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Aqueous Solution Chemistry of Zirconium(IV). 1. Kinetic Studies on Hydrogen Ion and General Acid (HX) Induced Dissociations of the Tetrameric Ion $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$

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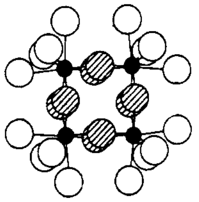
Received March 18, 1980

The tetramer to monomer conversion $[Zr_4(OH)_8(H_2O)_{16}]^{8+} \rightarrow Zr(H_2O)_8^{4+}$, i.e., $Zr_4 \rightarrow Zr$, was initiated by diluting aqueous solutions of Zr(IV) (ca. 10^{-2} M) in $HClO_4$ (ca. 0.5 M) to $[Zr(IV)] \leq 10^{-4}$ M and increasing $[H^+]$ to a value in the range 2.0–4.0 M ($I = 4.0$ M ($NaClO_4$)). Reactions were carried out in the presence of 2-thenoyltrifluoroacetone (HT), which complexes rapidly with Zr^{4+} (but not Zr_4) and, since ZrT^{3+} is colored (λ_{max} 366 nm), provides the means of monitoring the reaction. Data conform to the simple rate law $k_H[H^+][Zr_4]$, where at 25 °C $k_H = 3.7 \times 10^{-3}$ M^{-1} s^{-1}. At $I = 2.0$ M ($NaClO_4$), k_H (25 °C) $= 0.95 \times 10^{-3}$ s^{-1}, and from the temperature-dependence activation parameters $\Delta H^* = 13.2$ kcal mol^{-1} and $\Delta S^* = -28$ cal K^{-1} mol^{-1} were obtained. Acids HX also induce the $Zr_4 \rightarrow Zr$ conversion, giving the rate law $k_H[H^+][Zr_4] + k_{HX}[HX][Zr_4]$. Second-order rate constants k_{HX} (M^{-1} s^{-1}) at 25 °C, $[H^+] = 2.0$ M, and $I = 2.0$ M are as follows: H_3PO_4 (80) > $H_2C_2O_4$ (44) > $H_4P_2O_7$ (40) > HF (30) > HSO_4^- (8.8) > CCl_3CO_2H (1.0) > CH_2ClCO_2H (0.4). Acetic acid (5×10^{-3} M), Cl^- (2 M), and NCS^- (1.2×10^{-3} M) have no effect on the conversion.

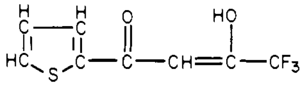
Introduction

Although substantial evidence for the Zr^{4+} aquo ion in solutions at low Zr(IV) concentrations (ca. 10^{-4} M) and high $[H^+]$ (1–2 M) has been reported,[1] the zirconyl ion ZrO^{2+} has yet to be identified. X-ray crystal structure determinations of "zirconyl" halides, $ZrOX_2{\cdot}8H_2O$ ($X^- = Cl^-, Br^-$, and I^-), have shown these to consist of cyclic tetrameric units $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ (hereafter Zr_4).[2,3]



Identical tetrameric units have also been shown to exist in solutions where $[Zr(IV)] = 2$–4 M and $[H^+] = 3.5$–9 M, with use of a low-angle X-ray scattering technique.[5,6] Extensive ultracentrifugation studies on more dilute solutions ($[Zr(IV)]$ = ca. 0.05 M) have demonstrated that such solutions are monodisperse for $[H^+]$ in the range 0.5–2.0 M, with a tetramer being the dominant species (>85%).[7] Under somewhat different conditions (mixed solvent at −70 °C), with $[Zr(IV)]$ = 1–2 M, NMR measurements[8] have indicated that the tetramer is predominant. At $[H^+] < 0.5$ M, higher polymeric species are formed.[1]

The manner of the tetramer to monomer conversion provides the subject of this paper. It has been demonstrated previously that the monobasic acid 2-thenoyltrifluoroacetone (HT)



HT

chelates (presumably via the two O atoms) to monomeric but not tetrameric Zr(IV).[9] Formation of colored ZrT^{3+} is rapid (equilibration rate constants 0.11 s^{-1} at 25 °C with $[Zr^{4+}] = 2.5 \times 10^{-4}$ M, $[HT] = 1.0 \times 10^{-5}$ M, $[H^+] = 2.0$ M, $I = 2.0$ M ($NaClO_4$)).[10] This provides the means of monitoring the rate-determining step in the $Zr_4 \rightarrow Zr$ conversion. A wide range of acids, HX, were also found to induce decomposition of Zr_4.

