1794 *Inorg. Chem.* **1984**, *23*, 1794-1798

Articles

Contribution from the Department of Chemistry,
University of Missouri, Columbia, Missouri 65211

Oxidation of Peroxotitanium(IV) by Chlorine and Cerium(IV) in Acidic Perchlorate Solution

RICHARD C. THOMPSON

Received July 27, 1983

The Cl_2–TiO_2^{2+} reaction proceeds by oxidation of trace amounts of H_2O_2 in equilibrium with the peroxo complex. The stability constant of peroxotitanium(IV) is 8.7×10^3 M^{-1} in molar perchloric acid at 25 °C. The complex is rapidly oxidized by cerium(IV) in acidic perchlorate solution ($k = 1.1 \times 10^5$ M^{-1} s^{-1} in molar perchloric acid at 25 °C) to form an intermediate that we identify as superoxotitanium(IV). This intermediate is proposed to decay by a first-order, internal redox process to form dioxygen and titanium(III). Peroxotitanium(IV) is re-formed during the decay by the rapid reaction of titanium(III) with the superoxotitanium(IV). The value of the decay constant is 0.11 s^{-1} in molar perchloric acid at 25 °C. In the presence of cerium(IV), no peroxotitanium(IV) is re-formed during the decay process, presumably due to rapid oxidation of the titanium(III) formed by the cerium(IV). In addition, a relatively slow oxidation of superoxotitanium(IV) by cerium(IV) was detected. The potential application of forming superoxo complexes in rather clean environments by the oxidation of precursor peroxo complexes with strong, 1-equiv oxidants such as cerium(IV) is discussed.

Introduction

We are exploring the redox chemistry of peroxo complexes of early transition elements in their highest oxidation states. These metal ions form labile peroxo and superoxo complexes with large stability constants.[1-3] Of interest is a comparison of the redox chemistry of these species with that of hydrogen peroxide and hydroperoxide, HO_2.

We have previously reported the reactions of peroxovanadium(V), VO_3^+ (or $VO(O_2)^+$), with a number of oxidants.[4,5] Aqueous chlorine was found to react only with traces of H_2O_2 in equilibrium with VO_3^+. Other oxidants (Co^{3+}, Ag^{2+}, SO_4F^-, and SO_4^-) reacted directly with the peroxo complex to form superoxovanadium(V), VO_3^{2+}. This radical cation was proposed to decay exclusively through an internal redox process to produce O_2 and VO^{2+}.

We have extended these studies to peroxotitanium(IV). We will write the free metal ion as TiO^{2+} and the peroxo complex as TiO_2^{2+}, though in neither case is the formulation certain.[6-9] In this paper we report the results obtained with the oxidants chlorine and cerium(IV) in acidic perchlorate solutions. In addition, the values of the stability constant and formation rate constant for TiO_2^{2+} under these conditions are summarized.

Experimental Section

Reagents. Solutions of $TiO(ClO_4)_2$ were prepared from freshly hydrolyzed $TiCl_4$ by ion exchange using a cation-exchange resin in the hydrogen ion form. Chloride ion was removed by rinsing the column with dilute perchloric acid. The TiO^{2+} was then eluted with 2 M $HClO_4$; only the center fraction was collected. These stock solutions were stable with respect to precipitation of hydrous TiO_2.

Solutions containing equal amounts of OCl^- and Cl^- were prepared and assayed as described previously.[5] Dilute solutions of cerium(IV) were prepared by the dissolution of reagent grade $(NH_4)_2Ce(NO_3)_6$ in perchloric acid. 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 Ce(IV) and H_2O_2 were analyzed by reaction with iodide followed by titration with thiosulfate. Titanium(IV) was assayed spectrophotometrically as the peroxide complex.[10] The $[HClO_4]$ in the TiO^{2+} stock solutions was determined by titrating the H^+ released when an aliquot was placed on a thoroughly rinsed column of cation-exchange resin in the H^+ form. Correction was made for the $[H^+]$ released by the TiO^{2+}.

Kinetic Procedures. The Cl_2–TiO_2^{2+} reaction was monitored spectrophotometrically at 410 nm, an absorption maximum for TiO_2^{2+}. The experimental procedures were the same as described in a previous paper for the Cl_2–VO_3^+ reaction.[5] A Durrum stopped-flow instrument was used for the other kinetic studies. The formation rates of TiO_2^{2+} were monitored at 410 nm, by using large excesses of hydrogen peroxide to produce pseudo-first-order conditions. The Cl_2–H_2O_2 reaction was monitored at the 325-nm absorption maximum for Cl_2, again by using large excesses of H_2O_2. Dilute oxidant concentrations were required to eliminate interference from bubbles of oxygen produced.

The Ce(IV)–TiO_2^{2+} reaction was followed either at 410 nm or at wavelengths where the absorbance was predominantly due to cerium(IV). Values of ϵ (M^{-1} cm^{-1}) determined at 25 °C in 1 M $HClO_4$ were as follows: TiO_2^{2+}, ϵ 717 at 410 nm, ϵ 113 at 310 nm; Ce(IV), ϵ 1480 at 310 nm, ϵ 516 at 360 nm, ϵ 144 at 410 nm. Small variations in these values were found at other temperatures. Minor corrections were made for contributions due to the absorptivity of the excess TiO^{2+}. No absorption by the superoxotitanium(IV) intermediate was detected at these wavelengths.

