{3+}}\text{”} \xrightarrow{\text{slow}} \mathrm{Ti^{III}} + \mathrm{O_2} \tag{2}$$

$$\text{“}\mathrm{Ti(O_2)^{3+}}\text{”} + \mathrm{Ti^{III}} \xrightarrow{\text{fast}} \mathrm{Ti(O_2)^{2+}} + \mathrm{Ti^{IV}} \tag{3}$$

this mechanism, since the decomposition of the superoxotitanium(IV) complex, which is perhydroxytitanyl(2+), $\mathrm{TiO(HO_2^\bullet)^{2+}}$, is retarded in the presence of $\mathrm{TiO^{2+}}$. The primary products $\mathrm{TiO^{2+}}$ and $\mathrm{HO_2^\bullet}$ are formed by reaction 4, and subsequently, the $\mathrm{HO_2^\bullet}$ radical reduces $\mathrm{TiO(HO_2^\bullet)^{2+}}$ according to reaction 5. Since $\mathrm{HO_2^\bullet}$ is generated very slowly and consumed

$$\mathrm{TiO(HO_2^\bullet)^{2+}} \underset{\text{fast}}{\overset{\text{slow}}{\rightleftharpoons}} \mathrm{TiO^{2+}} + \mathrm{HO_2^\bullet} \quad k_1, k_{-1} \tag{4}$$

$$\mathrm{TiO(HO_2^\bullet)^{2+}} + \mathrm{HO_2^\bullet} \xrightarrow{\text{fast}} \mathrm{Ti(O_2)^{2+}} + \mathrm{O_2} + \mathrm{H_2O} \quad k_2 \tag{5}$$

rapidly, it is always present at low concentration. Therefore, dismutation of $\mathrm{HO_2^\bullet}$ is not expected to compete with reaction 5. Rate law I was deduced by assuming that $\mathrm{HO_2^\bullet}$ is present at

$$-\mathrm{d}[\mathrm{TiO(HO_2^\bullet)^{2+}}]/\mathrm{d}t = 2k_1[\mathrm{TiO(HO_2^\bullet)^{2+}}]/\{1 + (k_{-1}/k_2)[\mathrm{TiO^{2+}}]/[\mathrm{TiO(HO_2^\bullet)^{2+}}]\} \tag{I}$$

steady-state concentration. For $(k_{-1}/k_2)[\mathrm{TiO^{2+}}]_{\mathrm{av}}/[\mathrm{TiO(HO_2^\bullet)^{2+}}]_{\mathrm{av}} < 1$ (av = average; $[\mathrm{TiO^{2+}}]_{\mathrm{av}} = [\mathrm{TiO^{2+}}]_0 + [\mathrm{TiO(HO_2^\bullet)^{2+}}]_0/4$, $[\mathrm{TiO(HO_2^\bullet)^{2+}}]_{\mathrm{av}} = [\mathrm{TiO(HO_2^\bullet)^{2+}}]_0/2$), first-order kinetics, described by rate law II, were observed over ~3 half-lives.

$$-\mathrm{d}[\mathrm{TiO(HO_2^\bullet)^{2+}}]/\mathrm{d}t \approx 2k_{\mathrm{I}}[\mathrm{TiO(HO_2^\bullet)^{2+}}]$$

$$k_{\mathrm{I}} = k_1/\{1 + (k_{-1}/k_2)[\mathrm{TiO^{2+}}]_{\mathrm{av}}/[\mathrm{TiO(HO_2^\bullet)^{2+}}]_{\mathrm{av}}\} \tag{II}$$

For $(k_{-1}/k_2)[\mathrm{TiO^{2+}}]_{\mathrm{av}}/[\mathrm{TiO(HO_2^\bullet)^{2+}}]_{\mathrm{av}} \approx 1$, however, the first-

