step in the primary redox path. It would, however, be expected to facilitate cleavage of the chelate ring(s), for incorporation of ligated halide is known markedly to enhance substitution lability at metal ion centers.[30] A sequence analogous to (10) may be envisaged for the Cr(IV)–I$^•$ reaction 5, but this almost certainly occurs after disruption of the bis-chelated structure. As in the proposed route pertaining to the Cr(V)–HSO_3^- system,[9] the Cr(V)–I$^•$ reaction, the most rapid among the electron-transfer steps, appears to be the only one involving interaction of a radical with an oxo-bound metal ion center.

It has been emphasized that autocatalysis of the type observed here and in the related Cr(V)-HSO_3^- reaction[9] reflects the capacity of both the reductant and the oxidant to undergo both one- and two-electron changes in the same medium. Analogous, but less striking, behavior in the Cr(V)–H_3PO_2 system[8] lends support to the proposed intervention of the unusual oxidation state P(II), and similar autocatalysis has been noted in the reductions of carboxylato-bound Cr(V) with SCN^- and with $S_2O_3^{2-}$,[31] although in the latter two instances competing scissions of the respective radical intermediates lead to a still more complicated kinetic picture. Among possible organic reductants, ascorbic acid reacts rapidly, generating an analogous profile, which, however, appears to be modified by strong association to the oxidant.[31]

Finally, it would be anticipated that other electron acceptors derived from transition metals in their higher oxidation states might exhibit related reduction patterns when treated with suitably versatile donors. Preliminary examinations[31] of the reductions of VO^{2+} and MoO_2^{2+} by vitamin B_{12s} (cob(I)alamin) indicates that this is the case.

Acknowledgment. The authors are grateful to Dr. Y.-T. Fanchiang for early experiments that initiated interest in this system. We also thank A. White for technical assistance.

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Redox Reactions of Superoxotitanium(IV) in Acidic Perchlorate Solution

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The ultraviolet absorption spectrum of superoxotitanium(IV), prepared by the rapid reaction of cerium(IV) and excess peroxotitanium(IV), TiO_2^{2+}, was determined. On the basis of extensive stopped-flow studies of the decay of superoxotitanium(IV), two forms of the complex formulated as TiO_2^{3+} and $TiO_2(OH)^{2+}$ are proposed. A value of 1.6 M^{-1} at an ionic strength of 1.0 M ($LiClO_4$) was determined for the hydrolysis constant of TiO_2^{3+}. The decay constant for TiO_2^{3+} (k_{d1}) is larger than that for $TiO_2(OH)^{2+}$ (k_{d2}); at 25 °C, the ratio $k_{d1}/k_{d2} \approx 13$. The redox reactions of superoxotitanium(IV) with a number of substrates were investigated by means of the multimixing, stopped-flow technique. On the basis of the variation of the second-order rate constants with [H^+], it is concluded that TiO_2^{3+} is the more reactive form of superoxotitanium(IV) toward the anionic or neutral reductants sulfur(IV), hexachloroiridate(III), iodide ion, and bromide ion. The hydrolyzed form $TiO_2(OH)^{2+}$ shows increased reactivity toward the cationic reductants iron(II), titanium(III), and oxovanadium(IV). It is proposed that reduction of superoxotitanium(IV) proceeds by a 1-equiv mechanism and is a facile process; the rate constants are only slightly less than that observed for protonated superoxide, HO_2. The rate constants for oxidation of superoxotitanium(IV), however, are orders of magnitude smaller than for HO_2. Rate constants (M^{-1} s^{-1}) determined in 1 M perchloric acid at 25 °C are as follows: 1.1×10^6 (I^-); 3.5×10^5 ($IrCl_6^{3-}$); 1.8×10^5 (Fe^{2+}); 1.3×10^4 (Ti(III)); 4.5×10^3 (S(IV)); 3.1×10^2 (VO^{2+}); ~13 (Cl_2); ~2 (Br^-).

Introduction

We have proposed that superoxotitanium(IV), tentatively formulated as TiO_2^{3+}, is formed by the rapid oxidation of peroxotitanium(IV), TiO_2^{2+}, by cerium(IV) in acidic perchlorate solution.[1] The strictly first-order decay of superoxotitanium(IV) produces half as much peroxotitanium(IV). We have interpreted these observations by the reaction scheme shown in eq 1 and 2.

$$TiO_2^{3+} = O_2 + Ti^{3+} \quad k_d \qquad (1)$$

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

The decay rate is relatively slow on the stopped-flow time scale ($k_d = 0.12\ s^{-1}$ in 1 M perchloric acid at 25 °C).[1] We therefore have been able to study the kinetics of reactions of superoxotitanium(IV) with selected reductants and oxidants by means of multimixing, stopped-flow procedures. In several cases the rate constants for the corresponding reactions of protonated superoxide, $HO_2^•$, have been determined by other investigators by pulse radiolysis techniques.[2–4] A comparison of these results enables us to assess the effect of metal ion coordination on the redox chemistry of superoxide.

In this paper we report the results of kinetic studies on the redox reactions of superoxotitanium(IV) with sulfur(IV), oxovanadium(IV), iron(II), titanium(III), hexachloroiridate(III), bromide ion, iodide ion, and chlorine. In addition, we have extended our earlier studies on the decay of superoxotitanium(IV) and have measured its absorption spectrum.

Experimental Section

Reagents. Solutions of H_2O_2, $TiO(ClO_4)_2$, $TiO(CF_3SO_3)_2$, $Ti(CF_3SO_3)_3$, $Fe(ClO_4)_2$, $VO(ClO_4)_2$, VO_2ClO_4, Na_2SO_3, and Ce(IV) were prepared by methods described previously.[1,5,6] Chlorine solutions were prepared by dissolution of the reagent-grade gas in perchloric acid. Sodium hexachloroiridate(III) was made by the hydrazine reduction of Johnson-Matthey $Na_2IrCl_6 \cdot 6H_2O$ or $(NH_4)_2IrCl_6$, followed by two recrystallizations from ethanol.[7]

All other chemicals were of reagent grade and were used without further purification. Deionized water was distilled twice before use; the last distillation was from alkaline permanganate.