Determination of the Stability Constant, K_1, for TiO_2^{2+}. Approximately equal concentrations of TiO^{2+} and H_2O_2 over the range $(0.200-1.41) \times 10^{-3}$ M were used. Spectrophotometric measurements were made at 410 nm. At least four determinations were made at each acidity and temperature. The data were consistent with the formation of a 1:1 complex. The percentage of the total $[H_2O_2]$ complexed as TiO_2^{2+} ranged from 49 to 88% in these experiments.

Data Treatment. The integrated form of the rate equation (6) for the Cl_2–TiO_2^{2+} (vide infra) was

$$A \ln (B + [TiO_2^{2+}]) + C \ln [TiO_2^{2+}] = (k_a/K_1)t + I \qquad (1)$$

where $A = [Ti(IV)]_T/B + 1$, $B = [Cl]_{T,0} - [TiO_2^{2+}]_0$, and $C =$

---

(1) Connor, J. A.; Ebsworth, E. A. V. *Adv. Inorg. Chem. Radiochem.* **1964**, *6*, 279.
(2) Djordjevic, C. *Chem. Br.* **1982**, *18*, 554.
(3) Czapski, G. *Annu. Rev. Phys. Chem.* **1971**, *22*, 171.
(4) Thompson, R. C. *Inorg. Chem.* **1982**, *21*, 859.
(5) Thompson, R. C. *Inorg. Chem.* **1983**, *22*, 584.
(6) Orhanovic, M.; Wilkins, R. G. *J. Am. Chem. Soc.* **1967**, *89*, 278.
(7) Ellis, J. D.; Thompson, A. K.; Sykes, A. G. *Inorg. Chem.* **1976**, *15*, 3172.
(8) Muhlebach, J.; Muller, K.; Schwarzenbach, G. *Inorg. Chem.* **1970**, *9*, 2381.
(9) Veber, M.; Csanyi, L. J. *Acta Phys. Chem.* **1977**, *23*, 297.
(10) Ellis, J. D.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1973**, 537.

Table I. Experimental Values of the Stability Constant, K_1, for Peroxotitanium(IV)[a]

T, °C	K_1, M^{-1} 1.0 M $HClO_4$	 1.0 M HCl	 0.10 M $HClO_4$, 0.90 M $LiClO_4$
25.0	$(8.7 \pm 0.2) \times 10^3$	$(8.2 \pm 0.3) \times 10^3$	$(8.5 \pm 0.3) \times 10^3$
17.0	$(1.5 \pm 0.1) \times 10^4$	$(1.5 \pm 0.1) \times 10^4$	$(1.4 \pm 0.1) \times 10^4$
10.0	$(2.5 \pm 0.1) \times 10^4$	$(2.3 \pm 0.1) \times 10^4$	$(2.4 \pm 0.1) \times 10^4$

[a] $[TiO^{2+}]_0 = (0.206-1.41) \times 10^{-3}$; $[H_2O_2]_0 = (0.200-1.26) \times 10^{-3}$ M.

Table II. Kinetic Results for the Formation of Peroxotitanium(IV)[a]

T, °C	$10^2 \times [H_2O_2]$, M	$[H^+]$, M	slope,[b] s^{-1}	k_f,[c] $M^{-1}\ s^{-1}$
25.0	2.06	1.0	3.32	161
25.0	1.03	1.0	1.72	167
25.0	1.17	0.20	1.57	134
25.0[d]	1.17	0.20	1.49	127
25.0	1.17	0.084	1.47	126
25.0[e]	1.17	0.084	1.32	113
17.0	2.06	1.0	2.21	107
17.0	1.03	1.0	1.10	107
10.0	2.06	1.0	1.38	67
10.0	1.03	1.0	0.65	63

[a] Conditions: $[TiO^{2+}]_0 = 4.78 \times 10^{-4}$ M; $I = 1.0$ M ($LiClO_4$) unless otherwise indicated. [b] Determined from plots of ln $[TiO_2^{2+}]$ vs. time. [c] $k_f = \text{slope}/[H_2O_2]_0$. [d] $[Cl^-] = 0.194$ M. [e] $[Cl^-] = 0.98$ M; $[Na^+] = 0.92$ M.