Experimental Section

Preparation of Zirconium Solutions. Pure (brilliant white) zirconyl chloride, $ZrOCl_2{\cdot}8H_2O$, was prepared by the following procedure[11] and used as a source of Zr(IV). Basic zirconium carbonate (2 mol, Magnesium Elektron Ltd) was dissolved in concentrated HCl (8 mol). When CO_2 evolution subsided, the mixture was heated to boiling and maintained at its boiling point for 1 h. It was then rapidly cooled, and the solid was filtered off and washed with cold concentrated HCl. Recrystallization (three times) was from 9 M HCl, following which the sample was air-dried to constant analysis ($AgNO_3$ titration for percent Cl^-). Solutions of tetramer, where Zr(IV) concentration (as monomer) is ca. 10^{-2} M, were prepared by dissolving the chloride salt of $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ in 0.50 M $HClO_4$.

Acids. Solutions containing acids HX were obtained by introducing amounts of Na_2SO_4, Na_2HPO_4, $Na_4P_2O_7{\cdot}10H_2O$, $Na_2C_2O_4$, NaF, NaCl, $NaSCN{\cdot}2H_2O$, $Na(CH_3CO_2)$, $Na(CClH_2CO_2)$, and CCl_3CO_2H, all BDH AnalaR, as required, into reactant solutions.

Complexing with HT. The reagent 2-thenoyltrifluoroacetone (HT) (BDH reagent grade) is a weak acid (acid dissolution constant 6.7×10^{-7} M)[12] which is present as HT at $[H^+]$ values used in this study. The complex ZrT^{3+} has an absorption maximum at 366 nm ($\epsilon = 2.4 \times 10^4$ M^{-1} cm^{-1}; cf. ϵ = ca. 80 M^{-1} cm^{-1} for HT),[9] and its formation equilibrium constant, as defined by (1), is reported to be 341 at 25

$$Zr^{4+} + HT \rightleftharpoons ZrT + H^+ \qquad (1)$$

°C, $[HClO_4] = 1.0$–2.0 M, and $I = 2.0$ M (Na/LiClO$_4$).[9] Spectra of HT and ZrT^{3+} (Figure 1) are in excellent agreement with those previously reported.[9] For confirmation that HT does not complex with Zr_4, HT was added to a 10^{-2} M Zr(IV) solution in 0.5 M $HClO_4$, when no development of absorbance at 366 nm was observed over a period of 24 h.

Kinetics. Solutions of tetramer (concentration (as monomer) $[Zr(IV)] = 0.01$ M in $[HClO_4] = 0.50$ M) were used in most cases. Identical results were obtained with a solution where $[Zr(IV)] = 0.05$ M and $[HClO_4] = 0.50$ M, conditions which overlap with those used in ultracentrifugation experiments and vouch for the predominance of tetrameric species. The H^+-induced decomposition was first studied at $I = 4.0$ M to establish the form of the rate law. Other H^+- and HX-induced dissociations were at $I = 2.0$ M. Ionic strengths were made up to the required value with $NaClO_4$ (BDH AnalaR). Runs were initiated by mixing solutions A and B, where A consisted of Zr(IV) stock solutions, $NaClO_4$, and HT and B consisted of $HClO_4$ and (where relevant) HX. From the preparation of A to the mixing with B ca. 5 min elapsed. Reproducible results were obtained on delaying mixing of A and B to 20 min. A run with solution A containing 0.5 M $HClO_4$ also gave identical behavior. Reactions were monitored at the ZrT^{3+} peak at 366 nm with Unicam SP500 and

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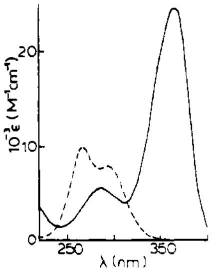

Figure 1. Absorption spectra of HT (---) and ZrT^{3+} (—) in 2 M $HClO_4$ (see ref 9).