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order plots were curved as predicted by rate law I (Figure 1). The curvature was not very pronounced over 1–2 half-lives (Figure 1). The applied experimental conditions (Table II) allowed us to determine the first-order rate constants k_I by using rate law II (the curved plots were evaluated over 1–2 half-lives). The $[TiO^{2+}]_{av}/[TiO(HO_2^\bullet)^{2+}]_{av}$ dependence of k_I (Table II) was investigated at 25 °C, 0.6 M H^+, and $I = 1.0$ ($LiClO_4$) by monitoring the re-formation of $Ti(O_2)^{2+}$ at 410 nm as described[4] by Thompson. Plots of k_I^{-1} vs $[TiO^{2+}]_{av}/[TiO(HO_2^\bullet)^{2+}]_{av}$ are linear (Figure 2). If $Ti(O_2)^{2+}$ were generated through complexation of TiO^{2+} by H_2O_2, k_I would *increase* with increasing $[TiO^{2+}]$. The opposite is observed. Clearly, $Ti(O_2)^{2+}$ is formed by reduction of $TiO(HO_2^\bullet)^{2+}$. A weighted least-squares fit provided $k_1 = (9.85 \pm 0.03) \times 10^{-2}$ s^{-1} and $k_{-1}/k_2 = (3.21 \pm 0.07) \times 10^{-3}$. The agreement between calculated and observed rate constants is excellent (Table II).

The rate constants k_{-1} and k_2 are not available from the literature, but $HO_2^\bullet$ and HF addition to TiO^{2+} may proceed at similar rates. The rate constant for the latter reaction is known[15] to be 1.86×10^3 M^{-1} s^{-1} at 25 °C and $I = 0.5$ ($LiClO_4$). On the other hand, dismutation of perhydroxyl radicals occurs[16] at a rate of $\sim 10^6$ M^{-1} s^{-1} at pH 0–1. A similar rate (k_2) is expected for the reaction of perhydroxytitanyl(2+) with perhydroxyl radicals. From this, we estimate $k_{-1}/k_2 \approx 2 \times 10^{-3}$, which compares very well with our experimental value of $(3.21 \pm 0.07) \times 10^{-3}$.

It was argued[14] that the superoxo complex of copper(II) decomposes via internal electron transfer, forming copper(I) and dioxygen. In fact, the one-electron oxidation of Cu^I by molecular oxygen is thermodynamically unfavorable in acid solution ($\Delta E = -0.034$ V), and O_2 and Cu^+ are stable products with respect to Cu^{2+} and $HO_2^\bullet$. Due to the lower potential of the TiO^{2+}/Ti^{3+} couple (0.03 V[17]), exactly the opposite holds for titanium: TiO^{2+} and $HO_2^\bullet$ are thermodynamically more stable than Ti^{3+} and O_2 ($\Delta E = 0.094$ V). Hence, it is not surprising that the decomposition of perhydroxytitanyl(2+) leads to the more stable products TiO^{2+} and $HO_2^\bullet$.

In order to get more information about the decomposition of $TiO(HO_2^\bullet)^{2+}$, its pH and temperature dependence has been studied. In principle, at each pH and temperature, the ratio $[TiO^{2+}]_{av}/[TiO(HO_2^\bullet)^{2+}]_{av}$ should be varied in order to determine k_1. Since we were not interested in the pH and temperature dependence of k_{-1}/k_2 (which would have required ca. 500 measurements instead of ca. 100), we studied the reaction at the constant and not too large $[TiO^{2+}]_{av}/[TiO(HO_2^\bullet)^{2+}]_{av}$ ratio of 38. Then, k_I is approximately equal to k_1. This simplification gives rise to a systematic error of ~10%, which may be $[H^+]$- and temperature-dependent.

The rate constants k_I were found to depend on $[H^+]$ according to eq 6 (Figure 3). No significant curvature was detectable at