Table III. Kinetic Results for the TiO_2^{2+}–Cl_2 System[a]

T, °C	$10^3 \times [TiO^{2+}]_0$, M	$10^3 \times [Cl_2]_0$, M	$10^2 \times [Cl^-]_0$, M	$10^2 k_a/K_1$,[b] s^{-1}
25.0	3.25	1.34	5.0	1.3_4 (1.5)[c]
25.0	5.55	1.68	5.1	1.3_6 (1.5)
25.0[d]	5.49	1.68	5.1	1.3_9 (1.5)
25.0	14.6	3.31	5.2	1.4_1 (1.5)
25.0	37.1	4.96	5.3	1.3_0 (1.5)
25.0[e]	5.57	1.41	19.7	1.3_9 (1.5)
25.0[f]	5.58	1.41	97.9	1.5_9 (1.5)
25.0[g]	5.56	1.41	39.2	1.2_1 (1.3)
25.0[h]	5.57	1.41	90.1	0.98_8 (1.0)
17.0	3.28	3.09	4.9	0.50_3 (0.60)
17.0	6.34	4.09	4.8	0.49_5 (0.60)
17.0[i]	10.1	2.93	4.6	0.50_8 (0.60)
10.0	3.28	3.09	4.9	0.20_4 (0.25)
10.0	6.23	6.06	4.8	0.20_8 (0.25)

[a] Conditions: $[H^+] = 0.91-0.99$ M; $[TiO_2^{2+}]_0 = (5.72-6.81) \times 10^{-4}$ M; $I = 1.0$ M unless otherwise indicated. [b] Slope of kinetic plot (eq 1). [c] Calculated from independently determined values listed in Tables I and IV. [d] Different TiO^{2+} stock solution used. [e] $[H^+] = 0.10$ M; $I = 1.0$ M ($LiClO_4$). [f] $[H^+] = 0.084$ M; $I = 1.0$ M (NaCl). [g] $k_a = 110\ M^{-1}\ s^{-1}$ used in analysis. [h] $k_a = 91\ M^{-1}\ s^{-1}$ used in analysis. [i] $[TiO_2^{2+}]_0 = 1.20 \times 10^{-3}$ M.

Table IV. Kinetic Results for the H_2O_2–Cl_2 Reaction[a]

T, °C	$10^2 \times [H_2O_2]_0$, M	$10^4 \times [Cl_2]_0$, M	slope,[b] s^{-1}	k_a,[c] $M^{-1}\ s^{-1}$
25.0	0.570	4.0	0.75_4	132
17.0	2.05	8.3	1.8_3	89
17.0	1.14	8.3	1.0_6	93
10.0	3.42	8.3	2.0_2	59
10.0	1.60	8.3	1.0_5	66

[a] Conditions: $[HClO_4] = 1.0$ M; $[Cl^-]_0 = 0.050$ M. [b] Determined from plots of ln $[Cl_2]$ vs. time. [c] $k_a = \text{slope}/[H_2O_2]_0$.

$-[Ti(IV)]_T/B - k_a/k_f$. Values of k_a/K_1 were obtained as the slopes of plots of the left side of eq 1 vs. time.

The reaction scheme proposed (vide infra) for the decay of superoxotitanium(IV), TiO_2^{3+}, formed by the reaction of *excess* Ce(IV) with TiO_2^{2+} leads to the rate expression (2). The $[TiO_2^{3+}]$ was taken

$$-d \ln [TiO_2^{3+}]/dt = k_d + k_5[Ce(IV)] \qquad (2)$$

to be proportional to $A - A_\infty$ at 360 nm. Plots of ln $(A - A_\infty)$ vs. time were approximately linear. Values of k_5 were estimated from the straight lines generated by plots of these slopes (identified as $k_d + k_5[Ce(IV)]_{av}$) vs. $[Ce(IV)]_{av}$, where $[Ce(IV)]_{av}$ is the average [Ce(IV)] during the decay process.

Results

Stability Constant and Formation Rate of Peroxotitanium(IV). The stability constant, as defined by eq 3, was determined spectrophotometrically under conditions appropriate to this study.

$$TiO^{2+} + H_2O_2 \underset{k_r}{\overset{k_f}{\rightleftharpoons}} TiO_2^{2+} + H_2O \quad K_1 \qquad (3)$$

The results summarized in Table I indicated that the value of K_1 is identical, within the substantial experimental uncertainty, in the three acidic media investigated. Values of $\Delta H° = -11._9$ kcal/mol and $\Delta S° = -22$ cal/(deg mol) were calculated from the temperature dependence.

Values of the formation rate constant, k_f, for TiO_2^{2+} were determined by means of the stopped-flow technique and are summarized in Table II. Our results are in excellent agreement with those previously reported.[6]

Oxidation of TiO_2^{2+} by Aqueous Cl_2. The stoichiometric ratio $\Delta[TiO_2^{2+}]/[Cl]_{T,0} = 0.94 \pm 0.01$ was determined for experiments with excess TiO_2^{2+}. This result is in reasonable agreement with the overall reaction

$$TiO_2^{2+} + Cl_2 + H_2O = TiO^{2+} + O_2 + 2Cl^- + 2H^+ \qquad (4)$$

The hydrolysis of chlorine was suppressed to ≤1% by use of sufficiently high concentrations of hydrogen and chloride ions, as summarized in Table III. The ratio [uncomplexed H_2O_2]/$[TiO_2^{2+}]$ varied from 0.003 to 0.035 over the range of experimental conditions. Nevertheless, the kinetic results indicated that the reaction proceeds by the H_2O_2 pathway, where the $[H_2O_2]$ is determined by the equilibrium shown in eq 3 and reaction 5. Application of the steady-state approximation for the $[H_2O_2]$ results in the rate expression (6).