Table I. Rate Constants at 25 °C and I = 4.0 M ($NaClO_4$) for the H^+-Induced Dissociation of Tetrameric Zr(IV) to Monomer[a]

$[H^+]$, M	$10^4[Zr(IV)]$,[b] M	10^3k_{obsd}, s^{-1}
2.0	1.0	7.3
2.0	2.0	7.6
2.0	3.0	7.2
2.0	4.0	7.7
2.0	5.0	7.6
2.5	5.0	9.7
3.0	5.0	10.8
3.5	5.0	12.5
3.75	5.0	14.2
4.0	5.0	15.3

[a] Reactions monitored by the complexing of HT (10^{-4} M) to monomer (λ 366 nm). [b] As monomer.

Perkin-Elmer 554 spectrophotometers. First-order rate constants were obtained from the slopes (×2.303) of plots of absorbance change, log ΔA, against time.

Concentrations of HT were such that $[ZrT^{3+}]$ remained negligible compared to total [Zr(IV)]. It was not always possible to vary the concentration of HX over as wide a range as is generally desirable, because several of the acids, HX, complex strongly with Zr(IV) giving ZrX^{3+}, hence, reducing substantially the amount of ZrT^{3+}.

Equilibrium Constants. The equilibrium constant (eq 1) determined by Zielen and Connick[9] using a spectrophotometric method, K_{ZrT} = 341 at 25 °C and I = 2.0 M ($Na/LiClO_4$), is used in this study. A value 280 ± 25 has been obtained by a kinetic method,[10] in satisfactory agreement.

An earlier value, K_{ZrT} = 1084 in $[HClO_4]$ = 4.0 M solution, was reported by McVey.[13] Equilibrium constants, K_{ZrX}, as defined in (2), were obtained by determining the decrease in $[ZrT^{3+}]$ for a given HX concentration.

$$Zr^{4+} + HX \rightleftharpoons ZrX^{3+} + H^+ \qquad (2)$$

Results

$[H^+]$-Induced Reaction. The effect of $[H^+]$ on the reaction $Zr_4 \rightarrow 4Zr$ was studied at 25 °C and I = 4.0 M ($NaClO_4$). No dependence on [HT] = (0.50–2.0) × 10^{-4} M was observed (±5%), and individual runs conform to the rate law (3) (plots

$$d[ZrT^{3+}]/dt = k_{obsd}[Zr_4] \qquad (3)$$

linear to >90% completion). Rate constants k_{obsd} (Table I) give a good fit to (4), with $[H^+]$ in the range 2.0–4.0 M

$$k_{obsd} = k_H[H^+] \qquad (4)$$

(Figure 2). Extrapolation to $[H^+]$ = 0 (through a region of $[H^+]$ where polymeric Zr species exist and (4) is unlikely to apply) provides no evidence for an $[H^+]$-independent pathway. From an unweighted least-squares treatment a value for the intercept 0.1 ± 0.3 s^{-1} is obtained which can be neglected. The fit to (4) gives k_H = (3.7 ± 0.2) × 10^{-3} M^{-1} s^{-1}. On the assumption that (4) applies also at I = 2.0 M with $[HClO_4]$ = 2.0 M, rate constants 10^3 k_H/M^{-1} s^{-1} = 0.20 (5.5 °C), 0.50 (15.8 °C), 0.95 (25.0 °C), and 2.2 (35.0 °C) give $\Delta H^‡$ = 13.2 ± 0.2 kcal mol^{-1} and $\Delta S^‡$ = −28 ± 2 cal K^{-1} mol^{-1}.

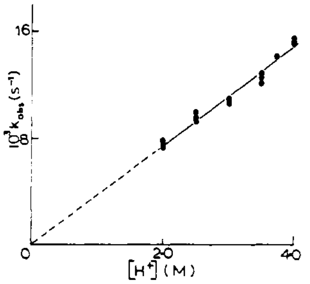

Figure 2. Dependence of first-order rate constants, k_{obsd}, on $[H^+]$ for the $Zr_4 \rightarrow Zr$ conversion. The broken line covers a region of H^+ in which other polymeric Zr species will be present.