$$k_I \cong k_1 = k_{1,0} + k_{1,H}[H^+] \tag{6}$$

any temperature (Figure 3). The substitution of perhydroxyl by water proceeds via a spontaneous ($k_{1,0}$) and an acid-catalyzed ($k_{1,H}$) pathway, as in the substitution[18] of oxide by hydrogen peroxide at TiO^{2+}. From the absence of any significant curvature in the $[H^+]$ dependence, it is concluded that the acid dissociation constant of the protonated perhydroxytitanyl(2+) is large, i.e. ≥ 10 M, and similar to that of protonated TiO^{2+}, $TiOH^{3+}$.[17] Such a low pK_a is in agreement with the $TiO(HO_2^\bullet)^{2+}$ structure. At each temperature the rate constants $k_{1,0}$ and $k_{1,H}$ were calculated by weighted least-squares fits ($w = 1/s^2(k_I)$). The agreement between observed and calculated rate constants is good (Table III, Figure 3). From the temperature dependence of $k_{1,0}$ and $k_{1,H}$ (Table IV) the activation parameters $\Delta H_{1,0}^\ddagger = 62 \pm 5$ kJ mol^{-1}, $\Delta S_{1,0}^\ddagger = -68 \pm 18$ J K^{-1} mol^{-1}, $\Delta H_{1,H}^\ddagger = 81 \pm 8$ kJ mol^{-1}, and $\Delta S_{1,H}^\ddagger = 7.6 \pm 3.3$ J K^{-1} mol^{-1} were obtained from plots of ln (k_i/T) vs $1/T$ ($w = k_i^2/s^2(k_i)$).

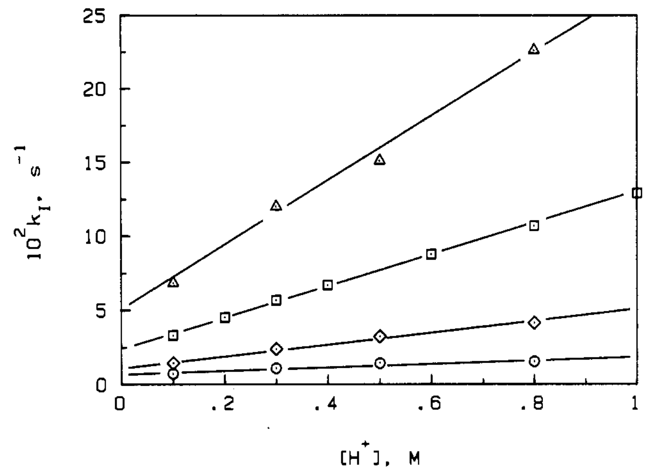

Figure 3. pH and temperature dependence of k_I: (circles) 9 °C; (diamonds) 17 °C; (squares) 25 °C; (triangles) 33 °C.

Table III. pH and Temperature Dependence of the $TiO(HO_2^\bullet)^{2+}$ Decay at $I = 1.0$ ($LiClO_4$)[a]

$[H^+]$, M	T, °C	$10^2 k_1$, s^{-1} obsd[b]	$10^2 k_1$, s^{-1} calcd[c]
0.10	9	0.72 ± 0.02 (5)	0.78
	17	1.43 ± 0.02 (5)	1.48
	25	3.33 ± 0.04 (5)	3.45
	33	6.85 ± 0.29 (4)	7.24
0.20	25	4.54 ± 0.04 (4)	4.52
0.30	9	1.09 ± 0.03 (4)	1.02
	17	2.40 ± 0.03 (4)	2.29
	25	5.69 ± 0.04 (8)	5.58
	33	12.0 ± 0.2 (4)	11.6
0.40	25	6.72 ± 0.05 (9)	6.65
0.50	9	1.45 ± 0.03 (5)	1.25
	17	3.24 ± 0.04 (5)	3.09
	33	15.1 ± 0.4 (3)	16.0
0.60	25	8.78 ± 0.02 (7)	8.79
0.80	9	1.55 ± 0.02 (4)	1.61
	17	4.15 ± 0.04 (5)	4.29
	25	10.7 ± 0.3 (10)	10.9
	33	22.6 ± 0.5 (4)	22.5
1.00	25	12.9 ± 0.1 (6)	13.1

[a] $[H_2O_2]_{tot} = 3 \times 10^{-4}$ M, $[Ce^{IV}]_{tot} = 2.5 \times 10^{-4}$ M, and $[Ti^{IV}]_{tot} = 5 \times 10^{-3}$ M. [b] Errors are standard deviations. Numbers of determinations are given in parentheses. [c] Calculated by using eq 6 with the parameters given in Table IV.

