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Kinetics of the Acid Decomposition of the Hydroxonickel(II) Tetramer

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The rate expression for the reaction of the hydroxonickel(II) tetramer with perchloric acid (10^{-3} to 10^{-1} *M*) is

$$\frac{-\mathrm{d}[\mathrm{Ni_4(OH)_4}^{4+}]}{\mathrm{d}t} = \frac{k_1k_2[\mathrm{Ni_4(OH)_4}^{4+}][\mathrm{H}^+]}{k_{-1} + k_2[\mathrm{H}^+]}$$

where k_1, the rate constant for a first-order, acid-independent reaction, is 690 $\sec^{-1}$ at 25° and $\mu = 1.5$ *M* $NaClO_4$. The value of $\Delta H_1^{\ddagger}$ is 17 kcal/mol and $\Delta S_1^{\ddagger}$ is 13 eu for this reaction, which is believed to be a distortion of the tetramer cluster in order to provide a site for H^+ attack. The ratio of k_{-1}/k_2 is 0.099 *M* and the reaction approaches a first-order dependence in $[H^+]$ at pH 3. After the kinetically observable reaction with one proton, the tetramer reacts rapidly with additional acid to give the aquonickel ion. The decomposition reaction is general acid catalyzed. The rate is affected little by the strength of various acids, but electrostatic attraction enhances the rate as evidenced by the negatively charged HSO_4^- ion reacting five times faster than hydrogen ion.

Introduction

A hydroxonickel(II) tetramer, $Ni_4(OH)_4^{4+}$, was proposed by Burkov, Lilić, and Sillén[2] from their studies of the potentiometric titration of 0.1–1.0 *M* nickel perchlorate with sodium hydroxide at 3.0 *M* ionic strength. In the present work potentiometric, spectrophotometric, and kinetic studies confirm the presence of a hydroxonickel(II) tetramer as the only major hydrolytic nickel species in solution under similar conditions at 1.5 *M* ionic strength.

The acid decomposition reaction in eq 1 is studied by

$$\mathrm{Ni_4(OH)_4}^{4+} + 4\mathrm{H}^+ \longrightarrow 4\mathrm{Ni}^{2+} + 4\mathrm{H_2O} \qquad (1)$$

stopped-flow spectrophotometry. Although a reaction stoichiometry requiring four protons per tetramer is confirmed, the kinetics of the decomposition at 10^{-3} *M* $[H^+]$ needs only one proton. There is rapid addition of the subsequent protons. At high acid concentrations the decomposition of $Ni_4(OH)_4^{4+}$ approaches a first-order, acid-independent reaction.

Experimental Section

Nickel perchlorate was prepared from nickel carbonate and perchloric acid and was recrystallized from water. Solutions of $Ni(ClO_4)_2$ were standardized by EDTA titration.

Solutions of hydrolyzed nickel were prepared by adding 1–5 ml of 1 *M* NaOH (carbonate free) to approximately 200 ml of $Ni(ClO_4)_2$ solution (0.1–0.5 *M*) adjusted with $NaClO_4$ to give an ionic strength of 1.5 *M*. (This is expressed as 1.5 *M* $(Na)ClO_4$.) A small quantity of nickel hydroxide precipitate was intentionally produced by this procedure and was removed by filtration through a 10-mμ filter (Type VFWP 0 4700, Millipore Corp., Bedford, Mass.). The filtrate contained Ni^{2+} and soluble, hydrolyzed nickel. No colloidal particles could be detected with a Tyndall beam. This method of preparation was far easier than attempting to avoid precipitation during the addition of NaOH to nickel solutions, but it was necessary to prove that the hydrolyzed form of nickel present was still the tetramer.