$$H_2O_2 + Cl_2 \xrightarrow{k_a} O_2 + 2H^+ + 2Cl^- \qquad (5)$$

Values of the rate parameter k_a appropriate to our experimental conditions were determined independently and are summarized in Table IV.

$$-d[TiO_2^{2+}]/dt = k_a k_r[TiO_2^{2+}][Cl_2]/(k_f[TiO^{2+}] + k_a[Cl_2]) \qquad (6)$$

Appropriate plots of the integrated form of eq 6, using our values of k_a and k_f, were strictly linear for at least 80% of the total reaction. The slopes of these plots, identified as k_a/K_1 by our analysis, are summarized in the last column by Table III. These values are independent of the initial reactant concentrations and the magnitude of the excess $[TiO^{2+}]$, in agreement with the rate expression. However, a small decrease in the value is observed as the product $[H^+][Cl^-]$ increases. This feature was also found for the Cl_2–VO_3^+ system and is consistent with previous proposals for the Cl_2–H_2O_2 reaction (7)–(9).[11,12] Reaction 7 is not significantly reversible provided

$$H_2O_2 + Cl_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} H^+ + Cl^- + HOOCl \qquad (7)$$

$$HOOCl \xrightarrow{k_3} O_2 + H^+ + Cl^- \qquad (8)$$

$$-d[H_2O_2]/dt = k_1 k_3[H_2O_2][Cl_2]/(k_2[H^+][Cl^-] + k_3) \qquad (9)$$

---

(11) Connick, R. E. *J. Am. Chem. Soc.* **1947**, *69*, 1509.

(12) Held, A. M.; Halko, D. J.; Hurst, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 5732.

Table V. Kinetic Results for the Reaction of Excess Peroxotitanium(IV) with Cerium(IV) in 1.0 M Perchloric Acid at 25 °C

λ, nm	$10^5 \times$ $[Ce(IV)]_0$, M	$10^5 \times$ $[TiO_2^{2+}]_0$, M	$10^3 \times$ $[Ti(IV)]_T$, M	$10^{-5}k_4$,[a] $M^{-1}\ s^{-1}$
310	5.00	8.19	7.96	1.1
310	5.00	8.19	15.9	1.1
310[b]	4.70	8.19	7.96	1.1
310[c]	4.70	8.19	7.96	0.72
310[d]	4.70	8.19	7.96	0.63
410	7.03	8.19	7.96	$1._3$
410	6.60	7.02	3.18	0.8

[a] Determined by plots of the integrated form of eq 10. [b] Added $[Ce(III)]_0 = 1.1 \times 10^{-2}$ M. [c] Added $[H_2SO_4] = 5.0 \times 10^{-3}$ M. [d] Added $[H_2SO_4] = 5.0 \times 10^{-3}$ M; added $[Ce(III)]_0 = 1.1 \times 10^{-2}$ M.

the product $[H^+][Cl^-]$ is less than 0.1, a condition fulfilled in most of our experiments.

Oxidation of Excess TiO_2^{2+} by Ce(IV). The rate of oxidation of hydrogen peroxide by cerium(IV) in acidic perchlorate solutions is far too rapid to be monitored by stopped-flow procedures.[13] However, we find that the TiO_2^{2+}–Ce(IV) reaction is measurable by this technique. Complete, rapid consumption of the cerium(IV) was observed at 310 nm, provided the initial concentration ratio $[TiO_2^{2+}]_0/[Ce(IV)]_0$ was greater than unity. Linear plots of ln $([TiO_2^{2+}]/[Ce(IV)])$ vs. time were obtained if a 1:1 stoichiometry was assumed. Values of the rate parameter k_4 appropriate to the rate expression (10) are summarized in Table V. The values are

$$-d[Ce(IV)]/dt = k_4[Ce(IV)][TiO_2^{2+}] \qquad (10)$$

unaffected by doubling the excess $[TiO^{2+}]$ or the addition of 1.1×10^{-2} M Ce(III). However, the presence of 5.0×10^{-3} M H_2SO_4 detectably lowers the value of k_4.[14]

The reaction was also monitored at the 410-nm absorption maximum of TiO_2^{2+}. The kinetic profiles exhibited a rapid decrease in absorbance followed by a slower increase, as shown in Figure 1. The kinetic data for the rapid reaction were adequately correlated by the integrated form of eq 10, again with the assumption of a 1:1 stoichiometry. As can be seen in Table V, the values of k_4 obtained at the two wavelengths are in reasonable agreement.