Table IV. Temperature Dependence of $k_{1,0}$ and $k_{1,H}$ at $I = 1.0$ ($LiClO_4$)

T, °C	$10^2 k_{1,0}$, s^{-1} obsd[a]	$10^2 k_{1,0}$, s^{-1} calcd[b]	$10^2 k_{1,H}$, M^{-1} s^{-1} obsd[a]	$10^2 k_{1,H}$, M^{-1} s^{-1} calcd[c]
9	0.66 ± 0.12	0.55	1.18 ± 0.23	1.59
17	1.08 ± 0.11	1.17	4.02 ± 0.29	4.22
25	2.38 ± 0.07	2.39	10.7 ± 0.1	10.7
33	5.06 ± 0.65	4.70	21.8 ± 1.7	25.7

[a] Errors are standard deviations. [b] Calculated by using the transition-state theory: $k_{1,0} = (\kappa k_B T/h) \exp\{-\Delta H_{1,0}^\ddagger/(RT)\} \exp\{\Delta S_{1,0}^\ddagger/R\}$ with $\kappa = 1$, $\Delta H_{1,0}^\ddagger = 62 \pm 5$ kJ mol^{-1}, and $\Delta S_{1,0}^\ddagger = -68 \pm 18$ J K^{-1} mol^{-1}. [c] Calculated as in footnote *b* with $\kappa = 1$, $\Delta H_{1,H}^\ddagger = 81 \pm 8$ kJ mol^{-1}, and $\Delta S_{1,H}^\ddagger = 7.6 \pm 3.3$ J K^{-1} mol^{-1}.

The EPR spectra of radicals formed in Ti^{III}/H_2O_2 mixtures are well-known.[19] There is a consensus that the two-line spectrum is due to two species that contain superoxide coordinated to Ti^{IV}.[6] No hyperfine coupling due to H becomes apparent, probably because H^+ exchange is too fast. We tentatively assign the (usually) intense line[6] at $g = 2.01339$ to $TiO(HO_2^\bullet)^{2+}$. The other

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Table V. Ionic Strength Dependence of the $TiO(HO_2^{\bullet})^{2+}$ Decay at 25 °C[a]

$[H^+]$, M	I	10^2k_I, s^{-1} obsd[b]	10^2k_I, s^{-1} calcd[c]
0.10	0.115	2.89 ± 0.04 (7)	3.02
0.15	0.165	3.41 ± 0.09 (5)	3.46
0.20	0.215	4.03 ± 0.05 (6)	3.96
0.25	0.265	4.54 ± 0.05 (5)	4.49
0.30	0.315	5.04 ± 0.06 (5)	5.00
0.40	0.415	6.10 ± 0.08 (6)	6.15
0.60	0.615	8.28 ± 0.03 (4)	8.28

[a] $[H_2O_2]_{tot} = 3 \times 10^{-4}$ M, $[Ce^{IV}]_{tot} = 2.5 \times 10^{-4}$ M, and $[Ti^{IV}]_{tot} = 5 \times 10^{-3}$ M. [b] Errors are standard deviations. Numbers of determinations are given in parentheses. [c] Calculated according to eq 8 with $k_{1,0} = (2.38 \pm 0.07) \times 10^{-2}$ s^{-1}, $k^0_{1,H} = (2.0 \pm 0.4) \times 10^{-2}$ M^{-1} s^{-1}, $z = 2.13 \pm 0.26$, and $A = 0.509$ $M^{1/2}$.

weak line[6] at $g = 2.01184$ may be due to an isomer, e.g. $Ti(OH)_2(HO_2^{\bullet})^{2+}$ [20] or more likely to the protonated species $Ti(OH)(HO_2^{\bullet})^{3+}$. pH-dependent EPR experiments should allow us to determine the pK_a of $Ti(OH)(HO_2^{\bullet})^{3+}$ and to discriminate between the isomer and the protonated species.

