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Equilibrium Studies and Redox Kinetics of the Peroxo Complex of Zirconium(IV) in Acidic Perchlorate Solution

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The complexation of zirconium(IV) by hydrogen peroxide has been studied in aqueous solutions containing (0.169–7.01) × 10^{-3} M Zr(IV), (0.364–5.17) × 10^{-3} M H_2O_2, and 1.00–1.96 M $HClO_4$. The peroxozirconium(IV) complex does not exhibit detectable absorption bands in the visible- or ultraviolet-wavelength regions. Therefore, the equilibrium concentrations of uncomplexed Zr^{4+} and H_2O_2 were measured by the use of the indicators 2-thenoyltrifluoroacetone and titanium(IV), respectively. The principal complex formed is a tetrameric species (4:2) containing four Zr(IV) and two peroxide ions. The value of the formation constant $K_{4:2}$ is $(2.4 \pm 0.2) \times 10^{19}$ M^{-5} at 25.0 °C in 1.96 M $HClO_4$. The thermodynamic parameters $\Delta H_f° = 11._2$ kcal/mol and $\Delta S_f°$ = 130 cal/(deg mol) were calculated from the temperature dependence of $K_{4:2}$ in 1.96 M $HClO_4$. The variation of the formation constant with acidity at an ionic strength of 2.0 M allows the tentative formulation of the peroxozirconium(IV) complex as $Zr_4(O_2)_2(OH)_4{}^{8+}$. The results of concentration-jump kinetic experiments have been interpreted in terms of the scheme

$$4{:}2 \underset{2}{\overset{1}{\rightleftharpoons}} 2{:}1 + 2Zr(IV) + H_2O_2 \qquad 2{:}1 \underset{4}{\overset{3}{\rightleftharpoons}} 2Zr(IV) + H_2O_2$$

where the steady-state approximation has been applied to the postulated 2:1 intermediate. Values of $k_1 = 1._3 \times 10^{-4}$ s^{-1} and $k_4 = 3._2 \times 10^3$ M^{-2} s^{-1} were determined at 25.0 °C in 1.96 M $HClO_4$. Kinetic studies of the oxidation of peroxozirconium(IV) by cerium(IV) and the reduction by sulfur(IV) in 1.96 M $HClO_4$ yielded a common rate expression: $-d[4{:}2]/dt = k_{redox}[4{:}2]$. At 25.0 °C the value of k_{redox} is $2._4 \times 10^{-3}$ s^{-1}. According to our interpretation, both systems proceed by a rate-determining ring-opening process on peroxozirconium(IV), followed by rapid attack on an exposed pendant $^{-}O_2H$ unit by the external reagent. The subsequent steps are rapid, and net stoichiometries of 4:1 and 2:1 are observed for the ratios Δ[cerium(IV)]/Δ[peroxozirconium(IV)] and Δ[sulfur(IV)]/Δ[peroxozirconium(IV)], respectively.

Introduction

The early transition elements in their highest oxidation states form labile peroxo and superoxo complexes with large stability constants.[1-3] Kinetic studies of the redox reactions of the peroxo complexes provide data that may be compared to the corresponding chemistry of hydrogen peroxide. We have found that oxidation of the peroxo complexes $VO(O_2)^+$ and $Ti(O_2)^{2+}$ by strong, 1-equiv oxidants rapidly produces the corresponding superoxo complexes in an environment free of objectionable contaminants.[4-6] The superoxo complexes are remarkably resistant to oxidation by several external reagents, in contrast to protonated superoxide, HO_2. However, an internal redox reaction with the formation of VO^{2+} or Ti^{3+} and dioxygen has been observed. The Ti^{3+} formed during the decay of $Ti(O_2)^{3+}$ rapidly reduces the superoxo complex to re-form approximately half of the precursor peroxo complex, $Ti(O_2)^{2+}$. In contrast, the VO^{2+} formed during the decay of $VO(O_2)^{2+}$ is unreactive.

We have extended these studies by the use of zirconium(IV), a metal ion that will almost certainly be inert to reduction. Virtually nothing is known about the peroxo complex(es) of zirconium(IV), although the early study of Connick and McVey clearly established that complexation does occur.[7] Consequently, a considerable portion of this paper is devoted to equilibrium studies of the interaction of zirconium(IV) and hydrogen peroxide in acidic perchlorate solutions. The investigation has been complicated by the unexpected observation that the peroxo complex(es) exhibit no detectable absorption bands in the ultraviolet- or visible-wavelength regions.

A second complication is that the aqueous chemistry of zirconium(IV) can be quite complex due to polymerization. However, Zielen and Connick have established that Zr^{4+} is the predominant species under certain conditions ([Zr(IV)] ≤ ca. 5 × 10^{-4} M in 2 M $HClO_4$ and ≤ca. 1 × 10^{-4} in 1 M $HClO_4$). With higher metal ion concentrations or lower acidities polymerization occurs, with $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ being the principal form under many conditions.[7-16]

In spite of these complexities, we have been able to determine the approximate formula and associated equilibria of the peroxozirconium(IV) complex over a modest range of conditions. In addition, we have investigated some redox chemistry of this complex.

Experimental Section

Reagents. Commercial $ZrOCl_2 \cdot 8H_2O$ was recrystallized twice from 8 M HCl. Excess 3 M $HClO_4$ was added to the moist crystals, and the solution was fumed repeatedly until tests for Cl^- were negative. White crystals formed upon cooling and were collected by filtration. A stock solution containing ca. 0.1 M Zr(IV) in 1 M $HClO_4$ was prepared. The solution was clear and has remained so for 1 year.

