Correspondence

Reaction of $HCrO_4^-$ with $Co(NH_3)_5H_2O$

Sir:

On the kinetics of association of $Co^{III}-OH_2$ ligands with $HOCrO_3^-$, reactions

$$HL + HOCrO_3^- \rightleftarrows LCrO_3^- + H_2O \qquad (1)$$
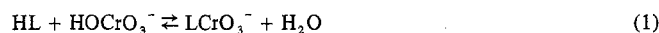
have been observed to follow two pathways, one involving a

Table I. Kinetic Parameters for Formation of Cr(VI) Complexes: $HL^{-n+1} + HCrO_4^- \rightleftarrows LCrO_3^{-n} + H_2O$

HL^{-n+1}	$K_a = \dfrac{[H^+][L^{-n}]}{[HL^{-n+1}]}$	K_{eq}	$k_f, M^{-1} sec^{-1}$	k_r, sec^{-1}	$k_f^{H^+}, M^{-2} sec^{-1}$	Ref
$HCrO_4^-$	3×10^{-6}	98	2	2.7×10^{-2}	6.6×10^5	a
$H_2PO_4^-$	6×10^{-8}	6			1.2×10^5	b
$H_2PO_3^-$	3×10^{-7}	8			5×10^5	c
$HS_2O_3^-$	5.4×10^{-2}	1×10^4	2×10^4	2		d
HSCN	>1	220			5.4×10^5	e
HCl	≫1	17		Too fast for T jump		e
$(NH_3)_5Co(OH)^{2+}$	$\sim 10^{-14}$	$\sim 9 \times 10^3$	80	$2.2 \times 10^{-2} + 64[H^+]$	4×10^5	f
$(NH_3)_5Co(OH_2)$	2×10^{-6}	9.8×10^{-3}	0.8			f
$(NH_3)_4Co(OH_2)(OH)^{2+}$	$\sim 10^{-10}$	$\sim 3 \times 10^3$			4×10^5	f

a J. H. Swinehart and G. W. Castellan, *Inorg. Chem.*, **3**, 278 (1964). *b* S. A. Frennesson, J. K. Beattie, and G. P. Haight, Jr., *J. Amer. Chem. Soc.*, **90**, 6018 (1968). *c* S. A. Frennesson, J. K. Beattie, and G. P. Haight, Jr., *Acta Chem. Scand.*, **23**, 3277 (1968). *d* K. Muirhead, G. P. Haight, Jr., and J. K. Beattie, *J. Amer. Chem. Soc.*, **94**, 3006 (1972). *e* Reference 1. *f* Reference 2.

proton attached to the ligand and one involving acid catalysis with the respective rate laws[1]

$$R_I = k_f[HL][HOCrO_3^-] \qquad (I)$$

$$R_{II} = k_f^{H^+}[H^+][L^-][HOCrO_3^-] \qquad (II)$$

So far all $k_f^{H^+}$ values are identical[1] within experimental error, being of the order of 5×10^5, consistent with the formation of weak

$$\begin{array}{c} L-CrO_3 \\ | \\ OH \end{array}$$

which reacts with H^+ to eliminate water. Values of k_f vary with the acidity of HL indicating a loose association

$$\begin{array}{c} O \quad LH \\ \diagdown / \\ O-Cr \\ \diagup \diagdown \\ O \quad OH \end{array}$$

in which the acidity of HL governs the rate of water elimination.

It is of interest to try to correlate the communication of Woods and Sullivan[2] containing a two-term rate law with the findings above

$$(NH_3)_5Co(H_2O)^{3+} + HOCrO_3^- \underset{k_r}{\overset{k_f}{\rightleftarrows}} Co(NH_3)_5OCrO_3^+ + H_3O^+ \qquad (2)$$
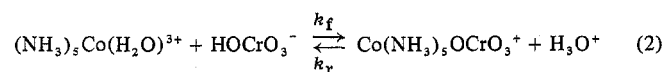
$$k_{obsd} = k_r + k_f^0[(NH_3)_5Co(H_2O)^{3+}] \qquad (III)$$

Woods and Sullivan[2] found that

$$k_f^0 = 0.80 + 1.68 \times 10^{-4}[H^+]^{-1} \qquad (IV)$$

Let us assume that $(NH_3)_5Co(OH_2)^{3+}$ will have to lose a proton to attack $HOCrO_3^-$ giving for the forward rate

$$R_V = k_f[(NH_3)_5CoOH^{2+}] + k_f^{H^+}[(NH_3)_5CoOH^{2+}][H^+] \qquad (V)$$

(1) C. T. Lin and J. K. Beattie, *J. Amer. Chem. Soc.*, **94**, 301 (1972).
(2) M. Woods and J. C. Sullivan, *Inorg. Chem.*, **12**, 1459 (1973).