The charge of perhydroxytitanyl(2+) has been determined from the ionic strength dependence of its decomposition kinetics. The rate of the acid-catalyzed pathway ($k_{1,H}$) depends on the ionic strength, because this reaction is bimolecular and involves two charged reactants, namely the proton and the charged superoxotitanium complex. The spontaneous reaction ($k_{1,0}$), however, is ionic strength independent. At higher ionic strength, the activity coefficient f is described accurately by eq 7.[21] At variable ionic

$$\log f = z^2[AI^{1/2}/(1 + I^{1/2}) - 0.1I] \qquad (7)$$

$$A = 0.509 \text{ at } 25\ °C$$

$$k_I \cong k_1 = k_{1,0} + k^0_{1,H}[H^+]10^{2z[AI^{1/2}/(1+I^{1/2})-0.1I]} \qquad (8)$$

strength eq 6 has to be replaced by eq 8, where $k^0_{1,H}$ is the rate constant $k_{1,H}$ at $I \rightarrow 0$, z the charge of the perhydroxytitanyl(2+) complex, and I the ionic strength. Since $k_{1,0}$ is independent of the ionic strength and is known from the previous experiments, eq 8 was linearized (eq 9). The decomposition of $TiO(HO_2^{\bullet})^{2+}$

$$\log \{(k_I - k_{1,0})/[H^+]\} = \log k^0_{1,H} + 2z[AI^{1/2}/(1 + I^{1/2}) - 0.1I] \qquad (9)$$

was measured at 25 °C in the absence of supporting electrolyte (Table V). The parameters $k^0_{1,H}$ and z were calculated by a least-squares fit to eq 9 using the weight $w = (\ln 10)^2(k_I - k_{1,0})^2/\{s^2(k_I) + s^2(k_{1,0})\}$, since both k_I and $k_{1,0}$ are subject to errors. $k^0_{1,H}$ and z were determined as $(2.00 \pm 0.38) \times 10^{-2}$ M^{-1} s^{-1} and 2.13 ± 0.26, respectively, which shows that the superoxotitanium(IV) complex carries a charge of 2+.

The present results are fully consistent with the existence of perhydroxytitanyl(2+) and argue against the alternative species, $Ti(OH)(O_2^{\bullet})^{2+}$. Free perhydroxyl radicals exhibit[16] p$K_a(HO_2^{\bullet}) = 4.8$, but they can also be protonated[22] with p$K_a(H_2O_2^{\bullet +}) \approx 1.0$–1.2. Evidence for the existence of $H_2O_2^{\bullet +}$ is available from the kinetics of the superoxide dismutation: if $H_2O_2^{\bullet +}$ were absent at pH 0–1, the rate constant would be expected to level off. This, however, was not observed,[23] since at pH ~2 the rate constant increases again with decreasing pH. This effect is not due to the increasing ionic strength, and therefore, we take it as a support for the existence of $H_2O_2^{\bullet +}$ in this pH range. $HO_2^{\bullet}$ radicals coordinated to TiO^{2+} are certainly more acidic than free $HO_2^{\bullet}$ but less acidic than $H_2O_2^{\bullet +}$. Therefore, the pK_a of $TiO(HO_2^{\bullet})^{2+}$ is expected to range between 1 and 4.8. Under the experimental conditions (pH 0–1) a hypothetical $Ti(OH)(O_2^{\bullet})^{2+}$ complex is expected to be protonated at the $O_2^{\bullet -}$ ligand.

Table VI. Oxidation of Ti^{III} by Molecular Oxygen at I = 1.0 (LiCl) and 25 °C

$[H^+]_{av}$,[a] M	$10^2[Ti^{III}]_0$, M	$10^4[O_2]_0$,[b] M	$10^2k_{II,obsd}$, M^{-1} s^{-1}	$10^2k_{II,obsd}[H^+]$, s^{-1}
0.202	2.0	7.94 ± 0.03[c]	9.58	1.94
0.241	3.0	7.3	8.20	1.98
0.301	3.0	6.6	6.51	1.96
0.402	1.0	8.82 ± 0.04[c]	4.98	2.00
	2.0	7.89 ± 0.02[c]	4.78	1.92
	3.0	7.7	4.88	1.96
	4.0	6.6	4.66	1.87
	5.0	8.6	4.85	1.95
0.502	4.0	7.9	3.81	1.91
0.602	4.0	8.2	3.11	1.87
0.698	4.0	7.3	2.77	1.93
0.852	2.0	9.22 ± 0.02[c]	2.34	1.99
0.93	1.0	10.4 ± 0.0[c]	2.26	2.10
				av $k_3K_a(Ti^{3+}) = (1.95 \pm 0.06) \times 10^{-2}$ s^{-1}