Titration of the hydrolyzed nickel solution with perchloric acid gives a sharp potentiometric break as seen in Figure 1. The total amount of bound hydroxide is close to that predicted using the equilibrium constant for the tetramer.[2] Table I gives data for one of the titrations performed with an electrode system similar to that of Burkov, Lilić, and Sillén. A calomel electrode containing 4 *M* NaCl is connected through a salt bridge of 1.5 *M* $NaClO_4$ to the titration vessel in which a glass electrode is mounted. The hydrolyzed nickel solution is thermostated at 25.0° and nitrogen is continuously bubbled through it. The change in millivolts during titration with $HClO_4$ is measured with a Beckman Research pH meter, Model 1019. The value of E_0, the constant reference cell potential, is determined by titrating well past the equivalence point and calculating the cell potential from the amount of acid present. An iterative calculation on the CDC 6500 computer gives the best value for the equivalence point in order to give a constant E_0 value. The value of *BZ*, the total hydroxide bound, is determined from the volume of acid added before the equivalence point.

For the hydrolysis reaction in eq 2 the polymer concentration

$$n\mathrm{Ni}^{2+} + n\mathrm{H_2O} \rightleftarrows \mathrm{Ni}_n(\mathrm{OH})_n{}^{n+} + n\mathrm{H}^+ \qquad (2)$$

equals BZ/n. A plot of log (BZ) against $-\log [H^+] + \log V_c$, where V_c is a volume correction, gives slopes varying from 3.8 to 4.0 for different titrations. Assuming $n = 4$ gives $\beta_{44} = [\mathrm{Ni_4(OH)_4}^{4+}][\mathrm{H}^+]^4/[\mathrm{Ni}^{2+}]^4$ and the values in the right-hand column of Table I. Two titrations gave log β_{44} values of $-27.01 \pm$

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[1] Correspondence to be addressed to this author.

[2] K. A. Burkov, L. S. Lilić, and L. G. Sillén, *Acta Chem. Scand.*, **19**, 14 (1965).

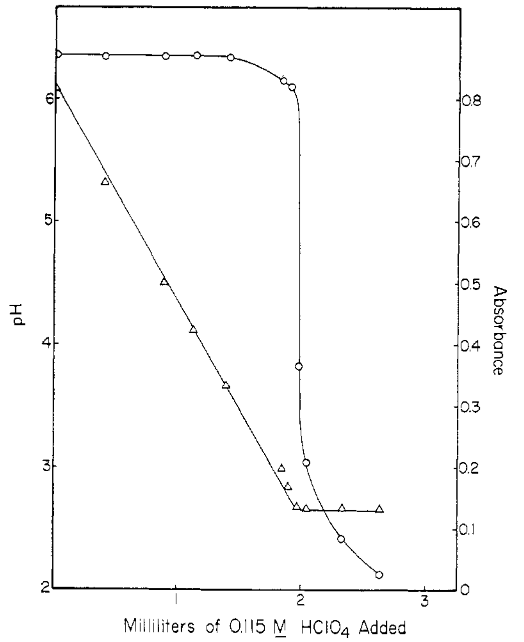


Figure 1.—Dependence of pH (○) and absorbance (Δ) in the titration of hydrolyzed nickel(II). The initial concentrations were $[Ni^{2+}]$ = 0.46 *M* and $[Ni_4(OH)_4^{4+}] = 3.83 \times 10^{-3}$ *M*. Other conditions: 25.0°, μ = 1.5 *M* (Na)ClO$_4$, 15-ml initial volume, 2-cm cells.

0.02 and −27.05 ± 0.04 at an ionic strength of 1.5 *M* (Na)ClO$_4$. This compares favorably with the value of −27.37 ± 0.07 at 3 *M* (Na)ClO$_4$.[2]

When hydrolysis of nickel perchlorate occurs, there is a large shift in its ultraviolet spectrum as seen in Figure 2. The absorbance is characteristic of $Ni_4(OH)_4^{4+}$ and is linear with the amount of tetramer present. Figure 1 displays the linearity of the absorbance with acid added and the agreement of the end point with a potentiometric curve. The molar absorptivity of the tetramer proved to be constant for solutions prepared over a 2.5-fold range of nickel concentrations and remained constant for at least 1 week. The average absorptivity determined for the tetramer at 235 mμ is 89.7 cm^{-1} *M*$^{-1}$. The linearity of the absorbance with acid added and the constant value of ϵ are additional evidence that $Ni_4(OH)_4^{4+}$ is the only major hydrolytic species.