Solutions of $TiO(ClO_4)_2$ were prepared as described previously.[6] Lithium perchlorate was prepared from reagent grade Li_2CO_3 and $HClO_4$ and was recrystallized four times. Hydrogen peroxide (Fisher, Certified, 30%, "stabilizer free") was used as supplied. Dilute solutions of cerium(IV) were prepared by the dissolution of reagent grade $(NH_4)_2Ce(NO_3)_6$ in perchloric acid. Fresh solutions of HT (2-thenoyltrifluoroacetone) were prepared daily. The decomposition of HT in acidic solutions is far too slow to be of concern,[8] and we did not detect any reaction between HT and H_2O_2 under our experimental conditions.

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. The analysis of Zr(IV) is complicated by polymerization of the metal ion. We have found that the EDTA method using xylenol orange as the indicator is quite satisfactory, provided the detailed procedure given by Pilkington and Wilson is rigorously followed.[17] Dilute solutions in which the zirconium(IV) is exclusively

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Table I. Formation Constants and Molar Extinction Coefficients Determined for $Ti(O_2)^{2+}$ and ZrT^{3+}

$[HClO_4]$, M[a]	T, °C	$10^{-4}K_{Ti(O_2)^{2+}}$, M^{-1}	$K_{ZrT^{3+}}$[b]	$\epsilon_{Ti(O_2)^{2+}}$, M^{-1} cm^{-1}[c]
1.96	25.0	1.16 ± 0.01	341[d]	735
1.96	17.0	1.94 ± 0.05	270 ± 4	780
1.96	10.0	3.20 ± 0.08	214 ± 2	793
1.40	25.0	1.15 ± 0.02	341[d]	770
1.00	25.0	1.14 ± 0.03	341[d]	770

[a] $I = 2.0$ M maintained with lithium perchlorate. [b] The value for ϵ at 25 °C, 2.40×10^4 M^{-1} cm^{-1}, was assumed at 17 and 10 °C in the calculation of the formation constant. [c] Values at 410 nm, the absorption maximum for $Ti(O_2)^{2+}$. [d] This value has been shown to be independent of $[H^+]$ at 25 °C and $I = 2.0$ M[8] and is in excellent agreement with our independent assays of Zr(IV) solutions by the method of Pilkington and Wilson.[17]

monomeric can also be analyzed by use of the indicator 2-thenoyltrifluoroacetone (HT).[7,8] We found that aliquots of the Zr(IV) stock solution could be diluted to 5×10^{-4} M in 2 M $HClO_4$, set aside overnight, and assayed by measuring the formation of ZrT^{3+} at its absorption maximum at 366 nm after addition of HT (eq 1). Agreement between

$$Zr^{4+} + HT \rightleftarrows ZrT^{3+} + H^+ \quad K_{ZrT^{3+}} \tag{1}$$

the results obtained with this method (using the previously established values for $K_{ZrT^{3+}} = 341$ and $\epsilon_{ZrT^{3+}} = 2.40 \times 10^4$ M^{-1} cm^{-1} at $I = 2$ M and $T = 25$ °C)[8] and the titrimetric procedure was satisfactory. Minor corrections for the absorbance due to HT ($\epsilon = 80$ M^{-1} cm^{-1}) were made. This result also indicates that olated polymers, which dissociate very slowly upon dilution, are not present in the Zr(IV) stock solution.

The analysis of solutions of Ce(IV), TiO^{2+}, and H_2O_2 has been previously described.[6] We found that reagent grade Na_2SO_3 was quite pure (<99.5%); fresh solutions in water were prepared for each set of experiments. $[HClO_4]$ in the Zr(IV) and 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 metal ion.

Equilibrium Studies. We were unable to detect any useful absorption bands for the peroxozirconium(IV) complex(es). For example, an equilibrated solution containing total concentrations of 5.68×10^{-4} M Zr(IV) and 2.82×10^{-4} M H_2O_2 in 2.0 M $HClO_4$ at 25 °C exhibited essentially no enhanced absorbance from 220 to 750 nm compared to that shown by the Zr(IV) and H_2O_2 separately. It was therefore necessary to measure accurately the free [Zr(IV)] and $[H_2O_2]$ in equilibrated solutions. This was accomplished by using TiO^{2+} and HT as indicators for H_2O_2 and Zr(IV), respectively. Solutions containing Zr(IV), TiO^{2+}, and H_2O_2 in (usually) 1.96 M $HClO_4$ were allowed to equilibrate at constant temperature (±0.1 °C). Equilibrium was assumed to be established when the absorbance due to peroxotitanium(IV), $Ti(O_2)^{2+}$, at its 410-nm absorption maximum became constant. $[H_2O_2]_{eq}$ was calculated by means of eq 2. The monomeric [Zr(IV)] was then determined

$$[H_2O_2]_{eq} = [Ti(O_2)^{2+}]_{eq}/\{K_{Ti(O_2)^{2+}}([Ti(IV)]_T - [Ti(O_2)^{2+}]_{eq})\} \tag{2}$$

by adding a known amount of HT and measuring the increased absorbance at the 366-nm absorption maximum of ZrT^{3+}. Control experiments demonstrated that HT does not interact detectably with TiO^{2+}, $Ti(O_2)^{2+}$, or the peroxozirconium(IV) complex(es) under our experimental conditions. It is known that HT does not complex $Zr_4(OH)_8{}^{8+}$,[8,18] although in our experiments the equilibrium concentration of this tetramer is negligible. Later experiments showed that dissociation of Zr(IV) from the peroxozirconium(IV) species is negligible during the minute or two required to assay the monomeric, equilibrium [Zr(IV)]; the latter was calculated by means of eq 3. [Zr(IV)] and $[H_2O_2]$ in the equilibrium peroxozirconium(IV) complex(es) were calculated from eq 4 and 5.

$$[Zr(IV)]_{eq} = [ZrT^{3+}]\{1 + [H^+]/(K_{ZrT^{3+}}([HT]_T - [ZrT^{3+}]))\} \tag{3}$$

$$[Zr(IV)]_{comp} = [Zr(IV)]_T - [Zr(IV)]_{eq} \tag{4}$$

$$[H_2O_2]_{comp} = [H_2O_2]_T - [Ti(O_2)^{2+}]_{eq} - [H_2O_2]_{eq} \tag{5}$$

This procedure requires accurate assays of the Zr(IV), TiO^{2+}, H_2O_2, and $HClO_4$ in the stock solutions, values of $K_{Ti(O_2)^{2+}}$ and $K_{ZrT^{3+}}$, and ϵ values for $Ti(O_2)^{2+}$ and ZrT^{3+}. The formation constants and molar extinction coefficients determined in this study are summarized in Table I. The entries are the average of at least four determinations at each temperature and acidity.