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Analytical Procedures. Sulfur(IV) solutions for the kinetic experiments were prepared in glass syringes by addition of a Na_2SO_3 solution to one containing perchloric acid and lithium perchlorate such that the final ionic strength was 1.0 M. Some volatilization of SO_2 occurred during this procedure. The [sulfur(IV)] in the syringe was determined by spectrophotometric assay of $SO_2(aq)$ ($\epsilon = 367^8$ and 126 M^{-1} cm^{-1} at 280 and 300 nm, respectively) and by use of the hydrolysis equilibrium

$$SO_2(aq) = H^+ + HSO_3^- \quad K_{SO_2} \tag{3}$$

A value of 0.0144 M for K_{SO_2} was used at 25 °C and $I = 1.0$ M.[9,10]

Chlorine solutions were transferred to a glass syringe before use. The $[Cl_2]$ in the syringe was determined by addition of an aliquot to a KI solution, followed by a spectrophotometric measurement at 469 nm, an isosbestic for I_2 and I_3^- ($\epsilon = 730$ M^{-1} cm^{-1}).[11]

Fresh solutions of $IrCl_6^{3-}$ were prepared for each experiment. They were assayed as $IrCl_6^{2-}$ ($\epsilon = 4100$ M^{-1} cm^{-1} at 487 nm)[7] after oxidation of an aliquot by gaseous Cl_2. The excess Cl_2 was removed by a stream of nitrogen.

The analytical methods used for the other reagents have been described previously.[1,5,6]

Kinetic Procedures. A Dionex multimixing accessory for the Durrum stopped-flow instrument was used in the kinetic determinations. This accessory utilizes three drive syringes and two separated mixing ports. Superoxotitanium(IV) was formed by rapidly mixing a cerium(IV) solution with a solution containing H_2O_2 and TiO^{2+} such that typically >98% of the peroxide was complexed as TiO_2^{2+}. The mixing of this solution with one containing the desired substrate was delayed by passage through a thermostated loop of Teflon tubing. The delay time is determined by the length and diameter of the loop and the velocity of the pneumatic drive of the stopped-flow instrument. This velocity is somewhat variable from day to day and was measured by means of a linear velocity transducer for each set of kinetic experiments. The delay time between the first and second mixings can be calculated from the loop dimensions, the drive velocity, and the total volume of solution passed through the mixing chambers during each actuation. The delay time was measured independently by use of the previously studied reaction 4.[1,12]

$$TiO^{2+} + H_2O_2 = TiO_2^{2+} + H_2O \tag{4}$$

Two solutions, containing TiO^{2+} and H_2O_2, respectively, were passed through the first mixer and then mixed with $HClO_4$. The delay time was calculated by measuring the extent of formation of TiO_2^{2+}. The agreement between the two methods was 5%; thereafter the velocity transducer method was used. Delay times typically ranged from 0.23 to 0.31 s. The dead time for complete mixing with this accessory was 9–11 ms.

The stopped-flow instrument without the multimixing accessory was used for the studies of the decay of superoxotitanium(IV).

A 1.0-mm slit width was used in all the kinetic experiments. We found that the extinction coefficients measured on the Durrum instrument under this condition were typically 10% lower than those determined on our Zeiss PMQ11 spectrophotometer. Therefore, the extinction coefficients of all absorbing species were determined at each wavelength on the Durrum instrument.

Determination of the Absorption Spectrum of Superoxotitanium(IV). Absorption due to superoxotitanium(IV) was observed only in the ultraviolet region. The superoxotitanium(IV) was formed by mixing a solution containing Ce(IV) with one containing excess TiO_2^{2+} on the stopped-flow instrument (path length 2 cm) such that the initial concentrations were $[Ce(IV)]_0 = 1.12 \times 10^{-4}$ M, $[TiO_2^{2+}]_0 = 1.41 \times 10^{-4}$ M, $[TiO^{2+}]_0 = 1.29 \times 10^{-3}$ M, and $[H_2O_2]_0 = 1.26 \times 10^{-5}$ M. The Ce(IV) oxidation of the small $[H_2O_2]$ to form HO_2 is very rapid. The fate of the HO_2 is uncertain—some will disproportionate, some will be oxidized to O_2 by Ce(IV), and some will combine with TiO^{2+} to form superoxotitanium(IV). We have assumed that half of the HO_2 formed in this minor pathway is rapidly converted to peroxotitanium(IV) and the rest to oxygen through rapid oxidation by cerium(IV). The Ce(IV)–TiO_2^{2+} reaction that forms superoxotitanium(IV) is rapid ($k = 1.1 \times 10^5$ M^{-1} s^{-1} in 1.0 M $HClO_4$ at 25 °C) but not instantaneous. Cerium(IV) is highly absorbing in the ultraviolet region, and it was essential to allow sufficient time in the spectral determinations for interference from this species to become negligible. Numerical integration of the scheme given in eq 13–17 in our previous paper,[1] where k_{15} and k_{16} were arbitrarily set at 10^6 M^{-1} s^{-1}, shows that 2.00 s after mixing [Ce(IV)] is less than 10^{-8} M. However, by this time [superoxotitanium(IV)] has passed through its maximum (9.7×10^{-5} M at 0.50 s) and has decayed to ca. 4.8×10^{-5} M. In addition, absorbance due to TiO^{2+} and TiO_2^{2+} must be taken into account. To overcome these difficulties in determining molar extinction coefficients for superoxotitanium(IV), the following procedure was adopted. The decay process was first monitored at 410 nm. The formation of TiO_2^{2+} was determined between 2.0 and 4.8 s after mixing. Equation 5 allows the quantity $\Delta[TiO_2^{2+}]$ to be accurately

$$A_{4.8s} - A_{2.0s} = 2(\epsilon_{TiO_2^{2+}})(\Delta[TiO_2^{2+}]_{4.8s-2.0s}) \tag{5}$$