The rates of acid decomposition of $Ni_4(OH)_4^{4+}$ were measured at 235 mμ using a Durrum-Gibson stopped-flow apparatus with a 2.0-cm observation cell. Oscilloscope time scans ranging from 5 to 100 msec/cm were used.

Results

Kinetics of the Tetramer Decomposition with HClO$_4$.—At low acidities the rate of change of the $Ni_4(OH)_4^{4+}$ concentration is first order in tetramer and first order in hydrogen ion as expressed in eq 3. The rate constant, k_p, is determined by plotting eq 4, where *a* is the initial

$$\frac{-d[Ni_4(OH)_4^{4+}]}{dt} = k_p[Ni_4(OH)_4^{4+}][H^+] \qquad (3)$$

$$\frac{1}{4a - b} \ln [(a - x)/(b - 4x)] = k_p t + c \qquad (4)$$

concentration of the tetramer, *b* is the initial concentration of acid, and *x* is the amount of polymer converted to Ni^{2+}. Individual k_p values are obtained from a least-squares program.

The first-order dependence in $[Ni_4(OH)_4^{4+}]$ is confirmed by the agreement of k_p values given in Table II for various concentrations of total nickel and polymer. Standard deviations are given for eight to ten runs at the same initial acidity; the hydrogen ion concentration is obtained from the amount of perchloric acid added.

Despite the linearity for first-order dependence in

Table I

Potentiometric Titration of Hydrolyzed Nickel(II) Solution[a]

HClO$_4$, ml	*E*, mV	10^3*BZ*, *M*	−Log [H$^+$]	Log β_{44}
0.00	42.3	14.52	6.493	−27.12
0.10	42.3	13.91	6.493	−27.13
0.24	42.8	13.07	6.484	−27.12
0.34	43.3	12.47	6.476	−27.10
0.45	43.6	11.79	6.471	−27.10
0.56	43.9	11.17	6.466	−27.10
0.66	44.4	10.57	6.457	−27.09
0.77	44.8	9.93	6.451	−27.09
0.88	45.3	9.31	6.442	−27.08
0.98	46.0	8.70	6.430	−27.06
1.08	46.3	8.12	6.425	−27.06
1.20	46.9	7.43	6.415	−27.06
1.30	47.5	6.85	6.405	−27.05
1.48	48.6	5.82	6.386	−27.04
1.58	49.6	5.25	6.369	−27.04
1.65	50.0	4.85	6.363	−27.01
1.75	50.9	4.29	6.347	−27.02
1.86	51.6	3.67	6.336	−27.01
1.96	52.9	3.10	6.314	−27.02
2.03	53.8	2.71	6.298	−27.00
2.06	54.2	2.54	6.292	−27.00
2.14	55.3	2.13	6.273	−27.00
2.20	56.6	1.77	6.251	−27.00
2.30	59.0	1.21	6.210	−27.00
2.38	61.3	0.80	6.172	−27.01
2.44	65.0	0.44	6.109	−27.02
2.48	68.0	0.25	6.058	−27.07
2.50	74.4	0.09	5.950	−27.05
			Av	−27.05 ± 0.04

[a] In 1.5 *M* (Na)ClO$_4$, at 25.0°; $[Ni^{2+}]$ = 0.46 *M*; [HClO$_4$] = 0.288 *M* used for titration; initial volume = 50 ml; E_0 = 426.8 ± 0.2 mV.