[a] $[H^+]_{av} = [H^+]_0 + 2[O_2]_0$. [b] Calculated as $(D_\infty - D_0)/[4(\Delta\epsilon_{270})]$, $\Delta\epsilon_{270} = 54.3$ M^{-1} cm^{-1}. [c] Determined from least-squares fits to the integrated form of rate law III ($\Delta\epsilon_{270} = 54.3$ M^{-1} cm^{-1}).

Crystal structures of superoxo complexes of cobalt(III) and iron(III) are known[24] to be of the η^1 type; i.e., superoxide is a monodentate ligand. No complex with protonated superoxide has been reported so far, but we expect that perhydroxyl acts also as a monodentate ligand, since one coordination site is already occupied by the proton.

Oxidation of Titanium(III) by Molecular Oxygen. We expected that oxygen addition to titanium(III) would provide an alternative route to perhydroxytitanyl(2+). The kinetics of this reaction were studied at 25 °C and I = 1.0 (LiCl).[25] Quantitative reduction of oxygen was observed when titanium(III) was in a more than 4-fold excess.

Neither peroxotitanium(IV) ($\epsilon_{412} = 717$ M^{-1} cm^{-1} [8]) nor perhydroxytitanyl(2+) ($\epsilon_{\sim 350} \approx 140$ M^{-1} cm^{-1} (maximum), $\epsilon_{\sim 300} \approx 70$ M^{-1} cm^{-1} (minimum), $\epsilon_{<250}$ large) were detected as intermediates. This is not surprising, since titanium(III) certainly would have reduced perhydroxytitanyl(2+) and also peroxotitanium(IV) rapidly. The latter reaction is known[26] to be slow, but it is still much faster than the oxidation of titanium(III) by molecular oxygen. The reduction of perhydroxyl radicals by titanium(III) is also expected to be fast, and therefore, the reaction of Ti^{III} with O_2 is rate-determining.

The kinetics of reaction 10 are described by rate law III.

$$4Ti^{3+} + O_2 + 2H_2O \xrightarrow{\text{slow}} 4TiO^{2+} + 4H^+ \quad k_{II} \qquad (10)$$

$$-d[O_2]/dt = k_{II}[O_2][Ti^{III}] \qquad (III)$$

Second-order rate constants k_{II} were obtained by using the integrated form of rate law III for $[Ti^{III}]_0 \leq 0.02$ M (the parameters $[O_2]_0$, k_{II}, and D_∞ were determined by least-squares fits). For $[Ti^{III}]_0 > 0.02$ M k_{II} was calculated from weighted least-squares fits to the expression $\ln |D_\infty - D| = A - k_{II}[Ti^{III}]_{av}t$ with $w = (D_\infty - D)^2$ and $[Ti^{III}]_{av} = [Ti^{III}]_0 - 2[O_2]_0$.

k_{II} is independent of $[O_2]_0$ and $[Ti^{III}]_0$ but depends on $[H^+]$ (Table VI). Plots of k_{II} vs $[H^+]^{-1}$ are linear, and the product of $k_{II}[H^+] = (1.95 \pm 0.06) \times 10^{-2}$ s^{-1} (Table VI) is constant. From the inverse acidity dependence of k_{II} and the absence of any $[H^+]$-independent term it is concluded that $TiOH^{2+}$ is the only reactive species. The rate-determining steps are described by reactions 11 and 12. Equation 13 was derived by treating reaction

$$Ti^{3+} + H_2O \underset{}{\overset{\text{fast}}{\rightleftharpoons}} TiOH^{2+} + H^+ \quad K_a(Ti^{3+}) \qquad (11)$$

$$TiOH^{2+} + O_2 \xrightarrow{\text{slow}} \text{products} \quad k_3 \qquad (12)$$

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(20) The yl oxygen of TiO^{2+} exchanges very rapidly via $Ti(OH)_2^{2+}$.[3]

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(25) In $CF_3SO_3^-$ media the rate law $-d[O_2]/dt = k[O_2]^{1/2}$ was observed. We are unable to interpret this. When TiO^{2+} was added, first-order kinetics were observed with rate constants slightly higher than in Cl^- media.