calculated. Our previous work demonstrated that eq 6 accurately relates

$$\Delta[TiO_2^{2+}] = \Delta[TiO^{2+}] = -0.50(\Delta[\text{superoxotitanium(IV)}]) \tag{6}$$

this quantity to $\Delta[TiO^{2+}]$ and Δ[superoxotitanium(IV)] during the same time period. The identical experiment was then performed at each desired wavelength in the ultraviolet region. Use of eq 5 and 6 allows an accurate calculation of the extinction coefficient for superoxotitanium(IV), ϵ_s, as summarized in eq 7. In a typical experiment at 260 nm, ΔA

$$\epsilon_s = \{A_{2.0s} - A_{4.8s} + 2\epsilon_{TiO^{2+}}(\Delta[TiO^{2+}]) + 2\epsilon_{TiO_2^{2+}}[TiO_2^{2+}]\}/(2\Delta[\text{superoxotitanium(IV)}]_{2.0s-4.8s}) \tag{7}$$

$= 0.038$, $\Delta[TiO^{2+}] = 1.28 \times 10^{-5}$ M $= \Delta[TiO_2^{2+}]$, and Δ[superoxotitanium(IV)] $= 2.56 \times 10^{-5}$ M. With use of $\epsilon_{TiO^{2+}} = 93.7$ M^{-1} cm^{-1} and $\epsilon_{TiO_2^{2+}} = 56$ M^{-1} cm^{-1}, the resulting value of ϵ_s is 816 M^{-1} cm^{-1}.

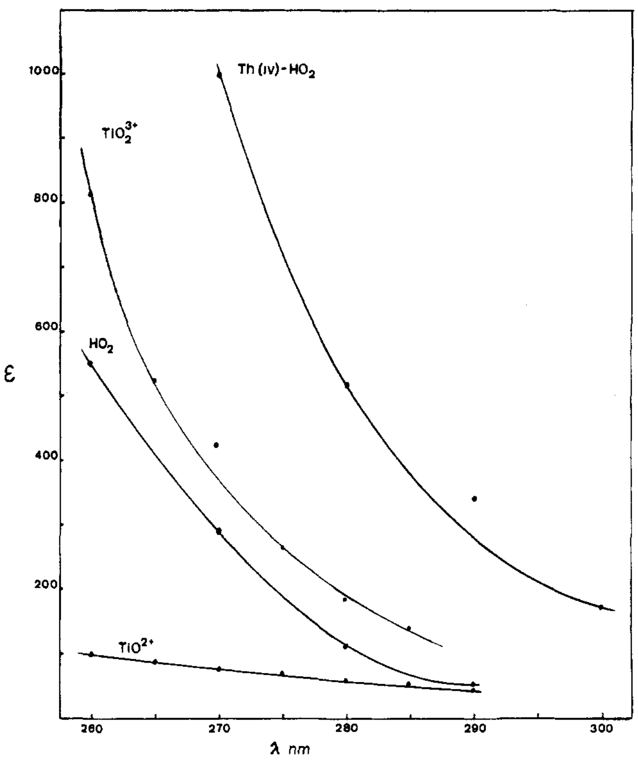

Figure 1. Absorption spectra of protonated superoxide,[13] superoxotitanium(IV), and superoxothorium(IV).[14]

Values of the extinction coefficients of TiO^{2+} and TiO_2^{2+} were determined at each wavelength, with use of the same fixed slit width of 1.0 mm as was used in the spectral determinations.

Data Treatment. Most of the kinetic experiments were performed with a large excess of the reductant or oxidant. Plots of ln $[A_\infty - A]$ or ln $[A - A_\infty]$ vs. t were linear in all cases under these conditions, usually for at least 3 half-lives.

Second-order conditions were employed for the very rapid reactions. The initial concentration of superoxotitanium(IV) was calculated as described in the previous section. It was difficult to determine accurately the reaction stoichiometries. Therefore, it was assumed that the ratio Δ[superoxotitanium(IV)]/Δ[substrate] was 1 for the iron(II), titanium(III), and hexachloroiridate(III) systems and 2 for the iodide system. The linearity of the second-order rate plots provides strong confirmation that these assumed stoichiometries are correct.

Results

Absorption Spectrum and Decay Kinetics of Superoxotitanium(IV). The absorption spectrum of superoxotitanium(IV) is shown in Figure 1. Significant absorptivity was found only

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Table I. Kinetic Results for the Decay of Superoxotitanium(IV)[a]

T, °C	[$HClO_4$], M	k_d, s^{-1} [b]	T, °C	[$HClO_4$], M	k_d, s^{-1} [b]
25.0[c]	1.00	0.11 ± 0.01	17.0	0.60	0.041 (0.040)
25.0[d]	1.00	0.10	17.0	0.40	0.032 (0.032)
25.0[e]	1.00	0.12 ± 0.01	17.0	0.20	0.023 (0.023)
25.0	1.00	0.11_8 (0.117)	17.0	0.15	0.020 (0.020)
25.0	0.80	0.10_4 (0.104)	17.0	0.125	0.019 (0.019)
25.0	0.60	0.089 (0.089)	10.0	1.00	0.025 (0.024)
25.0	0.40	0.072 (0.071)	10.0	0.80	0.023 (0.022)
25.0	0.20	0.046 (0.048)	10.0	0.60	0.019 (0.019)
25.0	0.10	0.036 (0.035)	10.0	0.40	0.015 (0.016)
17.0	1.00	0.051 (0.052)	10.0	0.20	0.010 (0.011)
17.0	0.80	0.044 (0.046)			