Spectral scans indicated the *formation* of TiO_2^{2+} during the second stage, slower reaction illustrated in Figure 1. The overall stoichiometric ratio $([TiO_2^{2+}]_0 - [TiO_2^{2+}]_\infty)/[Ce(IV)]_0$ was determined to be 0.50 ± 0.02, where $[TiO_2^{2+}]_\infty$ is the final, stable concentration of peroxotitanium(IV) at the conclusion of the slower reaction. This result is consistent with the net reaction (11). However, all of the cerium(IV) is consumed

$$TiO_2^{2+} + 2Ce(IV) + H_2O = TiO^{2+} + O_2 + 2Ce(III) + 2H^+ \qquad (11)$$

in the rapid reaction, and peroxotitanium(IV) is regenerated to the extent of half the initial cerium(IV) concentration during the slower reaction under these conditions.

The slower component of the kinetic profiles measured at 410 nm exhibited first-order behavior. Plots of ln $(A_\infty - A)$ vs. time, beginning at the point of minimum absorbance in the kinetic trace, were strictly linear for up to 90% of total reaction. The slopes of these plots are listed in Table VI. The values are essentially independent of the initial concentrations of the reactants and excess TiO^{2+} but decrease as the hydrogen ion concentration is lowered.

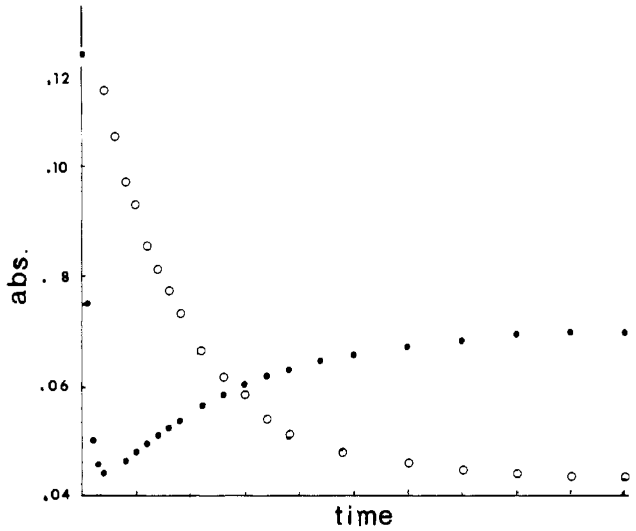

Figure 1. Kinetic plot of absorbance vs. time for the Ce(IV)–TiO_2^{2+} reaction. Conditions: $[TiO_2^{2+}]_0 = 8.19 \times 10^{-5}$ M; $[Ce(IV)]_0 = 7.03 \times 10^{-5}$ M; $[TiO^{2+}]_0 = 7.88 \times 10^{-3}$ M; $[HClO_4] = 1.0$ M; $T = 25$ °C; wavelength 410 nm; path length 2.0 cm. Time scale: 0.10 s per major division, open circles; 2.0 s per major division, blackened circles.

Oxidation of TiO_2^{2+} by Excess Ce(IV). These reactions were usually monitored at 360 nm, where the absorbance is predominantly due to cerium(IV). The cerium(IV) was consumed in two stages, the second significantly slower than the first. The overall stoichiometric ratio $[TiO_2^{2+}]_0/([Ce(IV)]_0 - [Ce(IV)]_\infty)$ was determined to be 0.50 ± 0.01, where $[Ce(IV)]_\infty$ is the final, stable concentration of cerium(IV) measured at the end of the slower reaction. Only the kinetic data for the slower reaction were analyzed. This analysis is more complicated than for the experiments in which excess TiO_2^{2+} was used, but we note that plots of ln $(A - A_\infty)$ vs. time were approximately linear. The slopes of these plots and the experimental conditions are summarized in Table VII. The values are independent of the excess $[TiO^{2+}]$ used but gradually increase as the excess [Ce(IV)] is increased.

Discussion

Both peroxovanadium(V) and peroxotitanium(IV) are quite unreactive toward chlorine, and instead oxidation proceeds through reaction of the traces of free hydrogen peroxide in equilibrium with the complexes. The only significant difference between the two reactions is the slower formation rate of TiO_2^{2+}; this rate constant must be included in the rate law for the TiO_2^{2+} reaction. The present results fortify the earlier suggestion[5] that a 2-equiv oxidation of hydrogen peroxide requires the prior formation of a peroxo complex with the oxidant. This pathway appears to be unfavorable when the peroxide moiety is complexed to a metal ion, at least when chlorine is the oxidant.

The values of k_a/K_1 determined by our independent experiments are given in parentheses in the last column of Table III. The agreement with the values determined by the kinetic analysis of the TiO_2^{2+}–Cl_2 reaction is satisfactory. The chlorine oxidation of these peroxo complexes provides an independent test of the equilibrium associated with the complex. This feature may be of particular importance for future studies where the formulation of both the metal ion and its peroxo complex is quite uncertain.

In the present system, the assignment of the formulas TiO^{2+} and TiO_2^{2+} is consistent with the experimental observation that no hydrogen ion dependence is detected in the equilibrium associated with the peroxo complex, at least in the range

---

(13) For a repudiation of contrary results, see: Samuni, A.; Czapski, G. *J. Chem. Soc., Dalton Trans.* **1973**, *487.*

(14) In 0.4 M H_2SO_4, the reaction is slow enough to be studied by conventional techniques. In this medium, even the H_2O_2–Ce(IV) reaction can be monitored by stopped-flow techniques. See: Czapski, G.; Bielski, B. H.; Sutin, N. *J. Phys. Chem.* **1963**, *67*, 201.