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11 as a rapid preequilibrium. On the basis of the literature value[27]

$$k_{\mathrm{II}} = k_3K_a(\mathrm{Ti}^{3+})/[\mathrm{H}^+] \qquad (13)$$

for $K_a(\mathrm{Ti}^{3+})$, k_3 was calculated as $4.25 \pm 0.13\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ at $I = 1.0$ (LiCl) and 25 °C.

The rate constant for the reaction of perhydroxyl with titanyl must be on the order of $2 \times 10^3\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ (see above). Thus, a free enthalpy of activation of ~0.56 eV is estimated to reach the transition state $[(\mathrm{TiO}\cdots\mathrm{HO}_2^{\bullet})^{2+}]^{\ddagger}$. A different transition state is formed by the oxidation of TiOH^{2+} with O_2. This reaction exhibits a free energy of activation of 0.72 eV, and furthermore, TiOH^{2+} and O_2 are less stable than TiO^{2+} and $\mathrm{HO}_2^{\bullet}$ by 0.23 eV. Therefore, the energy of the transition state $[(\mathrm{TiOH}\cdots\mathrm{O}_2)^{2+}]^{\ddagger}$ lies 0.95 eV above the $\mathrm{TiO}^{2+} + \mathrm{HO}_2^{\bullet}$ level. The transition state $[(\mathrm{TiOH}\cdots\mathrm{O}_2)^{2+}]^{\ddagger}$ is less stable than $[(\mathrm{TiO}\cdots\mathrm{HO}_2^{\bullet})^{2+}]^{\ddagger}$ by ~0.39 eV and arises either from outer-sphere electron transfer or from oxygen addition to TiOH^{2+}, which would lead to $\mathrm{Ti(OH)(O}_2^{\bullet})^{2+}$ as a primary product. This shows that $\mathrm{Ti(OH)(O}_2^{\bullet})^{2+}$ is less stable than $\mathrm{TiO(HO}_2^{\bullet})^{2+}$.

The stability constant for perhydroxytitanyl(2+) formation, $K_{\mathrm{HO}_2^{\bullet}} \approx k_{-1}/k_{1,0}$ is estimated as $\sim 8.4 \times 10^4\ \mathrm{M}^{-1}$ and the reduction potential of $\mathrm{TiO(HO}_2^{\bullet})^{2+}$ as ~1.35 V. We were unable to oxidize $\mathrm{Ti(O}_2)^{2+}$ by cyclic voltammetry in 0.1–1.0 M HClO_4 using a SnO_2 or a glassy-carbon electrode, presumably because the electron transfer at the electrode is too slow.

The $\mathrm{TiO(HO}_2^{\bullet})^{2+}$ ion is a slightly weaker oxidizing agent than the free $\mathrm{HO}_2^{\bullet}$ radical, but in contrast to the case for free $\mathrm{HO}_2^{\bullet}$, it is most likely a much poorer reducing agent, since molecular oxygen coordinated to TiO^{2+} would be formed as an unstable product. Probably for this reason, dismutation of perhydroxytitanyl(2+), reaction 14, is too slow to be observed in competition with reactions 4 and 5.

$$2\mathrm{TiO(HO}_2^{\bullet})^{2+} \rightarrow \mathrm{Ti(O}_2)^{2+} + \mathrm{TiO(O}_2)^{2+} + \mathrm{H_2O} \qquad (14)$$

Acknowledgment. P. Compte recorded the CV's. Professor Dr. R. C. Thompson, Dr. E. Müller, and Dr. R. Humphry-Baker contributed helpful comments on the manuscript. The work was supported by the National Energy Research Foundation.

Registry No. $\mathrm{Ti(O}_2)^{2+}$, 12179-34-9; $\mathrm{TiO(HO}_2^{\bullet})^{2+}$, 110487-74-6; TiOH^{2+}, 21029-47-0.