Studies of the Rates of Approach to Equilibrium. The concentration-jump method was used. In a typical experiment, 150 μL of an equilibrated solution containing total concentrations of 4.26×10^{-2} M Zr(IV) and 2.08×10^{-2} M H_2O_2 in 2.0 M $HClO_4$ was injected into 7.00 mL of 2.27×10^{-4} M Zr(IV) and 2.35×10^{-4} M HT in 2.0 M $HClO_4$ at constant temperature (±0.1 °C). The approach to equilibrium was monitored at the 366-nm absorption maximum of ZrT^{3+}. At least 20 data points were collected for each experiment.

Values of the forward and reverse rate constants for the formation of ZrT^{3+} were determined by stopped-flow procedures. A solution containing 1.99×10^{-4} M Zr(IV) in 2.0 M $HClO_4$ was rapidly mixed with an equal volume of 3.06×10^{-4} M HT in 2.0 M $HClO_4$ at 25.0 °C. Plots of $\ln (A_\infty - A)$ vs. t were linear. The perturbations in [Zr(IV)] and [HT] were sufficiently small to allow analysis of the kinetics by relaxation methods.[19] The forward rate constant was calculated by means of eq 6 and the reverse rate constant from this value and the known equilibrium

$$\text{slope} = -k_f\{[Zr(IV)]_{eq} + [HT]_{eq} + 1/K_{ZrT^{3+}}\} \tag{6}$$

constant $K_{ZrT^{3+}}$. These rate constants proved to be too small to allow kinetic studies of the rates of complexation between Zr(IV) and H_2O_2.

Kinetic Procedures for Redox Reactions of the Peroxozirconium(IV) Complex(es). The cerium(IV) reactions were monitored spectrophotometrically over the wavelength region 280–360 nm. Dimerization of the Ce(IV) is negligible over the range of concentrations used in 2.0 M $HClO_4$.[20] The reactions were initiated by injection of an equilibrated solution containing Zr(IV) and H_2O_2 in the ratio ≥2.0 into a solution containing the Ce(IV) at constant temperature. The kinetic data for experiments with a small stoichiometric excess of Ce(IV) were adequately correlated by eq 7. A nonlinear adjustment of the data in which A_∞,

$$-\ln (A - A_\infty) = k_{Ce(IV)}t + I \tag{7}$$

$k_{Ce(IV)}$, and the intercept I were adjustable parameters was used since the slow oxidation of water by Ce(IV) was not completely negligible. The difference between the best fit and experimentally estimated A_∞ values was ≤0.010 absorbance unit. The stoichiometric ratio $\Delta[Ce(IV)]/[H_2O_2]_{0,T} = 1.96 \pm 0.09$ was determined for the 10 kinetic experiments performed under these conditions. Values of ϵ for Ce(IV) were determined at each wavelength and temperature in separate experiments by measuring the change in absorbance after addition of insufficient standardized H_2O_2. The stoichiometry of the very rapid Ce(IV)–H_2O_2 reaction has been previously established as 2:1.[21]

Some experiments were performed with large excesses of the peroxozirconium(IV) complex(es). After an initial rapid but not instantaneous consumption of Ce(IV), plots of $A - A_\infty$ vs. t were linear to 95% of total reaction. The Ce(IV) consumed during the initial rapid reaction was estimated by extrapolation of the straight line plot to time zero. The percent of the total $[H_2O_2]_0$ that reacted rapidly with the Ce(IV) was calculated by means of eq 8 and ranged from 1.9 to 3.3%. Rate constants

$$\%\ [H_2O_2]_{T,rapid} = \{[Ce(IV)]_{0,T} - [Ce(IV)]_{0,extrap}\} \times 100/\{2[H_2O_2]_{0,T}\} \tag{8}$$

were calculated from the slopes of the linear portion of the kinetic plots by eq 9–11. In these expressions (4:2) represents the concentration of

$$-(\text{slope}) = \epsilon l k_{Ce(IV)}/(4[4{:}2]_{av}) \tag{9}$$

$$[4{:}2]_{av} = [4{:}2]_0 - [Ce(IV)]_{0,extrap}/8 \tag{10}$$

$$[4{:}2]_0 = [H_2O_2]_{0,T}/2 - \{[Ce(IV)]_{0,T} - [Ce(IV)]_{0,extrap}\}/4 \tag{11}$$

the predominant form of the peroxozirconium(IV) complex according to our interpretation of the equilibrium data (vide infra).

The SO_2 system was usually monitored at the 280-nm absorption maximum of SO_2. The reactions were initiated by the addition of an aliquot of an equilibrated solution containing Zr(IV) and H_2O_2 in the ratio ≥2.0 into a solution containing the SO_2 in 2.0 M $HClO_4$ at constant temperature. $[SO_2]_0$ was calculated on the basis of the amount of a S(IV) solution originally added. The S(IV) solution was prepared by dissolution of a weighed sample of Na_2SO_3 in water and was freshly made up for each series of experiments. The reaction vessel was a

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Table II. Equilibrium Results for the Complexation of Peroxide by Zirconium(IV) in 1.96 M Perchloric Acid at 25.0 °C