[a] Unless otherwise noted, reactions were monitored by measuring the regrowth of TiO_2^{2+} at 410 nm. Ionic strength maintained at 1.0 M with $LiClO_4$. Conditions: $[TiO_2^{2+}]_0 = (3.86–4.19) \times 10^{-4}$ M, $[Ce(IV)]_0 = (1.57–2.83) \times 10^{-4}$ M, and $[TiO^{2+}]_0 = (3.31–3.78) \times 10^{-3}$ M unless otherwise indicated. [b] Obtained from the slope of plots of $-\ln [A_\infty - A]$ vs. time, where k_d = slope/2. Values in parentheses were obtained by use of eq 12. [c] Value for k_d is averge of four experiments monitored from 260 to 275 nm, with $[TiO^{2+}]_0 = 1.31 \times 10^{-3}$ M. [d] $[TiO^{2+}]_0 = 1.42 \times 10^{-2}$ M. [e] $[Cu^{2+}]_0 = 9.87 \times 10^{-3}$ M and $[TiO^{2+}]_0 = 5.80 \times 10^{-3}$ M.

in the ultraviolet region, and the extinction coefficients were independent of acidity from 0.20 to 1.00 M perchloric acid. The spectrum is very similar in shape to that of HO_2 and superoxothorium(IV).[13,14]

The strictly first-order decay of superoxotitanium(IV) was previously monitored by observing the formation of peroxotitanium(IV) at its absorption maximum at 410 nm. We have extended these studies, and the results are summarized in Table I. Little if any effect due to the excess [TiO^{2+}] was observed over the range $(0.13–1.42) \times 10^{-2}$ M. The decay constant was insensitive to the presence of Cu^{2+}, a species known to be an effective scavenger of free HO_2.[15-17] The decay rate was also monitored by observing the decrease in absorbance of superoxotitanium(IV) in the ultraviolet region. Plots of $-\ln [A - A_\infty]$ vs. time were very linear for at least 3 half-lives, and the slopes were identical within experimental error to those determined at 410 nm.

The values of the decay constant k_d decrease with decreasing acidity, as was observed previously.[1] Our present, more extensive results are consistent with the scheme shown in eq 8–11.

$$TiO_2^{3+} + H_2O = TiO_2(OH)^{2+} + H^+ \quad \text{rapid, } K_h \tag{8}$$

$$TiO_2^{3+} = Ti^{3+} + O_2 \quad k_{d1} \tag{9}$$

$$TiO_2(OH)^{2+} \overset{H^+}{=} Ti^{3+} + O_2 + H_2O \quad k_{d2} \tag{10}$$

$$\text{superoxotitanium(IV)} + Ti^{3+} = TiO_2^{2+} + TiO^{2+} \text{ rapid} \tag{11}$$

This scheme would require three adjustable parameters to fit the observed [H^+] dependence at a given temperature. Therefore, we instead have simultaneously fit all the data at various acidities and temperatures to eq 12

$$k_d = \{k_{d1}[H^+] + k_{d2}K_h\}/\{[H^+] + K_h\} \tag{12}$$

where

$$k_{d1} = (k_bT/h) \exp(\Delta S^*_{d1}/R) \exp(-\Delta H^*_{d1}/RT) \tag{13}$$

$$k_{d2} = (k_bT/h) \exp(\Delta S^*_{d2}/R) \exp(-\Delta H^*_{d2}/RT) \tag{14}$$

This procedure uses 18 data points to determine 5 parameters, if we make the reasonable assumption that the hydrolysis constant K_h varies only slightly from 10 to 25 °C. The resulting best-fit parameters determined from a nonlinear least-squares adjustment of the data are $K_h = 1.6 \pm 0.3$ M, $\Delta H^*_{d1} = 18._9 \pm 0.5$ kcal/mol, $\Delta S^*_{d1} = 25 \pm 2$ cal/(deg mol), $\Delta H^*_{d2} = 14 \pm 2$ kcal/mol, and $\Delta S^*_{d2} = 3 \pm 6$ cal/(deg mol). The calculated values of k_d from these parameters are given in parentheses in Table I.

Table II. Kinetic Results for the Reduction of Superoxotitanium(IV) by Sulfur(IV)[a]

T, °C	[$HClO_4$], M	no. of expts	$10^{-3}k_{S(IV)}$, M^{-1} s^{-1} [b]
25.0	1.00	7	4.5 ± 0.4
25.0	0.80	8	4.7 ± 0.3
25.0	0.60	6	4.9 ± 0.4
25.0	0.40	14	5.3 ± 0.2
25.0	0.20	9	5.9 ± 0.4
25.0	0.15	4	6.8 ± 0.2
25.0	0.125	4	7.3 ± 0.2
25.0	0.10	4	7.1 ± 0.3
17.0	0.20	3	5.3 ± 0.1
10.0	0.20	5	3.8 ± 0.3

[a] Monitored at 410 nm. Ionic strength maintained at 1.0 M with $LiClO_4$. After first mixing, $[Ce(IV)]_0 = (1.70–2.23) \times 10^{-4}$ M, $[TiO_2^{2+}]_0 = (2.88–7.42) \times 10^{-4}$ M, and $[TiO^{2+}]_0 = (3.40–7.22) \times 10^{-3}$ M. After second mixing, $[\text{superoxotitanium}]_0 = (0.82–1.1) \times 10^{-4}$ M and $[\text{sulfur(IV)}]_0 = (0.91–5.49) \times 10^{-3}$ M. [b] Determined from the slope of plots of $-\ln [A_\infty - A]$ vs. time, where $k_{S(IV)} = \text{slope}/\{[S(IV)]_0 - [\text{superoxotitanium(IV)}]_0/2]\}$.

Kinetic Results for Redox Reactions of Superoxotitanium(IV) with Various Reagents. All of these studies used multimixing, stopped-flow procedures. Superoxotitanium(IV) was generated after the first mixing by the reaction of excess peroxotitanium(IV) and cerium(IV). The residence time of this solution prior to mixing with the substrate solution was typically 0.23–0.31 s, a period long enough for >99.9% consumption of the cerium(IV) and maximal production of superoxotitanium(IV). Substrate concentrations were adjusted such that the reaction rate was rapid relative to decay of the superoxo complex, except where noted. The substrates investigated are unreactive toward peroxotitanium(IV) on the time scale of the reactions of interest.