(15) Latimer, W. M. "Oxidation Potentials", 2nd ed.; Prentice-Hall: New York, 1952.

Table VI. Kinetic Results for the Decay of the Intermediate Formed in the Reaction of Excess Peroxotitanium(IV) with Cerium(IV)[a]

T, °C	$[HClO_4]$, M	$10^4 \times [Ce(IV)]_0$, M	$10^4 \times [TiO_2^{2+}]_0$, M	$10^3 \times [Ti(IV)]_T$, M	slope,[b] s^{-1}
25.0	1.0	0.703	0.819	7.96	0.19
25.0	1.0	0.660	0.702	3.18	0.24
25.0	1.0	2.87	2.93	7.96	0.22
25.0	0.40	2.84	2.93	4.78	0.14
25.0	0.20	2.84	2.93	4.78	0.088
25.0	0.10	2.84	2.93	4.78	0.065
17.0	1.0	2.84	2.93	4.78	0.11
10.0	1.0	2.84	2.93	4.78	0.057

[a] Monitored by measuring the regrowth of TiO_2^{2+} at 410 nm. Ionic strength maintained at 1.0 M with $LiClO_4$. [b] Obtained from plots of $\ln (A_\infty - A)$ vs. time.

Table VII. Kinetic Results for the Slower Component of the Reaction of Peroxotitanium(IV) with Excess Cerium(IV) in 1.0 M Perchloric Acid[a]

T, °C	$10^4 \times [Ce(IV)]_0$, M	$10^4 \times [TiO_2^{2+}]_0$, M	$10^3 \times [Ti(IV)]_T$, M	slope,[b] s^{-1}
25.0[c]	1.93	0.702	4.78	0.1_6
25.0	6.98	2.93	7.96	0.2_0
25.0	6.94	2.93	3.18	0.2_0
25.0	8.23	2.93	4.78	0.2_8
25.0	10.7	3.51	7.96	0.3_3
17.0	7.16	2.93	4.78	0.1_0
17.0	9.48	2.93	4.78	0.1_9
10.0	9.48	2.93	4.78	0.1_1
10.0	9.48	2.93	0.96	0.1_1

[a] Wavelength 360 nm unless otherwise indicated. [b] Estimated from plot of $\ln (A - A_\infty)$ vs. time. [c] Wavelength 310 nm.

0.10–1.0 M. The alternative proposal[8] that the equilibrium is

$$TiO^{2+} + H_2O_2 \rightleftarrows TiO_2(OH)^+ + H^+ \qquad (12)$$

below pH 1 is at odds with these observations. The problem of establishing reliable formulas for peroxo complexes of early transition metals in their highest oxidation state persists in spite of numerous investigations.[1]

Cerium(IV) oxidation of peroxotitanium(IV) in perchloric acid solutions is clearly a complicated process. While the net reaction shown in eq 11 is the conversion of the coordinated peroxide moiety to dioxygen, the kinetic results indicate a two-stage mechanism. The reaction scheme (13)–(17) is in harmony with our observations. The values of the rate constants listed are at 25 °C and 1 M $HClO_4$.

$$TiO_2^{2+} + Ce(IV) \xrightarrow{k_4} TiO_2^{3+} + Ce(III) \qquad k_4 = 1.1 \times 10^5\ M^{-1}\ s^{-1} \qquad (13)$$

$$TiO_2^{3+} \xrightarrow{k_d} O_2 + Ti^{3+} \qquad k_d = 0.11\ s^{-1} \qquad (14)$$

$$Ti^{3+} + TiO_2^{3+} + H_2O \xrightarrow{\text{fast}} TiO^{2+} + TiO_2^{2+} + 2H^+ \qquad (15)$$

$$Ti^{3+} + Ce(IV) + H_2O \xrightarrow{\text{fast}} TiO^{2+} + Ce(III) + 2H^+ \qquad (16)$$

$$TiO_2^{3+} + Ce(IV) + H_2O \xrightarrow{k_5} O_2 + TiO^{2+} + Ce(III) + 2H^+ \qquad k_5 = \text{ca. } 400\ M^{-1}\ s^{-1} \qquad (17)$$

The central feature of this scheme is the formation of a superoxo complex of titanium(IV) in reaction 13. We have formulated this unstable complex as TiO_2^{3+} for simplicity, but our data by no means establish the exact structure. The magnitude of the rate constant k_4 requires that a direct oxidation of the peroxotitanium(IV) must occur. The rate constant for dissociation of peroxide from TiO_2^{2+}, k_r in eq 3, is approximately 0.019 s^{-1} at 25 °C in 1 M $HClO_4$.