Table II. Rate Constants, k_{obsd}, at 25 °C, $[HClO_4]$ = 1.5 or 2.0 M as Indicated, and I = 2.0 M for the Zr(IV) Tetramer[a] to Monomer Conversion in the Presence of Acids HX[b]

10^4[HX], M	10^3k_{obsd},[d] s^{-1}	10^3k_{obsd},[e] s^{-1}
	HX = HSO_4^-	
3.0		3.5
4.0	4.9	
6.0		6.2
8.0	8.7	
9.0		8.3
12.0	11.3	10.5
16.0	16.1	
20.0	19.9	
	HX = H_3PO_4	
1.0	8.5	7.3
2.0	16.1	15.2
3.0	24.3	23.1
4.0	34.3	32.3
	HX = $H_4P_2O_7$	
1.0	5.1	5.2
2.0	8.8	8.4
3.0	14.4	13.8
4.0	18.5	18.2
	HX = HF	
1.0	4.5	
2.0	8.3	
3.0	10.8	
4.0	13.4	
	HX = $H_2C_2O_4$	
1.0	5.9	
2.0	9.8	
3.0	15.2	
4.0	19.7	
	HX = CCl_3CO_2H	
16.0	3.1	
	HX = CH_2ClCO_2H	
40.0	3.5	
	HX = CH_3CO_2H	
50.0	1.9	

[a] Total Zr(IV) generally 5 × 10^{-4} M. [b] Reactions monitored by formation of ZrT^{3+}, the rate of which is rapid[c] (λ 366 nm). [c] Concentration of HT 1 × 10^{-4} M. [d] $[H^+]$ = 2.0 M. [e] $[H^+]$ = 1.5 M.

Effect of Cl^- and NCS^-. Replacement of 2 M $HClO_4$ by 2 M HCl had no effect on the rate of the $Zr_4 \rightarrow 4Zr$ conversion. It was also shown that NCS^- (1.2 × 10^{-3} M) had no effect.

HX-Induced Reactions. The effects of different acids HX on the $Zr_4 \rightarrow 4Zr$ reaction were studied at 25 °C and I = 2.0 M ($NaClO_4$). While acetic acid does not give any increase in rate, all other HX species tested produced appreciable effects (Table II). With HX = HSO_4^-, H_3PO_4, and $H_4P_2O_7$ a linear dependence on [HX] (concentrations <1.0 mM) was

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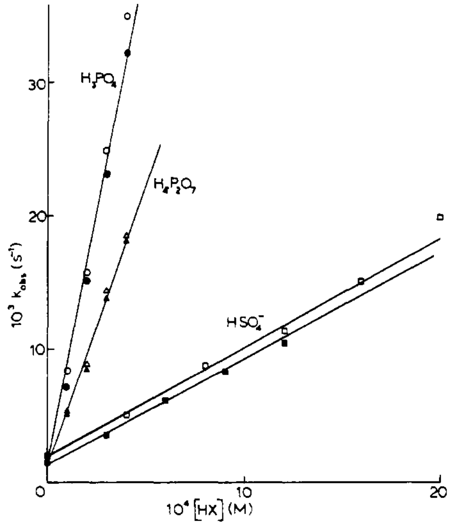


Figure 3. Dependence of first-order rate constants, k_{obsd}, on [HX] for the general acid induced $Zr_4 \rightarrow Zr$ conversion at 25 °C and I = 2.0 M ($NaClO_4$). With HX = HSO_4^-, two [H^+] values, 1.5 (■) and 2.0 M (□), were investigated. Two similarly spaced lines are also apparent in the studies at the same two [H^+] values with HX = H_3PO_4 (● and ○) and $H_4P_2O_7$ (▲ and △) although (because of the steeper gradients) separate lines are more difficult to draw in this case.