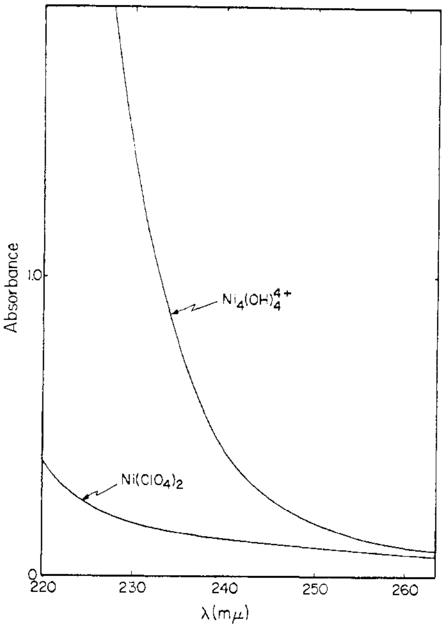


Figure 2.—Ultraviolet spectra of nickel perchlorate and the hydroxonickel(II) tetramer. Conditions: $[Ni^{2+}]$ = 0.46 *M*, $[Ni_4(OH)_4^{4+}] = 3.44 \times 10^{-3}$ *M*, 25.0°, μ = 1.5 *M* (Na)ClO$_4$, 2-cm cells.

TABLE II

RATE CONSTANTS FOR THE ACID DECOMPOSITION OF THE HYDROXONICKEL(II) TETRAMER[a]

$10^3[H^+]_i$, M	$10^3[Ni_4(OH)_4{}^{4+}]_i$, M	$[Ni^{2+}]$, M	$10^{-3}k_p$,[b] M^{-1} sec^{-1}
2.30	0.55–1.91	0.09–0.24	6.9 ± 0.5
4.60	0.55–1.91	0.09–0.24	7.1 ± 0.4
7.20	0.55–1.91	0.09–0.24	6.4 ± 0.3
17.20	0.55–1.91	0.09–0.24	6.2 ± 0.4
28.80	1.00–1.91	0.14–0.24	5.7 ± 0.2
43.10	1.00–1.91	0.14–0.24	4.8 ± 0.2
57.50	1.52–1.91	0.24	4.6 ± 0.3

[a] At 25.0° and $\mu = 1.5$ M (Na)ClO$_4$. [b] Standard deviations are given for eight to ten runs.

hydrogen ion at low acid concentrations, the value of k_p is not constant as the acid concentration is increased. This is seen in Figure 3. At higher acidities the $[H^+]$ is nearly constant during the reaction so that deviations from eq 4 do not interfere. The variation of k_p with $[H^+]$ suggests the mechanism given in eq 5 and 6,

$$Ni_4(OH)_4{}^{4+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \{Ni_4(OH)_4{}^{4+}\}^* \tag{5}$$

$$\{Ni_4(OH)_4{}^{4+}\}^* + H^+ \xrightarrow{k_2} \text{products} \tag{6}$$

where $\{Ni_4(OH)_4{}^{4+}\}^*$ is a more reactive form of the tetramer. A steady-state approximation for this intermediate leads to eq 7 and to the hydrogen ion

$$\frac{-d[Ni_4(OH)_4{}^{4+}]}{dt} = \frac{k_1k_2[Ni_4(OH)_4{}^{4+}][H^+]}{k_{-1} + k_2[H^+]} \tag{7}$$

dependence for k_p given in eq 8. The rate constants

$$k_p = k_1k_2/(k_{-1} + k_2[H^+]) \tag{8}$$

k_1 and the ratio of k_{-1}/k_2 are obtained by plotting $1/k_p$ against $[H^+]$ as shown in Figure 4. A least-squares analysis gives $k_1 = 690 \pm 10$ sec^{-1} and $k_{-1}/k_2 = 0.099 \pm 0.001$ M at 25°.