10^4 × init concn, M[a]			10^4 × equil concn, M[b]				
Zr(IV)	H_2O_2	TiO^{2+}	$Ti(O_2)^{2+}$	H_2O_2	Zr(IV)	*R*[c]	$10^{-19}K_{4:2}$, M^{-5} [d]
1.69	3.64	2.32	1.49	1.55	0.762	1.56	2.05
2.82	3.64	2.32	1.36	1.22	1.01	1.70	2.38
5.08	3.64	2.32	1.05	0.717	1.60	1.86	2.35
5.08	2.55				1.65		
6.20	3.64	2.32	0.871	0.519	1.98	1.88	2.37
7.30	5.78	2.31	1.36	1.24	1.43	1.85	2.13
7.33	3.64	2.32	0.671	0.351	2.51	1.84	2.27
8.46	3.64	2.32	0.521	0.250	3.02	1.90	2.48
9.32	3.53	41.2	1.91	0.0418	6.22	1.96	2.91
9.39	10.7	10.4	5.56	0.993	1.70	1.86	2.16
9.39	5.13				1.70		
9.52	7.23	2.30	1.42	1.39	1.45	1.83	2.13
9.59	3.64	2.32	0.368	0.162	3.86	1.84	2.21
9.59	3.64	9.28	0.969	0.100	4.69	1.91	2.45
12.8	15.4	11.7	7.49	1.54	1.42	1.78	2.59
15.2	14.3	11.4	6.22	1.04	1.79	1.92	2.89
27.1	24.4	11.1	8.10	2.32	1.48	1.82	2.27
28.2	21.1	11.6	6.10	0.955	2.35	1.85	2.11
42.2	25.2	11.6	4.56	0.560	3.27	1.94	2.34
42.3	21.1	11.6	1.70	0.148	6.27	1.88	2.49
70.0	41.8	17.3	7.18	0.614	3.68	1.95	2.34
70.1	37.7	17.3	4.28	0.283	5.18	1.96	2.76
							av (2.4 ± 0.2) × 10^{19}

[a] Concentrations of Zr(IV) are given as if only the monomeric form were present. [b] Values of $[H_2O_2]_{eq}$ and $[Zr(IV)]_{eq}$ calculated by means of eq 2 and 3, respectively. [c] R = $[Zr(IV)]/[H_2O_2]$ in the peroxozirconium(IV) complex(es). [d] $K_{4:2}$ is defined by eq 13; $[4:2]_{eq}$ was taken as $\{[Zr(IV)]_{comp} - [H_2O_2]_{comp}\}/2$.

Table III. Equilibrium Results in 1.96 M Perchloric Acid at 17.0 and 10.0 °C

10^4 × init concn, M[a]			10^4 × equil concn, M[b]				
Zr(IV)	H_2O_2	TiO^{2+}	$Ti(O_2)^{2+}$	H_2O_2	Zr(IV)	*R*[c]	$10^{-19}K_{4:2}$, M^{-5} [d]
17.0 °C							
5.08	3.64	4.64	1.92	0.364	2.33	2.02	1.78
7.33	3.64	9.28	1.88	0.131	4.11	1.98	1.63
9.52	7.23	3.69	2.43	1.00	1.91	2.01	1.43
15.2	14.3	11.4	6.93	0.805	2.36	1.96	1.56
27.1	24.4	11.1	9.22	2.49	1.63	2.02	1.44
28.2	21.1	11.6	6.92	0.763	3.07	1.88	1.14
70.0	41.8	17.3	7.73	0.418	5.23	1.92	1.19
							1.5 ± 0.2 (av)
10.0 °C							
5.07	4.36	4.63	2.60	0.400	2.56	1.84	0.827
7.31	5.08	9.25	3.27	0.171	4.18	1.91	0.839
9.52	7.23	3.69	2.68	0.837	2.26	1.96	0.964
15.2	14.3	11.4	7.59	0.628	3.11	2.00	0.814
28.0	25.1	19.7	11.4	0.432	4.25	1.80	0.860
56.2	31.5	14.5	5.81	0.210	7.43	1.92	0.865
69.3	51.7	25.2	17.0	0.648	4.40	1.90	0.980
							0.88 ± 0.05 (av)

[a] Concentrations of Zr(IV) are given as if only the monomeric form were present. [b] Values of $[H_2O_2]_{eq}$ and $[Zr(IV)]_{eq}$ calculated by means of eq 2 and 3, respectively. [c] *R* = $[Zr(IV)]/[H_2O_2]$ in the peroxozirconium(IV) complex(es). [d] $K_{4:2}$ is defined by eq 13; $[4:2]_{eq}$ was taken as $\{[Zr(IV)]_{comp} - [H_2O_2]_{comp}\}/2$.

spectrophotometer cell that was tightly stoppered to prevent loss of gaseous SO_2. With excess $[SO_2]$, plots of ln $(A - A_\infty)$ vs. t were strictly linear for greater than 90% of total reaction; the slopes of these plots are identified as k_{SO_2}. Equation 12 correlated the kinetic data when peroxide was in excess relative to the SO_2.

$$-\ln \{([H_2O_2]_{0,T} - [SO_2]_0)/2 + (A - A_\infty)/(4\epsilon_{SO_2})\} = k_{SO_2}t + 1 \qquad (12)$$

In one experiment HT was present and the reaction was monitored by measuring the growth of ZrT^{3+} at 366 nm. A plot of ln $(A_\infty - A)$ vs. t was linear, and the slope is taken as k_{SO_2}.

Results

Equilibrium Studies. We were unable to determine directly the extent of complexation between Zr(IV) and H_2O_2 due to the absence of detectable absorption bands for the peroxo complex. Consequently, it was essential to measure accurately the free [Zr(IV)] and $[H_2O_2]$ in equilibrated solutions. 2-Thenoyltrifluoroacetone (HT) was used as the indicator for the former and titanium(IV) for the latter. This procedure requires accurately standardized reagents and both formation constants and molar extinction coefficients of $Ti(O_2)^{2+}$ and ZrT^{3+}. Values of K_f and ϵ were determined at each acidity and temperature; the values are listed in Table I.