We propose that in the absence of external oxidants the decay of superoxotitanium(IV) involves a relatively slow internal redox reaction to produce dioxygen and titanium(III), as shown in eq 14. This is a surprising result, given the weak oxidizing strength of titanium(IV) and other possible routes for superoxide decomposition. However, there is good evidence that the decay of the superoxo complex of copper(II) also involves a first-order, internal redox reaction to produce dioxygen and copper(I).[16] The standard electrode potentials for the Cu(II)–Cu(I) and Ti(IV)–Ti(III) couples are 0.15 and 0.1 V, respectively.[15]

The regrowth of peroxotitanium(IV) observed in the reaction of *excess* peroxotitanium(IV) and cerium(IV) is accounted for by reaction 15, which we propose to be quite rapid. The first-order kinetics associated with this regrowth may be summarized by eq 18 according to our interpretation. Values

$$2d[TiO_2^{2+}]/dt = -d[TiO_2^{3+}]/dt = 2k_d[TiO_2^{3+}] \qquad (18)$$

of k_d are therefore half the slopes of the kinetic plots summarized in Table VI. Activation parameters for the decay of superoxotitanium(IV) in molar perchloric acid, as calculated from the temperature dependence of k_d, are $\Delta H^\ddagger = 14{.}_4$ kcal/mol and $\Delta S^\ddagger = -15$ cal/(deg mol).

The formation and decay of superoxotitanium(IV) are not completely separable processes under our experimental conditions, in that some decay occurs during the latter stages of reaction 13. However, the rates sufficiently different to permit the kinetic analysis of each.

Our justification for reactions 16 and 17 in the reaction scheme is more speculative. The pertinent data are those obtained with excess cerium(IV). Reaction 16 has apparently not been studied, but it is certainly reasonable to assume that it is very rapid in perchloric acid solution. If only reactions 14 and 16 were occurring during the decay of superoxotitanium(IV), the rate expression would be

$$-d[Ce(IV)]/dt = -d[TiO_2^{3+}]/dt = k_d[TiO_2^{3+}] \qquad (19)$$

The first-order kinetics predicted by this expression are consistent with the kinetic analysis as summarized in Table VII. While the observed slopes are comparable to the values of k_d determined in the absence of cerium(IV), they are always larger and increase as the excess cerium(IV) concentration is increased.[17] Consequently, we have included reaction 17 in our scheme. Our data are insufficient to extract an accurate rate constant, but we have estimated a value as described in the experimental section.

The value of the decay constant for superoxotitanium(IV) is dependent on the hydrogen ion concentration. The magnitude of the effect suggests that at least two different species are present in significantly varying ratios over the limited

---

(16) Meisel, D.; Levanon, H.; Czapski, G. *J. Phys. Chem.* **1974**, *78*, 779.

(17) If reaction 16 were not competitive with reaction 15, reaction 13 would be rapid enough to yield the rate expression 19, except the apparent rate constant would be $2k_d$.

acidity range investigated and that our formulation of TiO_2^{3+} may be an oversimplification. It is interesting that all recent ESR studies of superoxotitanium(IV) report a two-lined spectrum.[18,19] While the assignment of these peaks has caused considerable controversy, the concensus is that two distinct species are present in our acidity range. Our results are in agreement with Samuni's careful analysis in which he concludes that the assignment of two different hydrolyzed forms of the superoxo complex may be correct.[18]

The formation constant for superoxotitanium(IV) is apparently very large.[3,20]

$$\text{Ti(IV)} + \text{HO}_2 \rightleftarrows \text{Ti}^{\text{IV}}\text{HO}_2 \quad K_f \qquad (20)$$

Our results are consistent with this equilibrium lying far to the right. Even in the presence of cerium(IV) no evidence for significant oxidation of free HO_2 was obtained, even though the rate constant for the HO_2–Ce(IV) reaction is very large.[21] Most previous studies of superoxotitanium(IV) have used solutions containing high concentrations of hydrogen peroxide. It is quite possible that the superoxotitanium(IV) formed in these studies also contained coordinate peroxide. The decay constants reported under these conditions are considerably larger than those we have determined.[3,22] The chemistry associated with the decay process has not been recognized previously.

A potential application of our results is the generation of superoxo complexes in a rather clean environment. The rapid oxidation of a slight excess of TiO_2^{2+} by Ce(IV) produces the superoxotitanium(IV) contaminated only by the excess TiO^{2+} and small concentrations of Ce(III). The possible extension of this procedure to other peroxo complex precursors must await further experimentation. In some cases strong one-equivalent oxidants other than cerium(IV) may be more appropriate.

An internal redox process is an important if not exclusive mode of decay for the superoxo complexes of copper(II), titanium(IV), and vanadium(V). On the basis of the limited data available, these complexes are rather resistant to reaction with external oxidants either by direct reaction or through dissociation of superoxide as free HO_2 in acidic solution. The reactivity of superoxo complexes toward external reductants is unknown, except for our proposal of a rapid reduction of superoxotitanium(IV) by titanium(III).

Registry No. Cl_2, 7782-50-5; Ce, 7440-45-1.