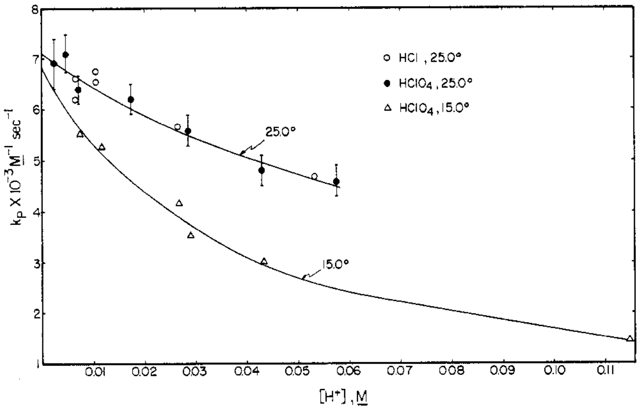


Figure 3.—Hydrogen ion dependence of the acid decomposition rate of the tetramer at $\mu = 1.5$ M (Na)ClO$_4$. The initial concentration of $Ni_4(OH)_4{}^{4+}$ varied from 0.55×10^{-3} to 1.91×10^{-3} M.

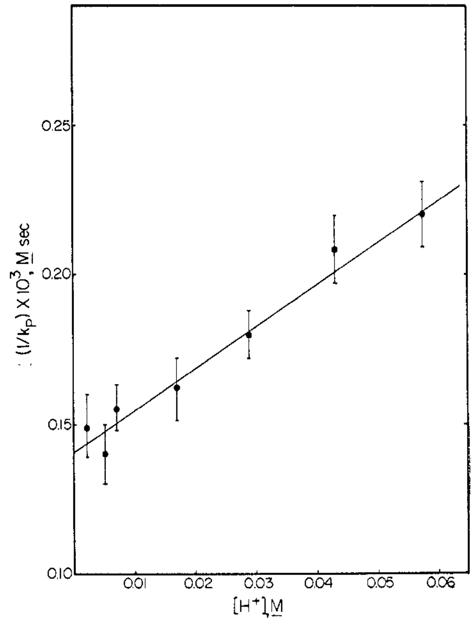


Figure 4.—Hydrogen ion dependence of the reciprocal of the rate constant for the perchloric acid decomposition of the tetramer, at 25.0°, $\mu = 1.5$ M (Na)ClO$_4$, and $[Ni_4(OH)_4{}^{4+}]_i = (0.55–1.91) \times 10^{-3}$ M.

The reaction of perchloric acid with $Ni_4(OH)_4{}^{4+}$ is studied at temperatures from 15 to 40°. In order to determine the activation parameters for k_1 and for k_{-1}/k_2 it is necessary to observe the decomposition rate for a number of acid concentrations at each temperature. Table III gives the value of k_p at various temperatures and acidities. The resolved rate constants are given in Table IV. The activation energies, enthalpies, and entropies evaluated from these constants also are shown in Table IV.

Effect of Other Acids on the Tetramer Decomposition.—Reactions with hydrochloric acid give the same results as those with perchloric acid. This is shown by the open circles in Figure 3 which fall within the experimental error for the perchloric acid reactions at 25°. The activation energy for k_p with HCl is the same as that with HClO$_4$.

On the other hand, when acetic, aminoacetic, and sulfuric acids are used, the rate behavior indicates that, in addition to hydrogen ion, the undissociated acids react with the tetramer. Assuming that the same reactive intermediate must form before any acid, HA, can react gives eq 9 in addition to the steps given in

$$\{Ni_4(OH)_4{}^{4+}\}^* + HA \xrightarrow{k_2'} \text{products} \tag{9}$$

eq 5 and 6. The rate of decomposition of the tetramer then equals $k_a[Ni_4(OH)_4{}^{4+}]$ where

$$k_a = \frac{(k_2[H^+] + k_2'[HA])k_1}{k_{-1} + k_2[H^+] + k_2'[HA]} \tag{10}$$

and the values for k_a are given in Table V. The actual value of k_2' cannot be determined because only the ratio of k_{-1}/k_2 is known. However, the ratio of k_2'/k_2 can be evaluated from the other constants as given in eq 11.