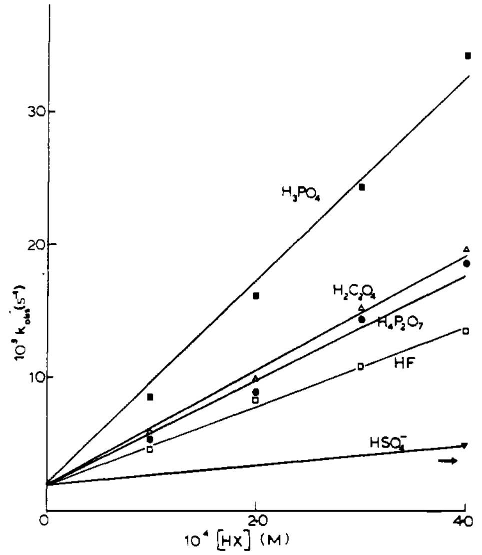


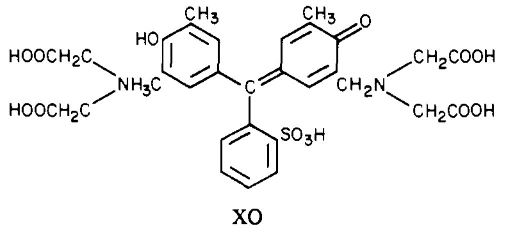
Figure 4. Dependence of first-order rate constants, k_{obsd}, on [HX] at 25 °C, [$HClO_4$] = 2.0 M, and I = 2.0 M. HX identities are as indicated.

first demonstrated with [$HClO_4$] = 2.0 M and then 1.5 M, when parallel lines were obtained (Figure 3). The full rate law is accordingly as in (5). Intercepts in Figure 3 correspond

$$k_{obsd} = k_H[H^+] + k_{HX}[HX] \qquad (5)$$

to $k_H[H^+]$ as determined previously. The dependences on different HX with [$HClO_4$] = 2.0 M are illustrated in Figure 4. Values of k_{HX} are listed in Table III alongside K_{ZrX}, defined in (2), and literature acid dissociation pK_a's for HX.

Effect of Xylenol Orange. Xylenol orange is a tetracarboxylic acid (XO) which is also known to complex with Zr^{4+}.[20] When attempts were made to use XO instead of HT it was found that a reaction occurred even at [$HClO_4$] = 0.5 M, indicating that XO itself induces the reaction $Zr_4 \rightarrow Zr$.



XO

Table III. Summary Rate Constants, k_{HX}, at 25 °C, [$HClO_4$] = 2.0 M, and I = 2.0 M for the Zr(IV) Tetramer to Monomer Conversion and Formation Constants for ZrX^{3+} as Defined in (2)[a]

HX	k_{HX}, M^{-1} s^{-1}	K_{ZrX}, M^{-1}	pK_a
CH_3CO_2H			4.50[d]
CH_2ClCO_2H	0.4	30 ± 15	2.66[e]
CCl_3CO_2H	1.0	70 ± 30	0.70[f]
HSO_4^-	8.8	460[b]	1.12,[g] 0.95[h]
HF	30	6.3×10^5 [b]	2.95[i]
$H_4P_2O_7$	40	$(7.0 \pm 3.0) \times 10^3$	0.79[j]
$H_2C_2O_4$	44	3×10^5 [c]	1.08[k]
H_3PO_4	80	$(5.0 \pm 2.0) \times 10^3$	1.70[l]

[a] Literature acid dissociation pK_a values at 25 °C for HX are also given (I = 1.0 M). [b] Reference 9. [c] Marov, I. N.; Rjabcikov, D. I. *Russ. J. Inorg. Chem.* (Engl. *Transl.*) 1962, *7*, 1036. [d] Kulba, F. Ya.; Yakovlev, Yu. B.; Mironov, V. E. *Ibid.* 1965, *10*, 886. Deneux, M.; Meilleur, R.; Benoit, R. L. *Can. J. Chem.* 1968, *46*, 1383. [e] At 20 °C. Hala, J.; Okac, A. *Coll. Czech. Chem. Commun.* 1962, *27*, 1697. [f] Deyrup, A. J. *J. Am. Chem. Soc.* 1934, *56*, 60. [g] Vdovenko, V. M.; Lazarev, L. N.; Khvorostin, Y. S. *Zh. Neorg. Khim.* 1967, *12*, 1152. [h] I = 2.0 M. [i] Farrer, H. N.; Rossotti, F. J. C. *J. Inorg. Nucl. Chem.* 1964, *26*, 1959. [j] Mitra, R. P.; Malhotra, H. C.; Jain, D. V. S. *Trans. Faraday Soc.* 1966, *62*, 167. [k] Moorhead, E. G.; Sutin, N. *Inorg. Chem.* 1966, *5*, 1866. [l] Ferrer, M.; Sykes A. G. *Inorg. Chem.* 1979, *18*, 3345.