(A) Reduction of Superoxotitanium(IV) by Sulfur(IV). A large excess [sulfur(IV)] was used in all the kinetic experiments. The reactions were monitored by measuring the formation of peroxotitanium(IV) at 410 nm. Plots of $-\ln [A_\infty - A]$ vs. time were linear for ca. 80% of the total reaction. Values of the rate parameter $k_{S(IV)} = \text{slope}/[\text{sulfur(IV)}]_{av}$ for various experimental conditions are summarized in Table II. The scatter in the values of the rate parameter was the largest for any system investigated in this study, but the results at a given acidity and temperature are consistent with rate expression 15. The yields of peroxotitanium(IV) were approximately 75% based on the initial superoxotitanium(IV) concentration. We were unable to establish whether dithionate, sulfate, or mixtures of both were the oxidation product(s).

$$-d[\text{superoxotitanium(IV)}]/dt = k_{S(IV)}[\text{superoxotitanium(IV)}][S(IV)] \tag{15}$$

A small increase in the value of $k_{S(IV)}$ with decreasing acidity was observed at 25 °C, a variation that is correlated empirically by eq 16.

$$k_{S(IV)} = (4.5 \pm 0.1) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}/[H^+]^{0.21\pm0.02} \tag{16}$$

(B) Reduction of Superoxotitanium(IV) by Oxovanadium(IV). A large excess [VO^{2+}] was used in all the kinetic experiments, which were usually monitored at 410 nm. The reproducibility and the linearity of the $-\ln [A_\infty - A]$ vs. time plots were extraordinary, the best of any system investigated in this study. Values of the rate parameter $k_{V(IV)} = k_{obsd}/[V(IV)]_{av}$ and the experimental conditions are summarized in Table III. The values of $k_{V(IV)}$ determined at 356 nm, an isosbestic for VO_2^+ and $VO(O_2)^+$, and at 455 nm, an absorption maximum for $VO(O_2)^+$, were virtually identical with those measured at 410 nm. The absorbance

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Table III. Kinetic Results for the Reduction of Superoxotitanium(IV) by Oxovanadium(IV)[a]

T, °C	[$HClO_4$], M	$10^2[VO^{2+}]_0$	k_{obsd}, s^{-1} [b]	$10^{-2}k_{V(IV)}$, M^{-1} s^{-1} [c]
25.0	0.80	2.02	6.31	3.1_3
25.0	0.60	2.01	6.49	3.2_4
25.0	0.40	0.672	2.23	3.3_4
25.0	0.40	1.34	4.36	3.2_6
25.0	0.40	2.00	6.69	3.3_5
25.0	0.40	2.67	8.85	3.3_2
25.0	0.40	3.36	11.1	3.3_1
25.0	0.20	2.02	7.03	3.4_9
25.0[d]	0.20	2.02	7.13	3.5_4
25.0[e]	0.20	2.02	6.89	3.4_8
25.0	0.15	2.02	7.09	3.5_2
25.0	0.125	2.03	7.16	3.5_3
25.0	0.10	2.03	6.99	3.4_5
15.0	0.20	2.02	3.30	1.6_4
13.7	0.20	1.91	2.77	1.4_5
10.0	0.20	1.91	1.97	1.0_3

[a] Monitored at 410 nm unless otherwise indicated. Ionic strength maintained at 1.0 M with $LiClO_4$. After second mixing, [superoxotitanium(IV)]$_0$ = (8.35–9.26) × 10^{-5} M and $[TiO^{2+}]_0$ = (0.679–1.14) × 10^{-2} M. [b] Determined from the slope of plots of $-\ln [A_\infty - A]$ vs. time. [c] Rate parameter $k_{V(IV)} = k_{obsd}/\{[VO^{2+}]_0 - [\text{superoxotitanium(IV)}]_0/2\}$. [d] Monitored at 356 nm. [e] Monitored at 455 nm.

change in the experiment at 455 nm establishes that VO_2^+ rather than $VO(O_2)^+$ is the principal oxidation product. The small variation of the rate parameter with acidity at 25 °C is adequately correlated by eq 17. Values of the activation parameters determined from the temperature dependence of $k_{V(IV)}$ in 0.20 M $HClO_4$ at an ionic strength of 1.0 M are $\Delta H^* = 12.9 \pm 0.4$ kcal/mol and $\Delta S^* = -4 \pm 1$ cal/(deg mol).

$$k_{V(IV)} = (359 \pm 3\ M^{-1}\ s^{-1}) \exp\{(-0.018 \pm 0.02)[H^+]\} \quad (17)$$

(C) Reduction of Superoxotitanium(IV) by Iron(II), Titanium(III), and Hexachloroiridate(III). These rapid reactions were briefly investigated under second-order conditions. The experimental details and values of the second-order rate constants k_{obsd} are summarized in Table IV. No [H^+] was detected for the iron(II) system, whereas a first-order dependence was found for the hexachloroiridate(III) reaction. A small inverse [H^+] dependence on k_{obsd} was found for the titanium(III) system.

(D) Reduction of Superoxotitanium(IV) by Iodide and Bromide Ions. Superoxotitanium(IV) is rapidly reduced by iodide ion. The values of the second-order rate constants given in Table IV decrease substantially with decreasing [H^+].

The kinetic profiles monitored at 410 nm for the bromide system are similar to those observed in its absence. A small enhancement in the first-order rate constant k_{obsd} (0.32 s^{-1} with 9.89 × 10^{-2} M Br^- compared with 0.23 s^{-1} with no added Br^-) was observed in 1 M $HClO_4$; no enhancement was detected under these conditions in 0.20 M $HClO_4$ at I = 1 M. The identical experiments were repeated at 265 nm in an effort to determine whether in fact bromide ion is weakly reactive toward superoxotitanium(IV). At this wavelength extinction coefficients for superoxotitanium(IV), Br_2, and Br_3^- are 520, 27, and 3.6 × 10^4 M^{-1} cm^{-1}, respectively.[18,19] In 1 M $HClO_4$, a small increase in absorbance with time was observed. The first-order rate constant is in reasonable agreement with that determined at 410 nm. Approximately 4.3 × 10^{-6} M (Br_2 + Br_3^-) was formed during the reaction, based on the absorbance change at 265 nm (a value[20] of 17 M^{-1} was used for the very rapid equilibrium $Br_2 + Br^- = Br_3^-$). No absorbance change with time was observed in 0.20 M $HClO_4$ at 265 nm, indicating that only traces of Br_2 and Br_3^- are formed, in amounts that coincidentally compensate for the decrease in absorbance due to loss of superoxotitanium(IV). We conclude that under our experimental conditions some reduction of superoxotitanium(IV) by bromide ion is competitive with the self-decay of superoxotitanium(IV) in 1 M perchloric acid, whereas in 0.20 M acid the competition is nearly absent.