$$\frac{k_2'}{k_2} = \frac{k_1[H^+] - ([H^+] + (k_{-1}/k_2))k_a}{[HA](k_a - k_1)} \tag{11}$$

Table VI summarizes the results for the values of k_2' for HSO$_4{}^-$, NH$_3$CH$_2$COOH$^+$, and CH$_3$COOH relative to the k_2 value for H$_3$O$^+$. The concentration of the conjugate bases of these acids did not affect the rate.

TABLE III
TEMPERATURE DEPENDENCE OF THE OBSERVED ACID DECOMPOSITION RATE CONSTANT AT $\mu = 1.5\ M$ (Na)ClO_4

Temp, °C	$10^3[H^+]_i$, *M*	$10^3(1/k_p)$, *M* sec
15.0	7.20	0.180
15.0	10.60	0.165
15.0	11.50	0.186
15.0	26.50	0.240
15.0	28.80	0.283
15.0	43.10	0.333
15.0	115.00	0.720
19.8	10.60	0.169
19.8	11.50	0.162
19.8	28.80	0.234
19.8	57.50	0.340
25.0	Data given in Table II	
30.1	10.60	0.127
30.1	11.50	0.116
30.1	26.50	0.170
30.1	28.80	0.143
35.1	10.60	0.149
35.1	11.50	0.129
35.1	28.80	0.160
39.6	10.60	0.085
39.6	11.50	0.088
39.6	26.50	0.105
39.6	28.80	0.093

TABLE IV
EFFECT OF TEMPERATURE ON THE RESOLVED RATE CONSTANTS FOR THE HYDROXONICKEL(II) TETRAMER ACID DECOMPOSITION AT $\mu = 1.5\ M$ (Na)ClO_4

Temp, °C	$10^{-2}k_1$, sec^{-1}	$10^2(k_{-1}/k_2)$, *M*
15.0	2.0	2.6
19.8	2.7	3.3
25.0	6.9	9.9
30.1	6.0	6.4
35.1	16.5	16.0
39.6	22.2	18.6

$E_1 = 18 \pm 2$ kcal/mol
$\Delta H_1^{\ddagger} = 17 \pm 2$ kcal/mol
$\Delta S_1^{\ddagger} = 13 \pm 3$ cal/°K mol

$E_{-1} - E_2 = 15 \pm 3$ kcal/mol
$\Delta H_{-1}^{\ddagger} - \Delta H_2^{\ddagger} = 15 \pm 3$ kcal/mol
$\Delta S_{-1}^{\ddagger} - \Delta S_{-2}^{\ddagger} = 22 \pm 4$ cal/°K mol

TABLE V
EFFECTS OF VARIOUS ACIDS ON THE TETRAMER DECOMPOSITION RATE AT $\mu = 1.5\ M$ (Na)ClO_4

HA	$10^3[H^+]$, *M*	10^3[HA], *M*	$10^3[A^-]$, *M*	k_a, sec^{-1}	Temp, °C
CH_3COOH	0.86	24.1	0.86	20	25.0
$H_3{}^+NCH_2COOH$	2.84	2.17	2.84	29	25.0
	7.98	17.20	7.98	114	25.0
HSO_4^-	7.90	0.28	3.82	47	13.5
	7.90	0.39	3.71	62	25.0
	15.3	1.07	7.13	87	14.9
	15.2	1.24	6.96	99	20.7
	15.0	1.38	6.82	143	25.0
	14.8	1.56	6.64	147	30.1
	14.7	1.73	6.47	213	35.1
	14.5	1.90	6.30	248	39.6