---

[18] Samuni, A. *J. Phys. Chem.* **1972**, *76*, 2207.
[19] Irvine, M. J.; Wilson, I. R. *Aust. J. Chem.* **1979**, *32*, 2283.
[20] Meisel, D.; Czapski, G.; Samuni, A. *J. Am. Chem. Soc.* **1973**, *95*, 4148.
[21] Samuni, A.; Czapski, G. *Isr. J. Chem.* **1970**, *8*, 551.
[22] Irvine, M. J.; Wilson, I. R. *Aust. J. Chem.* **1979**, *32*, 2131.

Contribution from the Department of Chemistry,
University of Florida, Gainesville, Florida 32611

Action of Strong Acids on $M_2(O_2CR)_4$ Species

JOSHUA TELSER and RUSSELL S. DRAGO*

Received April 26, 1983

Treatment of acetonitrile solutions of $Rh_2(O_2CCH_2CH_2CH_3)_4$ and $Mo_2(O_2CCH_3)_4$ with stoichiometric amounts of the strong noncomplexing acids CF_3SO_3H and $HBF_4{\cdot}Et_2O$ gives $Rh_2(O_2CCH_2CH_2CH_3)_2^{2+}$ and $Mo_2(O_2CCH_3)_2^{2+}$, respectively. The rhodium complex is characterized in solution by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. Two derivatives of $Mo_2(O_2CCH_3)_2^{2+}$ were isolated, $[Mo_2(O_2CCH_3)_2(CH_3CN)_4](CF_3SO_3)_2$ (**1**) and $[Mo_2(O_2CCH_3)_2(CH_3CN)_5](BF_3OH)$ (**2**), and characterized by IR and UV–vis spectroscopy.

Introduction

The metal carboxylate dimers $M_2(O_2CR)_4$, where M = Cr, Mo, Ru, Re, Rh, and Cu, have been extensively studied.[1-8] These systems are of interest for several reasons. The presence of two metals in close proximity leads to the possibility of metal synergism; that is, one metal can influence the chemistry at the other metal site, leading to different reactivity than would be expected for monomeric metal systems.[2] Synergism from metal clusters is proposed in a number of biological systems such as the ferredoxins, nitrogenase,[3] cytochrome oxidase, and copper type 3 proteins.[4] Synergism in metal clusters has also been proposed to model metal-surface reactions.[5] Metal carboxylate dimers are ideal systems for studying synergism, for with variation of the metals and their oxidation states there can be wide variation in the metal–metal interaction. Metal–metal bond orders range from 4 in the Mo_2 system to 0 in the Cu_2 system where the Cu atoms are indirectly antiferromagnetically coupled.

In earlier studies from this laboratory,[2] the influence of a synergistic metal–metal interaction on the coordination of ligands to the termini of the metal–metal bond axis was investigated. The metal–metal interaction was found to lead to very effective metal-to-ligand π-back-bonding. Variation in the bridging carboxylate was also shown to have an effect on the metal–terminal ligand bond strength. Our interest in extending this research involves probing the synergistic mechanisms that are possible by having "edge" instead of terminal coordination positions available.

Ligand coordination to these edge (equatorial) positions has been reported for molybdenum(II) carboxylates. The carboxylate becomes monodentate in the process.[7,8] Species such as $Mo_2^{4+}(aq)$[9] and $Rh_2^{4+}(aq)$[10] have been reported, indicating

---

[1] Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley-Interscience: New York, 1982; and references therein. Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 225.
[2] (a) Richman, R. M.; Kuechler, T. C.; Tanner, S. P.; Drago, R. S. *J. Am. Chem. Soc.* **1977**, *99*, 1055. (b) Drago, R. S.; Tanner, S. P.; Richman, R. M.; Long, J. R. *Ibid.* **1979**, *101*, 2897. (c) Drago, R. S.; Long, J. R.; Cosmano, R. *Inorg. Chem.* **1981**, *20*, 2920. (d) Drago, R. S.; Long, J. R.; Cosmano, R. *Ibid.* **1982**, *21*, 2196. (e) Drago, R. S. *Ibid.* **1982**, *21*, 1697.
[3] Eichhorn, G. L. Ed. "Inorganic Biochemistry"; American Elsevier: New York, 1973.
[4] Solomon, E. I.; Dooley, D. M.; Wang, R.-H.; Gray, H. B.; Cerdonio, M.; Mogno, F.; Romani, G. L. *J. Am. Chem. Soc.* **1976**, *98*, 1029.
[5] Muetterties, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91.
[6] Sheldon, R. A.; Kochi, J. K. "Metal-Catalyzed Oxidations of Organic Compounds"; Academic Press: New York, 1981; p 320.
[7] Girolami, G. S.; Mainz, V. V.; Andersen, R. A. *Inorg. Chem.* **1980**, *19*, 805.
[8] Cotton, F. A.; Lay, D. G. *Inorg. Chem.* **1981**, *20*, 935.
[9] Bowen, A. R.; Taube, H. *J. Am. Chem. Soc.* **1971**, *93*, 3287.
[10] Maspero, F.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 7361.

0020-1669/84/1323-1798$01.50/0 © 1984 American Chemical Society