(E) Kinetic Results for the Superoxotitanium(IV)–Chlorine System. The rate of disappearance of superoxotitanium(IV) in the presence of dissolved chlorine was monitored at 260 nm. Linear first-order rate plots were obtained in all cases. Values of the measured first-order rate constant k_{obsd} and the experimental conditions are summarized in Table IV. The values of k_{obsd} are *smaller* than those observed in the absence of Cl_2 at low [Cl_2] and greater at a large [Cl_2].

(F) Qualitative Observations. No effect of 2 × 10^{-3} M HN_3, NH_3OH^+, $N_2H_5^+$, BrO_3^-, or HSO_5^- was observed in 1 M $HClO_4$ at 25 °C on the decay of superoxotitanium(IV) monitored at 410 nm. We conclude that these reagents are unreactive under these conditions.

Discussion

The only significant difference in the absorption spectra of protonated superoxide, superoxotitanium(IV), and superoxothorium(IV) is a shift toward longer wavelengths for the d^0 and f^0 metal ion complexes. The ultraviolet absorption of superoxotitanium(IV) has extended the range of feasible studies of this transient species. In particular, we have measured the decay process by following the disappearance of superoxotitanium(IV) as well as the formation in the decay product peroxotitanium(IV). The excellent agreement between the two methods provides additional confirmation of the decay scheme given in eq 1 and 2. We have also confirmed that titanium(III) rapidly reduces superoxotitanium(IV) to form peroxotitanium(IV) by a brief kinetic study of reaction 2.

We have previously suggested,[1] on the basis of the variation of the decay constant with acidity, that two different forms of superoxotitanium(IV) exist in rapid equilibrium over the hydrogen ion concentration range 0.10–1.0 M. ESR studies show a two-lined spectrum in this acidity region, and Samuni has proposed the existence of two different hydrolyzed forms on the basis of a careful analysis of the ESR data.[21,22] The results of the extensive decay studies summarized in Table I have enabled us to estimate a hydrolysis of 1.6 M^{-1} for reaction 8 at an ionic strength of 1.0 M. The exact formulation for the two forms of superoxotitanium(IV) is speculative, but our analysis indicates that the unhydrolyzed form we identify at TiO_2^{3+} decays more rapidly than $TiO_2(OH)^{2+}$ ($k_{d1}/k_{d2} \approx 13$ at 25 °C).

The ratio $[TiO_2^{3+}]/[TiO_2(OH)^{2+}]$ varies from ca. 0.63 to 0.063 over the 1.0–0.10 M [H^+] range used in this study. Our kinetic data indicate that TiO_2^{3+} is the more reactive form toward the anionic and neutral reductants examined. This is clearly the case with iodide ion; the limited results available are correlated by eq 18. Similarly, the hexachloroiridate(III) results are in reasonable accord with eq 19. The sulfur(IV) results are more difficult to assess, since the ratio $[HSO_3^-]/[SO_2(aq)]$ varies from ca. 0.014 in 1.0 M $HClO_4$ to 0.14 in 0.10 M $HClO_4$. The bisulfite ion is often the more reactive[23] and is the only species reactive toward H_2O_2.[8] We observe a mild inverse [H^+] dependence for the sulfur(IV)–superoxotitanium(IV) system as given by eq 16. There are numerous possible schemes that may be used to fit the data, but the general conclusion that may be reached in that TiO_2^{3+} is more reactive than $TiO_2(OH)^{2+}$ if it is reasonably assumed that HSO_3^- is more reactive than $SO_2(aq)$.

$$-d[\text{superoxotitanium(IV)}]/dt = (2.8 \times 10^6\ M^{-1}\ s^{-1})[I^-][TiO_2^{3+}] \quad (18)$$

$$-d[\text{superoxotitanium(IV)}]/dt = ((8 \pm 1) \times 10^5\ M^{-1}s^{-1})[IrCl_6^{3-}][TiO_2^{3+}] \quad (19)$$

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Table IV. Kinetic Results for Other Redox Reactions of Superoxotitanium(IV)[a]