The experimental results are summarized in Tables II–IV. The feasible range of concentrations was limited by several factors. (1) An appreciable fraction of the Zr(IV) and H_2O_2 must be complexed to allow an accurate determination of the composition of the complex(es). (2) Neither reactant could be present in large excess since the equilibrium concentration of each must be measured. (3) The equilibrium concentration of Zr(IV) must be low enough to ensure that it is monomeric, or at least predominantly so. This feature severely restricts the lower range of acidities. (4) We were primarily interested in identifying conditions where a single peroxo complex predominates.

Table IV. Equilibrium Results at 25.0 °C and I = 2.0 M ($LiClO_4$) in 1.40 and 1.00 M Perchloric Acid

10^4 × init concn, M[a]			10^4 × equil concn, M[b]				
Zr(IV)	H_2O_2	TiO^{2+}	$Ti(O_2)^{2+}$	H_2O_2	Zr(IV)	R[c]	$10^{-20}K_{4:2}$, M^{-5}[d]
				1.40 M $HClO_4$			
5.08	3.64	4.64	1.29	0.334	1.08	1.98	6.66
7.33	3.64	9.28	0.943	0.0983	2.13	2.00	6.53
9.52	7.23	3.69	1.87	0.891	0.829	1.94	5.62
15.2	14.3	11.4	5.94	0.953	0.996	1.93	3.82
26.7	24.1	15.7	9.50	1.34	0.994	1.93	3.57
28.2	21.1	11.6	5.80	0.869	1.21	1.88	3.91
70.0	41.8	17.3	5.86	0.447	2.19	1.91	3.51
							4.8 ± 1.3 (av)
				1.00 M $HClO_4$			
5.08	3.64	4.64	1.11	0.275	0.620	1.97	98.3
7.33	3.64	9.28	0.607	0.0614	1.40	2.00	104
9.52	7.23	3.69	1.74	0.788	0.433	1.94	100
15.2	14.3	11.4	5.72	0.890	0.494	1.92	74.6
27.1	24.4	11.1	8.04	2.29	0.384	1.89	55.1
28.2	21.1	11.6	5.61	0.822	0.633	1.88	49.5
70.0	41.8	17.3	5.64	0.425	1.08	1.93	67.7
							78 ± 19 (av)

[a] Concentrations of Zr(IV) are given as if only the monomeric form were present. [b] Values of $[H_2O_2]_{eq}$ and $[Zr(IV)]_{eq}$ calculated by means of eq 2 and 3, respectively. [c] $R = [Zr(IV)]/[H_2O_2]$ in the peroxozirconium(IV) complex(es). [d] $K_{4:2}$ is defined by eq 13; $[4:2]_{eq}$ was taken as $\{[Zr(IV)]_{comp} - [H_2O_2]_{comp}\}/2$.

In several experiments the addition of TiO^{2+} was omitted and the initial $[H_2O_2]$ decreased by the equilibrium $[Ti(O_2)^{2+}]$ found when the experiment was performed in the usual way. The free, equilibrium [Zr(IV)] determined in the pairs of trials were in good agreement. This is an important result in that it demonstrates that neither TiO^{2+} nor $Ti(O_2)^{2+}$ is incorporated into the peroxozirconium(IV) complex(es). Also, it was shown that the equilibrium $[Ti(O_2)^{2+}]$ was not altered during the time required to assay the uncomplexed [Zr(IV)] by the HT method.

The results show that the ratio of [Zr(IV)] to $[H_2O_2]$ in the peroxo complex is close to 2:1 over most of the experimental conditions. The data are adequately correlated by postulating the *principal* equilibrium as eq 13. The scatter in the values of

$$4Zr(IV) + 2H_2O_2 \rightleftarrows 4{:}2 \quad K_{4:2} \tag{13}$$

$K_{4:2}$ in 1.96 M $HClO_4$ may be due to the presence of additional complexes in minor amounts, but some scatter would be anticipated given the sensitivity of $K_{4:2}$ to small errors in the equilibrium concentrations. The equilibrium [4:2] varied from 2.32 × 10^{-5} to 1.66 × 10^{-3} M. Values of the thermodynamic parameters $\Delta H_f° = 11._2$ kcal/mol and $\Delta S_f°$ = 130 cal/(deg mol) were calculated from the temperature dependence of $K_{4:2}$ in 1.96 M $HClO_4$.

By far the largest variation in the measured values of $K_{4:2}$ occurred at lower acidities where $LiClO_4$ was added to maintain constant ionic strength. A similar problem was observed by previous workers in studies of the polymerization of zirconium(IV) and was attributed to the complexing of a small amount of zirconium by an impurity in the lithium perchlorate.[7] We suspect that the same feature obtains in the present study. We note that the values of $K_{4:2}$ (Table IV) do tend to level off at higher concentrations of Zr(IV), conditions where the impurity would have less effect on the results. In any event, the equilibrium constant is extremely sensitive to $[H^+]$. A plot of log $K_{4:2}$ vs. log $[H^+]$ is linear, with a slope of $-8._7$. We conclude that between eight and nine protons are released in the formation of the tetrameric peroxo complex.