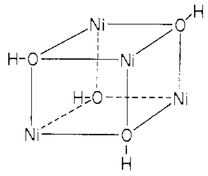
TABLE VI
RELATIVE RATE CONSTANTS FOR VARIOUS ACIDS AT $\mu = 1.5\ M$ (Na)ClO_4

HA	pK_a	Temp, °C	k_2'/k_2
H_3O^+	−1.74	25.0	1.0
HSO_4^-	1.13	15–40	5.0 ± 1.5
$H_3NCH_2COOH^+$	2.43	25.0	0.7
CH_3COOH	4.54	25.0	0.09

The protonation constants used to calculate the concentrations of the acid species were log $K_{HA} = 4.54$ for acetic acid determined at 20° and 1 *M* $NaClO_4$,[3] log $K_{H_2A} = 2.43$ for aminoacetic acid determined at 20° and 1 *M* $NaClO_4$,[3] and log $K_{HSO_4} = 1.13$ at 25° and 1.5 *M* $NaClO_4$.[4] The hydrogen sulfate reactions were studied at various temperatures and the protonation constant was calculated from $\Delta H_{HSO_4} = 5.5$ kcal/mol in 2 *M* (Na)ClO_4.[5] Within the experimental errors of the evaluation of k_2'/k_2, temperature had no effect for HSO_4^- compared to H_3O^+, and therefore the activation energies for these two rate constants must be nearly the same.

Discussion

The structure for $Ni_4(OH)_4{}^{4+}$ is not known, but the fact that the tetramer occurs as a unique polymeric species suggests a special stability for this stoichiometry. A study of a hydrolytic polymer of lead(II), $Pb_4(OH)_4{}^{4+}$, by solution X-ray scattering measurements[6] and by Raman and infrared[7] spectra shows a compact ion which is a distorted cube consisting of lead and oxygen atoms arranged tetrahedrally. A similar arrangement is reasonable for $Ni_4(OH)_4{}^{4+}$ and is shown in I. This structure permits each nickel to interact with three hydroxide ions and each hydroxide ion to interact with three nickel ions and allows for the possibility of metal–metal interaction. This type of tetrahedral nickel cluster has been reported[8] in an X-ray crystal study of $[Ni(acac)(OCH_3)(CH_3OH)]_4$ where the $^-OCH_3$ groups are in positions similar to the ^-OH groups in I.



I

The observed kinetics of acid decomposition of $Ni_4(OH)_4{}^{4+}$ are consistent with the proposed structure. There is no evidence of direct acid attack on $Ni_4(OH)_4{}^{4+}$ which agrees with the hydroxide ions being fully coordinated. There is a high enthalpy of activation ($\Delta H_1^{\ddagger} = 17.4$ kcal/mol) in going from the stable form of $Ni_4(OH)_4{}^{4+}$ to a form which can react with acid. This process also has a positive entropy of activation ($\Delta S_1^{\ddagger} = 13$ eu) indicating the breakup of an ordered structure. This suggests that $\{Ni_4(OH)_4{}^{4+}\}^*$ is sufficiently distorted from the original polymer to permit acid attack on one of the hydroxides. An extreme distortion would give an eight-membered ring of alternating nickel and

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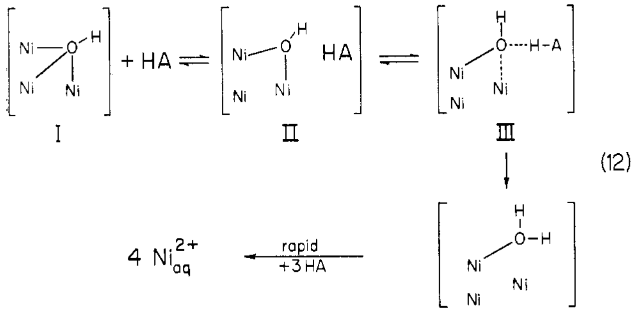
[7] V. A. Maroni and T. G. Spiro, *Inorg. Chem.*, **7**, 188 (1968).