reagent; wavelength, nm	Init concn, M	$[HClO_4]_0$, M	10^5[superoxotitanium(IV)]$_0$, M	k_{obsd}
Fe^{2+}; 410	4.36×10^{-5}	1.00	3.9	$1.8 \times 10^5\ M^{-1}\ s^{-1}$
Fe^{2+}; 410	4.36×10^{-5}	0.60	4.1	$1.8 \times 10^5\ M^{-1}\ s^{-1}$
Fe^{2+}; 410	4.36×10^{-5}	0.20	3.7	$1.7 \times 10^5\ M^{-1}\ s^{-1}$
Ti^{3+}; 410	1.14×10^{-4}	1.00	4.7	$1.3 \times 10^4\ M^{-1}\ s^{-1}$
Ti^{3+}; 410	9.58×10^{-5}	0.20	1.7	$2.2 \times 10^4\ M^{-1}\ s^{-1}$
$IrCl_6^{3-}$; 487	1.03×10^{-4}	1.00	2.9	$3.5 \times 10^5\ M^{-1}\ s^{-1}$
$IrCl_6^{3-}$; 487	8.90×10^{-5}	0.80	6.7	$3.3 \times 10^5\ M^{-1}\ s^{-1}$
$IrCl_6^{3-}$; 487	1.04×10^{-4}	0.60	2.8	$2.1 \times 10^5\ M^{-1}\ s^{-1}$
$IrCl_6^{3-}$; 487	1.01×10^{-4}	0.40	2.3	$1.4 \times 10^5\ M^{-1}\ s^{-1}$
$IrCl_6^{3-}$; 487	1.09×10^{-4}	0.20	2.7	$7.5 \times 10^4\ M^{-1}\ s^{-1}$
Cl_2; 260	2.01×10^{-4}	1.00	$10._1$	$0.15\ s^{-1}$
Cl_2; 260	6.38×10^{-4}	1.00	$10._1$	$0.17\ s^{-1}$
Cl_2; 260	2.27×10^{-3}	1.00	$10._1$	$0.22\ s^{-1}$
Cl_2; 260	1.85×10^{-2}	1.00	9.4	$0.40\ s^{-1}$
Cl_2; 260	1.32×10^{-2}	0.20	$12._0$	$0.27\ s^{-1}$
I^-; 469	6.02×10^{-5}	1.00	2.5	$1.1 \times 10^6\ M^{-1}\ s^{-1}$
I^-; 469	6.02×10^{-5}	0.60	2.8	$7.6 \times 10^5\ M^{-1}\ s^{-1}$
I^-; 469	6.02×10^{-5}	0.20	2.9	$3.1 \times 10^5\ M^{-1}\ s^{-1}$
Br^-; 410	9.89×10^{-2}	1.00	$11._6$	$0.32\ s^{-1}$
Br^-; 265	9.89×10^{-2}	1.00	6.9	$0.29\ s^{-1}$
Br^-; 410	9.89×10^{-2}	0.20	$12._0$	$0.082\ s^{-1}$
Br^-;[b] 265	9.89×10^{-2}	0.20	9.5	

[a] Conditions: I = 25 °C and I = 1.0 M ($LiClO_4$) unless otherwise indicated. Second-order rate constants obtained from plots of ln {[reagent]/[superoxotitanium(IV)]} vs. time. First-order rate constants obtained from plots of ln $[A_\infty - A]$ or ln $[A - A_\infty]$ vs. time. [b] No absorbance change observed during experiment.

However, the hydrolyzed form of superoxotitanium(IV) appears to play a more significant role in the reductions by cationic metal ions. We conclude that iron(II) is about equally reactive toward the two forms, on the basis of the lack of an observable $[H^+]$ dependence. The assessment for titanium(III) depends on the relative reactivity of Ti^{3+} and $TiOH^{2+}$ ($K_h = 2.3 \times 10^{-3}$).[24] We observe an inverse $[H^+]$ dependence, but the data are too limited to allow a conclusion regarding the more reactive form of superoxotitanium(IV). The results for oxovanadium(IV) show no hydrogen ion dependence other than a mild variation that is likely due to a medium effect as shown in eq 17. Taken at face value, this implies that the two forms of superoxotitanium(IV) are about equally reactive. However, the conversion of VO^{2+} to VO_2^+ is accompanied by the loss of two hydrogen ions. This raises the (less likely) possibility that the lack of an observable $[H^+]$ dependence may be due to a cancellation of effects if TiO_2^{3+} were the more reactive form of superoxotitanium(IV).

We propose that the reductions of superoxotitanium(IV) investigated in this study involve a 1-equiv process as the principal pathway. In every case peroxotitanium(IV) is a major reduction product. The oxovanadium(IV) system appears to proceed by an outer-sphere process, since the likely product of an inner-sphere reduction, $VO(O_2)^+$, was not detected. However, the available data do not allow an outer-sphere or inner-sphere designation for most of the other reductions. Although the η^2 or triangular geometry has been established for peroxo complexes of d^0 metal ions, the structure of their superoxo complexes is not known.

The rate constants for the rapid reductions of superoxotitanium(IV) we have investigated are dependent on both the charge and the reducing strength of the substrate. Oxidations of superoxotitanium(IV) appear to be sluggish. Even cerium(IV) in perchlorate media oxidizes superoxotitanium(IV) with a rate constant no greater than ca. 400 $M^{-1}\ s^{-1}$ in molar perchloric acid at 25 °C.[1] We briefly investigated the chlorine system since Cl_2 is reported to oxidize HO_2 with a rate constant of $10^9\ M^{-1}\ s^{-1}$.[4] The kinetic results summarized in Table IV obey pseudo-first-order kinetics. The observed rate constants are comparable to those observed in the absence of chlorine but are clearly smaller at low $[Cl_2]$ and larger at high $[Cl_2]$. A plot of $k_{obsd} - k_d$ vs. $[Cl_2]_{av}$, where $[Cl_2]_{av}$ is taken as $[Cl_2]_0 - 0.25$[superoxotitanium(IV)]$_0$, is reasonably linear with a slope of 13 ± 1 $M^{-1}\ s^{-1}$ and an intercept of 0.05 ± 0.01 s^{-1}. If we assume the reaction scheme shown in eq 20–22, the value of k_2 is 13 $M^{-1}\ s^{-1}$, some 8 orders of magnitude

$$\text{superoxotitanium(IV)} = O_2 + Ti^{3+} \quad k_d \tag{20}$$

$${}^1/_2Cl_2 + Ti^{3+} = Ti(IV) + Cl^- \quad \text{fast} \tag{21}$$

$$ {}^1/_2Cl_2 + \text{superoxotitanium(IV)} = O_2 + Cl^- + Ti(IV) \quad k_2 \tag{22}$$

lower than that reported for the Cl_2–HO_2 reaction.[4] The small positive intercept might be taken as reflecting a competitive loss of HO_2 from superoxotitanium(IV) followed by rapid oxidation by Cl_2. However, the lack of an effect of copper(II) on the decay kinetics argues against a detectable net loss of HO_2 from superoxotitanium(IV) in the presence of excess TiO^{2+}.