Table V. Kinetic Results of Concentration-Jump Experiments with the Peroxozirconium(IV) Complex in 2.00 M Perchloric Acid[a]

	10^4 × init concn, M[b]			10^4 × $[Zr(IV)]_{eq}$, M[c]	10^3 × k_{obsd}, s^{-1}[d]
T, °C	Zr(IV)	H_2O_2	HT		
25.0	17.2	7.17	1.89	3.62	1.77
25.0	11.7	4.36	1.91	3.53	1.66
25.0	11.2	4.36	2.30	3.08	1.33
25.0	10.9	4.36	2.30	2.88	1.30
25.0	7.96	2.93	2.31	2.72	0.905
25.0	6.56	2.35	2.90	2.47	0.803
25.0	5.03	1.77	4.36	2.10	0.630
25.0	4.75	1.77	4.36	1.96	0.528
17.0	17.2	7.17	2.01	3.88	0.630
17.0	11.2	4.36	2.44	3.28	0.507
17.0	10.9	4.36	2.44	3.08	0.457
17.0	7.96	2.93	2.46	2.91	0.357
17.0	5.03	1.77	2.78	2.66	0.278
17.0	6.56	2.35	4.19	2.24	0.252
17.0	4.75	1.77	4.55	2.11	0.280
10.0	17.2	7.19	2.76	4.07	0.258
10.0	11.2	4.36	3.12	3.47	0.205
10.0	10.9	4.36	2.73	3.30	0.192
10.0	7.96	2.93	3.15	3.03	0.147
10.0	5.03	1.77	5.93	2.34	0.117

[a] Monitored at 366 nm. [b] Most of the initial [Zr(IV)] and $[H_2O_2]$ were in the peroxozirconium(IV) complex (see Experimental Section for details). [c] Calculated by means of eq 3. [d] Defined as the slope of $-\ln \Delta$ vs. t plots.

Studies of the Rates of Approach to Equilibrium. The concentration-jump method was used. An aliquot of an equilibrated, concentrated solution of the peroxozirconium(IV) complex was injected into a solution containing dilute Zr(IV) and HT. The rate at which the new equilibrium position was attained was monitored by measuring the growth of ZrT^{3+} due to reaction 14.

$$4{:}2 \rightleftarrows 4Zr(IV) + 2H_2O_2 \tag{14}$$

The experimental conditions are summarized in Table V. The perturbation in [4:2] ranged from 6 to 29%. Plots of $-\ln \Delta$ vs. t, where $\Delta = [4{:}2] - [4{:}2]_{eq}$, were linear. The slopes of these plots, k_{obsd}, are listed in the table. The simplest scheme we have found that correlates the relaxation rates with the equilibrium concentrations of 4:2, Zr(IV), and H_2O_2 is given by eq 15 and 16.

$$4{:}2 \underset{2}{\overset{1}{\rightleftarrows}} 2{:}1 + 2Zr(IV) + H_2O_2 \tag{15}$$

$$2{:}1 \underset{4}{\overset{3}{\rightleftarrows}} 2Zr(IV) + H_2O_2 \tag{16}$$

Application of the steady-state approximation to the concentration of the postulated intermediate 2:1 leads to eq 17 and 18, where

$$-\frac{d[4{:}2]}{dt} = \frac{k_1k_3[4{:}2] - k_2k_4[Zr(IV)]^4[H_2O_2]^2}{k_2[Zr(IV)]^2[H_2O_2] + k_3} \tag{17}$$

$$-d(\ln \Delta)/dt = k_{obsd} = a/\{(K_{4:2}/k_4)b + 1/k_1\} \tag{18}$$

$a = \{[4{:}2]_{eq} + \Delta - K_{4:2}[[Zr(IV)]_{eq} - 4\Delta]^4[[H_2O_2]_{eq} - 2\Delta]^2\}/\Delta$, $b = [[Zr(IV)]_{eq} - 4\Delta]^2[[H_2O_2]_{eq} - 2\Delta]$, and $K_{4:2} = k_2k_4/k_1k_3$.

Table VI. Equilibrium Rate Constants[a] and Activation Parameters for the Peroxozirconium(IV) Complex

T, °C	10^4k_1, $s^{-1\,b}$	$10^{-3}k_4$, $M^{-2}\ s^{-1\,b}$
25.0	1.3 ± 0.1	3.2 ± 0.3
17.0	0.60 ± 0.06	0.98 ± 0.08
10.0	0.28 ± 0.02	0.36 ± 0.02

$\Delta H_1^{*} = 21._4$ kcal/mol $\Delta H_4^{*} = 23._7$ kcal/mol
$\Delta S_1^{*} = -3$ cal/(mol deg) $\Delta S_4^{*} = 37$ cal/(mol deg)

[a] Determined from plots of eq 18 by use of the k_{obsd} values from Table V. [b] Uncertainties are average deviations and indicate only the internal consistency of the data.

Equation 18 is formulated in the manner given for the following reasons. The higher order Δ terms are retained to accommodate relatively large perturbations in the equilibrium concentrations. The kinetic data allow an accurate determination of [Zr(IV)] as a function of time. The corresponding concentrations of 4:2 and H_2O_2 were calculated by assuming a value of 2.00 for the ratio of [Zr(IV)] to $[H_2O_2]$ in the 4:2 complex. While this procedure is adequate for the kinetic analysis, the resulting variation in the $K_{4:2}$ values was much larger than in the equilibrium studies where $[H_2O_2]_{eq}$ was also measured. Accordingly, the kinetic data for each experiment were analyzed by using the $K_{4:2}$ value determined in the above manner. This appears to be the best way to ensure consistency between the equilibrium concentrations and the rate constants.

Plots of a vs. b were very linear for all the experiments. The slope of these plots is $k_{obsd}K_{4:2}/k_4$, and the intercept is k_{obsd}/k_1 according to our interpretation. Values of k_1 and k_4 determined at each temperature and the associated activation parameters are listed in Table VI.

The data were also analyzed in a slightly different manner. The expression for $d\Delta/dt$, derived from eq 17, was solved by numerical integration using various trial values for k_1 and k_4. The best agreement between the calculated and experimental Δ vs. t curves was invariably generated with the same values of k_1 and k_4 listed in Table VI. This result would be anticipated, but it does assuage our concern over why the ln Δ vs. t plots were linear (vide infra).