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Cluster Synthesis. 15. Square-Pyramidal Coordination of Sulfur in Metal Cluster Complexes. Synthesis and Structural Characterizations of $\mathrm{Ru_4(CO)_7(\mu\text{-}CO)_2(PMe_2Ph)_2(\mu_4\text{-}S)(\mu_5\text{-}S)[W(CO)_4PMe_2Ph]}$ and $\mathrm{Os_5(CO)_{15}(\mu_5\text{-}S)[W(CO)_4PPh_3]}$

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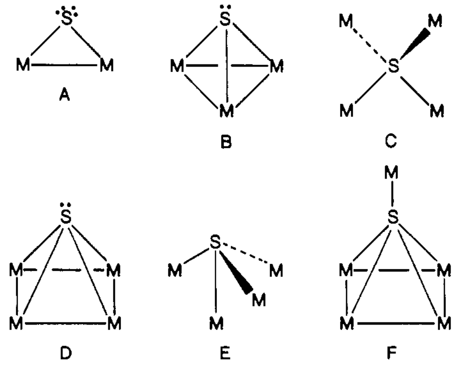
Received April 14, 1987

The compounds $\mathrm{Ru_4(CO)_7(\mu\text{-}CO)_2(PMe_2Ph)_2(\mu_4\text{-}S)(\mu_5\text{-}S)[W(CO)_4PMe_2Ph]}$ (**2**) and $\mathrm{Os_5(CO)_{15}(\mu_5\text{-}S)[W(CO)_4PPh_3]}$ (**4**) have been obtained in yields of 40% and 35% by the irradiation of solutions containing $\mathrm{W(CO)_5(PMe_2Ph)}$ and $\mathrm{Ru_4(CO)_9(PMe_2Ph)_2(\mu_4\text{-}S)_2}$ and solutions containing $\mathrm{W(CO)_5(PPh_3)}$ and $\mathrm{Os_5(CO)_{15}(\mu_4\text{-}S)}$, respectively. Both products were characterized by X-ray diffraction analyses. For **2**: space group $P2_1/c$, $a = 12.408$ (2) Å, $b = 29.353$ (7) Å, $c = 13.903$ (2) Å, $\beta = 111.69$ (1)°, $V = 4705$ (2) Å^3, $Z = 4$. For **4**: space group $P2_1/c$, $a = 19.839$ (9) Å, $b = 16.461$ (6) Å, $c = 27.407$ (10) Å, $\beta = 92.94$ (3)°, $V = 8939$ (7) Å^3, $Z = 8$. Both products contain pentacoordinate, square-pyramidal, quintuply bridging sulfido ligands formed by the addition of a $\mathrm{W(CO)_4PR_3}$ group to a quadruply bridging sulfido ligand of the original complex. The W–S bond lengths of 2.486 (2) Å in **2** and 2.52 (2) Å in **4** are not significantly different from those for W–S bonds to tetravalent sulfido ligands. The attachment of the tungsten-containing group to the sulfido ligand does not produce any significant structural changes upon the bonding of the sulfido ligand to the clusters in either case.

Introduction

The strong affinity of sulfur for the elements of the transition series serves as a basis for a variety of important naturally occurring metal sulfur compounds. Metal sulfides constitute the most important class of mineral ores.[1] Metal–sulfur complexes play a central role in the activity of a variety of biologically important enzymes and coenzymes.[2] Metal–sulfur compounds have been shown to have an enormous commercial value as hydrodesulfurization catalysts.[3]

Recent studies of metal complexes have shown that the coordination chemistry of sulfur is extremely rich and varied.[4] Sulfido ligands commonly exhibit doubly (A), triply (B), and quadruply (C and D) bridging bonding modes. The ligand is remarkably flexible. M–S–M bond angles may be as small as 65° or as large as 140°.[5] A recent report of an "inverted" tetrahedral coordination E, demonstrates how extreme these distortions may become.[6] The only known examples of pentacoordinate sulfur exist in an unusual class of metal-rich minerals known as pentlandites.[7]



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