[8] J. A. Bertrand and R. I. Kaplan, Abstracts, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, No. O 20

hydroxide ions, but a lesser degree of disruption of I is more likely.

The fact that the dissociation of the tetramer is general acid catalyzed indicates that the mechanism does not involve a complete protonation of the tetramer followed by a rate-determining nickel dissociation step. Rather, the proton-transfer reaction must be part of the rate-determining step. However, the results in Table VI indicate that the reaction is relatively insensitive to the pK_a values of the acids. Thus, for the two positively charged acids, H_3O^+ and $H_3NCH_2COOH^+$, a difference of more than 4 in the pK_a values has almost no effect on the rate of the acid reaction. Only with acetic acid does the rate begin to fall off with acid strength. The larger k_2' value for HSO_4^- can be accounted for because of electrostatic attraction in an encounter complex with the tetramer. Similar encounter complexes were proposed in the acid catalysis of proton transfer from the primary hydration sphere of metals to bulk water.[9] As with the tetramer decomposition rate, enhancement was observed for HSO_4^- over hydrogen ion.

The proposed structure of the tetramer, the activation parameters, and the behavior of the acid reactions are consistent with a detailed mechanism such as that shown in eq 12. A corner of the cube of I is shown.



(12)

The suggested mechanism is the formation of an encounter complex between $\{Ni_4(OH)_4^{4+}\}^*$ and the acid HA in II. Structure II, which reacts with HA, has two nickels bound to a hydroxide ion and would not be expected to be a strong base. The fact that k_2' is little affected by the strength of HA means that the proton must be transferred to a moderately strong base. The base strength of the active intermediate is sufficiently strong that it does not discriminate between the strength of the acids until the pK_a of the acid becomes greater than 2.5. Therefore, structure III is proposed in the reaction mechanism, where a nickel–hydroxide bond breaks to give a moderately strong base which accepts a proton from HA. The base strength of III would be similar to that of $NiOH^+$ which has a $p\beta_{11}$ value of 10.[2] The rate-determining step is believed to involve a proton transfer to a structure such as III in which the nickel–hydroxide bond is almost completely broken.

The enthalpy of activation for the acid-independent rate constant, k_1, is large ($\Delta H_1^{\ddagger}$ = 17 kcal/mol) and is approximately the same as that observed[10] for the breaking of a hydroxide bridge in the hydrolytic dimer $Cr_2(OH)_2^{4+}$. A comparison of the enthalpy of activation for substitution reactions of Cr(III) and Ni(II) indicates that the $\Delta H^{\ddagger}$ values for chromium are usually twice as large as those for the corresponding nickel reactions.[11]

The large positive value for the activation entropy with $Ni_4(OH)_4^{4+}$ ($\Delta S_1^{\ddagger}$ = 13 eu) also is unusual for first-order bond breakage in hydrolytic systems. The breaking of one of the hydroxide bridges in the hydrolytic dimer of Fe(III),[12] $Fe_2(OH)_2^{4+}$, has an activation entropy of 3 eu and a similar reaction of Cr(III) using $[(phen)_2CrOH]_2^{4+}$ has an activation entropy of 0.5 eu.[13]

The entropy and enthalpy of activation for k_1 indicate that the process involved is more than a simple hydroxide bond cleavage and must involve a greater disruption of the initial polymer. This is consistent with a change from a compact to a more open structure for the tetramer.

In conclusion for the reaction of the nickel tetramer with 10^{-3} M or greater concentrations of acid, the rate-determining step is early in the breakup of the hydrolytic species and requires the addition of only one proton. At higher acid concentrations an acid-independent, first-order distortion of the tetramer must occur first. Thus, the kinetic evidence, as well as the thermodynamic evidence, points to a special stability for the tetramer, which suggests a clustered structure as in I. Many other hydrolytic species have preferred stoichiometries and may exist as clusters. Similar kinetic behavior should be expected.

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