In one experiment the dissociation of the 4:2 complex was essentially driven to completion. A 150-μL aliquot of an equilibrated solution containing total concentrations of 5.08×10^{-3} M Zr(IV) and 2.53×10^{-3} M H_2O_2 was injected into 9.00 mL of a 1.30×10^{-3} M HT solution in 2.0 M $HClO_4$ at 25.0 °C. While the time for total reaction was quite long (ca. 10 h), a plot of ln $(A_\infty - A)$ vs. t was linear with a slope of 1.4×10^{-4} s^{-1}. This value is in good agreement with the average value of 1.3×10^{-4} s^{-1} for k_1 determined at the same acidity and temperature by the relaxation experiments.

Our attempts to measure the rate of complex formation between Zr(IV) and H_2O_2 by the stopped-flow technique using HT as the indicator were unsuccessful. The rates proved to be much faster than the indicator reactions. Preliminary values of $k_f = 34$ M^{-1} s^{-1} and $k_r = 0.20$ s^{-1} were determined at 25.0 °C in 2.0 M $HClO_4$ (eq 19).

$$Zr^{4+} + HT \underset{k_r}{\overset{k_f}{\rightleftharpoons}} ZrT^{3+} + H^+ \qquad (19)$$

Redox Kinetic Studies. The stoichiometric results for the cerium(IV)-peroxozirconium(IV) reaction are in harmony with eq 20. The results of the kinetic experiments are summarized

$$4{:}2 + 4Ce(IV) = 4Zr(IV) + 4Ce(III) + 2O_2 \qquad (20)$$

in Table VII. The data are consistent with the rate expression 21, an unexpected result in that the rate is independent of the

$$-d[4{:}2]/dt = k_{Ce(IV)}[4{:}2] \qquad (21)$$

oxidant concentration under our experimental conditions. The values of $k_{Ce(IV)}$ are in agreement regardless of whether Ce(IV) or the 4:2 complex is in excess if it is assumed that four Ce(IV) ions are rapidly consumed following the rate-determining event for a 4:2 ion.

Table VII. Kinetic Results for Oxidation of the Peroxozirconium(IV) Complex by Cerium(IV) in 2.0 M Perchloric Acid

		10^4 × init concn, M			10^3 × $k_{Ce(IV)}$, $s^{-1\,b}$
T, °C	λ, nm	Zr(IV)	H_2O_2	Ce(IV)[a]	
25.0	310	1.85	0.893	2.34	2.6
25.0	340	4.68	2.28	5.66	2.9
25.0	310	13.7	6.71	1.85 (1.59)	2.4
25.0	340	30.7	15.0	5.24 (4.72)	2.6
17.0	340	4.68	2.28	5.93	1.3
17.0	360	9.26	4.52	12.0	1.4
17.0	310	18.1	8.84	1.84 (1.49)	1.1
17.0	340	30.7	15.0	5.24 (4.62)	1.3
10.0	280	0.936	0.451	1.27	0.60
10.0	310	1.85	0.893	2.43	0.64
10.0	340	4.68	2.29	5.63	0.68
10.0	360	9.26	4.52	10.5	0.70
10.0	360	12.3	4.52	10.3	0.70
10.0	280	9.26	4.52	1.25 (1.03)	0.59
10.0	310	18.1	8.85	1.93 (1.49)	0.53
10.0	310	24.3	8.85	1.91 (1.43)	0.56
10.0	310	30.7	15.0	1.83 (1.03)	0.52
10.0	310	41.0	15.0	1.83 (0.99)	0.53
10.0	340	30.7	15.0	5.17 (4.40)	0.62

[a] Values in parentheses are the $[Ce(IV)]_0$ values obtained by extrapolation of the linear portion of the $A - A_\infty$ vs. t plots. [b] Defined by eq 21 and obtained from plots of eq 7 (excess [Ce(IV)]) or from the slopes of $A - A_\infty$ vs. t plots by eq 9 (excess [peroxozirconium(IV) complex]).

Table VIII. Kinetic Results for Reduction of the Peroxozirconium(IV) Complex by Sulfur Dioxide in 2.0 M Perchloric Acid[a]

	10^4 × init concn, M			10^3 × k_{SO_2}, $s^{-1\,b}$
T, °C	Zr(IV)	H_2O_2	S(IV)	
25.0	17.2	8.37	5.60	2.4
25.0	11.5	5.62	7.00	2.4
25.0	5.92	2.89	3.86	2.4
25.0[c]	4.58	2.24	3.15	2.4
17.0	17.2	8.37	5.68	1.2
17.0	5.92	2.89	3.92	1.2
10.0	17.2	8.37	5.63	0.56
10.0	5.92	2.89	3.88	0.60

[a] Monitored at 280 nm unless otherwise indcated. [b] Defined by eq 23. [c] λ = 366 nm, with [HT] = 1.00×10^{-4} M.

Very little free H_2O_2 is present in the experiments with excess [4:2], far too little to account for the observed rapid, initial consumption of Ce(IV). Further, the rate of the Ce(IV)-H_2O_2 reaction is "instantaneous" on the time scale of our experiments.[22] Therefore, we attribute this rapid reaction to the presence of an additional, more reactive peroxozirconium(IV) complex present in the equilibrium mixture. This is not cause for concern, in that the additional species account for ≤3% of the total initial $[H_2O_2]$. Indeed, the equilibrium data gave some hint of the presence of a minor, additional species. The experiments with large excess [4:2] is the only type of study we have performed that is sensitive to the presence of the minor species.

The stoichiometric results for the SO_2 system are consistent with eq 22. The kinetic results are summarized in Table VIII.

$$4{:}2 + 2SO_2 = 4Zr(IV) + 2HSO_4^- \qquad (22)$$

The kinetic analysis is straightforward, in that the results are independent of the reactant in excess and of whether the disappearance of SO_2 or the appearance of Zr(IV) is monitored. However, the rate expression (23) is again unusual in that the rate is independent of the reductant concentration.

$$-d[4{:}2]/dt = k_{SO_2}[4{:}2] \qquad (23)$$

Our attempts to determine the kinetics of the Ce(IV) or SO_2 reactions at lower acidities were unsuccessful. The observed rates

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[22] Samuni, A.; Czapski, G. *J. Chem. Soc., Dalton Trans.* **1973**, 487.

decreased with decreasing [H^+] at $I = 2$ M, but the kinetic profiles were not consistent with eq 21 and 23 and instead gave indications of a biphasic process.