Even the weak oxidant titanium(IV) is capable of oxidizing *coordinated* superoxide. If rapid oxidations of HO_2 are usually inner-sphere processes, as has been proposed for copper(II),[3,15–17] then the slow rates of oxidation of superoxotitanium(IV) by *external* reagents may well arise from the blocking of an inner-sphere attack. This would suggest but by no means establish an η^2 structure for superoxotitanium(IV). Another factor may be a lengthening of the O–O bond in the superoxo complex, a feature that would promote reduction but hinder oxidation.

The rates of reduction of HO_2 by Fe^{2+} and VO^{2+} have been studied by pulse radiolysis techniques. The former reaction is proposed to be inner sphere and controlled by water substitution of Fe^{2+}.[2] The VO^{2+} reaction is definitely inner sphere; $VO(O_2)^+$ is the major oxidation product.[3] The ratio $k_{HO_2}/k_{\text{superoxotitanium(IV)}}$ is 6.7 for Fe^{2+} and 35 for VO^{2+} in 1 M acid at 25 °C. Thus, some rate retardation is seen for the reduction of superoxotitanium(IV) relative to that of HO_2, but the effect is not large. In contrast, an enormous rate retardation occurs for oxidation or superoxotitanium(IV) relative to HO_2. As a result, certain reactions of the superoxo complex can be studied that are not observed for HO_2. The radiolysis of bromide solutions was one of the earliest and most extensively studied systems.[25] To the best of our

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knowledge, no reaction between HO_2 and Br^- has been observed. This is probably due both to a slow reaction rate and the very rapid oxidation of HO_2 by any of the possible products (Br_2, Br_2^-, and Br_3^-).[25-27] In contrast, the lifetime of superoxotitanium(IV) is long relative to that of HO_2, and the oxidation of the superoxo complex by Br_2 or Br_3^- would be expected to be very slow on the basis of our results with the stronger oxidant Cl_2. We observe a small rate enhancement for both the disappearance of superoxotitanium(IV) and the formation of peroxotitanium(IV) in the presence of 0.1 M bromide ion in molar perchloric acid. Spectral evidence for the concomitant formation of small amounts of Br_2 and Br_3^- was obtained.[28] If we assume that TiO_2^{3+} is the reactive species toward Br^-, as appears to be the case for I^-, then the limited data in Table IV allow an estimate of 2 M^{-1} s^{-1} for the rate constant of the TiO_2^{3+}–Br^- reaction. The rate constant for a possible HO_2–Br^- reaction would not be expected to be very much greater, so it is hardly surprising that this reaction was not observed in the radiolysis experiments.

The multimixing procedure used in this study should be applicable to relatively long-lived superoxo complexes of other d^0 and f^0 metal ions. The technique has been used previously to study reactions of a peroxo–superoxo complex of vanadium(V) formulated as $VO_3^+ \cdot O_2H$.[3] This complex was found to be more susceptible to oxidation than we have observed for superoxotitanium(IV). Measurable rates were obtained with iodine and benzoquinone, although again the rate constants are considerably smaller than for the analogous reactions of HO_2. The technique should also allow studies of the redox properties of unstable peroxo complexes such as $CrO(O_2)_2$.[29] An important objective in these studies is to increase our understanding of how metal ions modify the chemistry of superoxide and peroxide. Both of these dioxygen species are thought to be important intermediates in the water–oxygen cycle.[30-32] The advantage of d^0 and f^0 metal ions is their ability to rapidly form peroxo and superoxo complexes with larger formation constants.[33-35]

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Nickel Catalysis of Olefin Epoxidation

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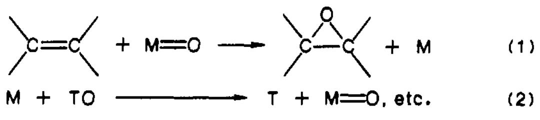
The catalytic epoxidation of olefins is examined with a wide variety of nickel(II) complexes derived from different tetraaza macrocycles (both neutral and anionic), Schiff bases, porphyrins, and bidentate phosphines. The most effective among these are the dicationic $Ni^{II}(cyclam)^{2+}$ and its unsaturated analogues $Ni^{II}(Me_4[14]tetraeneN_4)^{2+}$ and $Ni^{II}(CR)^{2+}$ as well as the Schiff base derivatives Ni^{II}(Tfaced) and Ni^{II}(Aceted). All of the nickel(II) complexes efficiently convert iodosylbenzene as the terminal oxidant to iodobenzene. However, despite extensive efforts to optimize the solvent, counterions, added donor ligands, and terminal oxidants, the conversions of olefins are restricted to modest yields of epoxides owing to competition from the oxidative attack on the solvent and the ligands. The catalytic activity is tentatively ascribed to an active oxo–nickel(IV) intermediate that is rather indiscriminate in oxygen atom transfer and in homolytic attack on solvent as well as ligand. A spectral transient is assigned to a (μ-oxo)nickel(III) dimer arising from the facile association of the putative oxo–nickel(IV) intermediate with the nickel(II) precursor. In these regards, the nickel catalysis of olefin epoxidation is strongly reminiscent of the behavior of cationic manganese(III) complexes under similar conditions.

Introduction

The epoxidation of olefins with terminal oxidants such as peroxides, iodosylbenzene, hypochlorite, amine oxides, etc. is catalyzed by a variety of metal complexes.[1] Metalloporphyrins have been studied extensively owing to their direct relationship to enzymatic oxidations with cytochrome P-450.[2] The same catalytic epoxidations are mimicked by metal complexes of other macrocycles in which (a more or less) square-planar array of nitrogen and oxygen atoms are coordinated to the metal center.[3]

At least three separate pathways have been identified for the catalytic epoxidation of olefins.[1] Among these, the oxygen rebound process outlined in Scheme I is particularly viable.[4,5] According to Scheme I, the metal catalyst (M) serves as a relay for oxygen atom transfer from the oxygen donor (TO) via the intermediacy of an oxo–metal species (M=O). The shuttling of the metal complex between the two states formally corresponds to an oxidative-addition–reductive-elimination sequence. As such, it is generally found that those metals that are capable of readily undergoing two-electron changes, such as iron(III), manganese(III), chromium(III), and ruthenium(IV), are effective in catalysis.[1-7]

Scheme I



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