Discussion

The potential complexity (i.e., polymeric nature) of Zr(IV) aqueous solutions was of concern to us at the outset in this study, and considerable care was required in defining a reliable approach. The fact that simple kinetics were observed for the reaction assigned[1] as the H^+-induced $Zr_4 \rightarrow Zr$ conversion, with a single rate-determining step, was particularly encouraging. From such studies it was found that the rate law takes the form $k_H[Zr_4][H^+]$ with no contribution from an [H^+]-independent term. Second-order rate constants k_H were independent of [HT], which complexes rapidly with Zr^{4+} but not with Zr_4. On varying the initial concentration of Zr(IV), equilibrated in 0.50 M $HClO_4$ prior to initiation of kinetic runs, so that conditions overlapped with those applying in ultracentrifuge experiments,[7] we observed identical kinetic behavior. Results obtained are consistent with the tetramer $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ being the single dominant species in solution, accounting for >90% of total Zr(IV).

The rate law observed clearly implicates $Zr_4 \rightarrow Zr_3$, or a step such as a single μ-hydroxo cleavage which is representative of this conversion, as the rate-determining process. Accordingly reactions $Zr_3 \rightarrow Zr$ are presumed to be relatively rapid, with no significant buildup of trimeric and dimeric intermediates. Zielen and Connick[9] have indicated that trimeric $Zr_3(OH)_4^{8+}$ may be present and relevant to interpretation of their studies on solutions with [Zr(IV)] = 0.02 M and [$HClO_4$] = 1–2 M. Also dimeric sulfato[14] and carbonato[15] complexes have been isolated. However evidence for such species playing a dominant role in the solution chemistry is at present lacking, and consideration of these species is not required in the interpretation of present results.

The rate-determining process in the $Zr_4 \rightarrow Zr_3$ conversion could involve the first μ-hydroxo bridge cleavage, with a reaction sequence (6)–(7), where only a section of the Zr_4 reactant is shown in these equations. The first stage here is a rapid protonation, so that k_H = kK. Alternatively the slow step could be [H^+]-independent cleavage of the second bridge in the manner of (8)–(9). This reaction sequence also requires

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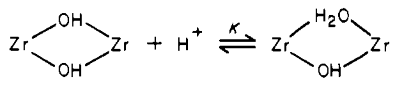
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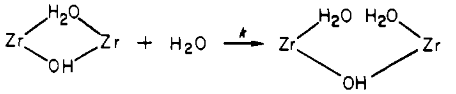
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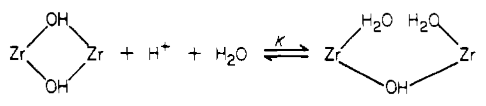
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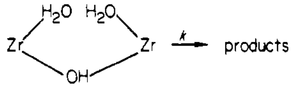
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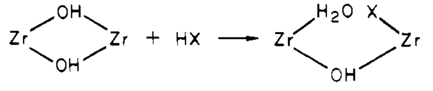
K to be small and $k_H = kK$. Interestingly hydroxo-bridged cleavage of $[(NH_3)_5CoOHCo(NH_3)_5]^{5+}$ gives $[H^+]$-independent and $[H^+]$-dependent terms $(a + b[H^+])$,[16,17] whereas with the analogous Cr(III) complex no b term is observed.[18] At this time there is no obvious rationalization of these different rate laws, and we find it difficult to choose between (6)–(7) and (8)–(9). Decomposition of $Ni_4(OH)_4^{4+}$ (which probably has a cubanelike structure) has also been studied,[19] where a change from zero- to first-order dependence on $[H^+]$ is observed as the latter increases from 10^{-3} to 10^{-1} M. Since protonation of a hydroxo bridge already bonded to three Ni(II) atoms cannot occur, a mechanism involving initial cleavage of a Ni–OH bond to give reactive $^*Ni_4(OH)_4^{4+}$ (eq 10) followed by reaction of this intermediate with H^+, provides a satisfactory explanation.