Discussion

The equilibrium studies demonstrate that the principal peroxozirconium(IV) species under our experimental conditions contains four zirconium(IV) ions and two peroxide units. In addition, between eight and nine protons are released in the formation of the tetramer. If we assume that the lower number is correct, we may tentatively formulate the peroxozirconium(IV) complex as $Zr_4(O_2)_2(OH)_4^{8+}$. This formula may be compared to that of the zirconium(IV) tetramer $Zr_4(OH)_8^{8+}$. Formally, two peroxide ions replace four bridging hydroxide ions. Clearly, a structure determination for the peroxo complex would be highly desirable if single crystals can be obtained.

Equilibrium studies have been reported for the peroxo complexes of plutonium(IV) under conditions similar to those used in this study.[23] The system was complicated by electron-transfer reactions that occurred after complex formation. Two peroxo complexes were detected which may be formulated as $Pu_2(O_2)^{4+}$ and $Pu_2(O_2)OH^{5+}$. Here great stability is exhibited by species containing two plutonium(IV) ions, whereas with zirconium(IV) there is an enormous stability associated with tetrameric species.

The kinetics of the conversion of $Zr_4(OH)_8^{8+}$ to monomeric zirconium(IV) have been reported.[18] The rate expression is summarized by eq 24. Values of $k_H = 9.5 \times 10^{-4}$ M^{-1} s^{-1} at 25

$$-d[Zr_4(OH)_8^{8+}]/dt = k_H[H^+][Zr_4(OH)_8^{8+}] \qquad (24)$$

°C and $I = 2.0$ M, $\Delta H^* = 13._2$ kcal/mol, and $\Delta S^* = -28$ cal/(mol deg) were determined. While we have not undertaken a study of the hydrogen ion dependence of the breakdown of peroxozirconium(IV), we have determined the first-order rate constant $k_1 = 1.3 \times 10^{-4}$ s^{-1} in 2.0 M $HClO_4$ at 25 °C. Thus the rate-determining step for the dissociation of the peroxozirconium(IV) complex is approximately 1 order of magnitude slower than the corresponding reaction of the zirconium(IV) tetramer. In neither case have the mechanistic features been established, but a ring-opening process is an attractive possibility.

The relaxation kinetic studies provide some useful information about the equilibria associated with the peroxozirconium(IV) complex. However, the scheme summarized in eq 15 and 16 is not unique and is surely an oversimplification, although the data do not warrant more elaborate interpretations. In addition to providing estimates of the initial dissociation and formation rate constants, our analysis suggests the presence of an intermediate peroxo complex at low concentrations, although our formulation of a 2:1 complex as the intermediate is speculative. We were initially concerned by the observation that plots of ln Δ vs. time (eq 18) were linear. While the perturbations in the equilibrium concentrations were relatively small, they are certainly larger than normally used in relaxation studies. However, the analysis appears to be internally consistent, and the question of just how small the perturbations must be to yield linearization of a rate equation is a difficult problem.[24] The agreement in the values of k_1 determined in the relaxation studies and that found when the dissociation of the peroxozirconium(IV) complex was driven to completion is gratifying.

The reduction of H_2O_2 by sulfur(IV) is quite rapid in acidic solution and is proposed to proceed via nucleophilic substitution by H_2O_2 on HSO_3^- to form a peroxomonosulfurous acid intermediate.[25,26] The oxidation of H_2O_2 by cerium(IV) is extremely rapid in perchloric acid solution.[22] It is therefore remarkable that we do not observe a direct reaction between the intact peroxozirconium(IV) tetramer and either sulfur(IV) or cerium(IV). Not only is the rate expression simply first order in the peroxo complex but the value of the rate constant is also identical within experimental error for both systems. We further note that these values are some 20 times larger than those determined for k_1 in the dissociation of peroxozirconium(IV). A possible explanation for these observations is that the ring-opening process in the dissociation reaction is reversible and yields an intermediate species containing a pendant ^-OOH group still attached to a zirconium(IV) center. In the redox systems this exposed HO_2^- group is rapidly attacked by sulfur(IV) or cerium(IV), but in the dissociation process ring closure is competitive with loss of peroxide and results in a smaller, composite rate constant k_1.

While the results obtained in this study have elucidated some aspects of the solution chemistry of peroxozirconium(IV), they have raised some questions for which we have no satisfactory answers. It is very surprising that no visible or ultraviolet absorption bands are observed for the peroxo complex. This feature has led earlier investigators to conclude falsely that no complexation of zirconium(IV) by peroxide occurs in strongly acidic solution.[27] Even if our formulation of $Zr_4(O_2)_2(OH)_4^{8+}$ is correct, what is the structure of the tetramer? Our results demonstrate that the presumably bridging peroxide groups are well protected from attack by several reagents that react very rapidly with hydrogen peroxide. Why is the relatively straightforward kinetic behavior observed with cerium(IV) and sulfur(IV) in 2 M perchloric acid not also found at lower acidities? We suspect that the tetrameric unit is reversibly re-formed as the free zirconium(IV) concentration increases during the reaction, but our results hardly settle the issue. As pointed out by Sykes,[18] it is unclear why HT should coordinate to Zr^{4+} but not $Zr_4(OH)_8^{8+}$. We find that HT also does not complex peroxozirconium(IV). The lower average charge per zirconium in the tetramers may be responsible for these observations.

Finally, we wish to suggest that some of our observations may have application in separation procedures that are complicated by the presence of zirconium(IV). Some preliminary experiments aimed at obtaining crystals of peroxozirconium(IV) suggest that quite concentrated solutions of this complex may be formed even under strongly acidic conditions and that these solutions exhibit remarkable stability.

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