$$Ni_4(OH)_4^{4+} \rightleftharpoons {}^*Ni_4(OH)_4^{4+} \qquad (10)$$

Activation parameters obtained for k_H (0.95×10^{-3} M^{-1} s^{-1} at 25 °C), $\Delta H^{\ddagger} = 13.2$ kcal mol^{-1} and $\Delta S^{\ddagger} = -28$ cal K^{-1} mol^{-1}, are very similar to those obtained for other μ-hydroxo bridge cleavage processes.[17] In particular parameters for the $[H^+]$-dependent bridge cleavage of $(NH_3)_5CoOHCo(NH_3)_5^{5+}$,[16] rate constant 5.3×10^{-3} M^{-1} s^{-1} (25 °C), $\Delta H^{\ddagger} = 12.0$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -28.7$ cal K^{-1} mol^{-1} ($I = 2.0$ M ($LiClO_4$)), are virtually identical. The sign (and magnitude) of the entropy term is consistent with an increase in solvation which is expected to accompany addition of H^+ to an 8+ complex with consequent increase in total positive charge.

As is now customary in this type of study, the effect of replacing $NaClO_4$ by $LiClO_4$ was tested. Previously it has been clearly demonstrated that spurious rate law terms can contribute when $NaClO_4$ is used.[20] However in this case it was concluded that Li^+ ions have a marked acceleration on the $Zr_4 \rightarrow 4Zr$ process and induce bridge cleavage even at $[H^+] = 0.50$ M, while Na^+ and K^+ have no such effect.[10] No similar effects of Li^+ have been reported for other μ-OH cleavage reactions.

The HX-induced pathways are independent of $[H^+]$. Reactions may be expressed as in (11), where in this case, since


(11)

there is no $[H^+]$ dependence, the first bridge cleavage process must be the one observed. We have no information as to whether HX first substitutes into a Zr(IV) coordination sphere or binds to the μ-OH group undergoing cleavage. The observation that chloride (2 M) does not induce dissociation is consistent with other observations that early transition-metal ions generally exhibit low affinity for Cl^-. No effect of NCS^- was observed, where in this case concentrations tested were small and comparable to those of HX. One of the strongest effects observed is that of HF, where fluoride is known to have a high affinity for Zr(IV). The order of effectiveness in terms of rate constants k_{HX} is $H_3PO_4 > H_2C_2O_4 > H_4P_2O_7 > HF > HSO_4^- > CCl_3CO_2H > CH_2ClCO_2H$, which bears a close resemblance to the thermodynamic ($k_{Zr,X}$) order rather than the pK_a order (Table III). Ligands which are able to chelate, e.g., H_3PO_4 and $H_2C_2O_4$, appear to have a bigger effect as compared to those which cannot or are less likely to chelate e.g., HF and CCl_3CO_2H.

Finally, while crucial to this study, it is not clear to us why HT should coordinate to Zr^{4+} and not Zr_4. Interestingly xylenol orange, the other "colored" ligand investigated, was found to coordinate to Zr_4 and itself induce decomposition.

Acknowledgment. We are indebted to Tioxide International for generous support of this work and to Dr. P. Howard for his helpful collaboration and direction. The enthusiasm (and help) of Dr. I. McAlpine of Magnesium Elektron Ltd and Dr. S. Jones of British Aluminum Co. Ltd at the outset of these studies was particularly encouraging. We also thank Magnesium Elektron Ltd for a gift of zirconium samples.

Registry No. $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$, 12399-00-7; H_3PO_4, 7664-38-2; $H_2C_2O_4$, 144-62-7; $H_2P_2O_7$, 2466-09-3; HF, 7664-39-3; HSO_4^-, 14996-02-2; CCl_3CO_2H, 76-03-9; CH_2ClCO_2H, 79-11-8.

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