This rearranges to

$$R_V = \frac{K_a k_f[(NH_3)_5CoOH_2^{3+}]}{[H^+]} + K_a k_f^{H^+}[NH_3]_5Co(OH_2)^{3+}]$$

which is equivalent to eq IV with $K_a k_f = 1.68 \times 10^{-4}$ and $K_a k_f^{H^+} = 0.80$.

In 1 M $NaNO_3$ (*vs.* 0.25 M $NaClO_4$ in Woods and Sullivan's system) K_a is reported[3] to be 2×10^{-6}

$$K_a k_f = 1.68 \times 10^{-4}$$

$$k_f = 84$$

$$K_a k_f^{H^+} = 0.80$$

$$k_f^{H^+} = 4 \times 10^5$$

Similarly $k_f^{H^+}$ for $(NH_3)_4Co(OH_2)(OH)^{2+}$ can be shown to be 4×10^5.

It appears that

$$\begin{array}{c} |/ \\ -Co-OH^{2+} \\ /| \end{array}$$
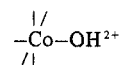
species coordinate to $HOCrO_3^-$ by the mechanism

$$\begin{array}{c} |/ \\ -Co-OH^{2+} + HOCrO_3^- \rightleftarrows \end{array} \quad \begin{array}{c} H \quad O \\ |/ \; | \; / \\ -Co-O-Cr-O^+ \\ /| \qquad \diagdown O \\ \qquad\qquad || \\ \qquad\qquad O \\ \qquad\qquad H \end{array}$$

$$\begin{array}{c} H \quad O \quad O^+ \\ |/ \; | \; |/ \\ -Co-O-Cr \quad + H^+ \rightarrow \\ /| \qquad | \\ \qquad O \\ \qquad H \end{array} \quad \begin{array}{c} O \\ |/ \; / \\ -Co=O=Cr-O^+ + 2H^+ \\ /| \qquad \diagdown \\ \qquad O \end{array}$$
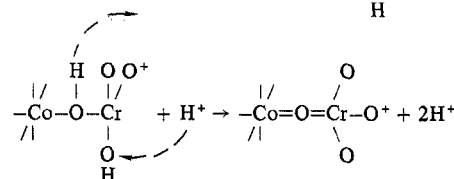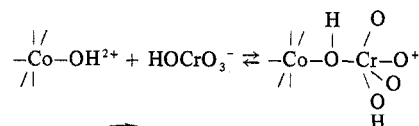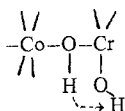
the rate of which is the same as for all other such proton-assisted combinations.

Inclusion of the hydroxycobalt(III) species in Table I shows that the constancy of $k_f^{H^+}$ is maintained. However, k_f is very high considering the weakness of $Co^{III}-OH$ species as acids. This would seem to rule out a weak association complex

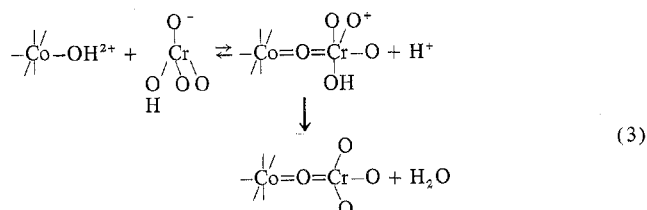(3) L. G. Sillen and A. E. Martell, *Chem. Soc., Spec. Publ.*, No. 17 (1964).

$$\begin{array}{c} \backslash / \quad \backslash / \\ -\text{Co}-\text{O}-\text{Cr} \\ /\backslash \quad | \quad | \\ \quad \text{H} \quad \text{O} \\ \quad \quad \backslash \text{--} \rightarrow \text{H} \end{array}$$

with internal proton transfer leading to water elimination. An alternative possibility is that a strong association takes place with proton elimination followed by proton-assisted water elimination

$$-\overset{\backslash/}{\underset{/|}{\text{Co}}}-\text{OH}^{2+} + \overset{\text{O}^-}{\underset{\underset{\text{H}}{\text{O}}}{\overset{|}{\underset{\text{O}}{\text{Cr}}}}} \rightleftarrows -\overset{\backslash/}{\underset{/|}{\text{Co}}}=\text{O}=\overset{\text{O}}{\underset{\text{OH}}{\overset{\text{O}^+}{\text{Cr}}}}-\text{O} + \text{H}^+$$

$$\downarrow \qquad\qquad (3)$$

$$-\overset{\backslash/}{\underset{/|}{\text{Co}}}=\text{O}=\overset{\text{O}}{\underset{\text{O}}{\overset{}{\text{Cr}}}}-\text{O} + \text{H}_2\text{O}$$

There would seem to be competition between loss of proton from the bridging oxygen, followed by rapid loss of water, and loss of water, followed by deprotonation of the bridging oxygen.

$CoOH^{2+}$ substrates differ from the other oxygen-containing substrates studied in two important respects: (1) the bridging oxygen in the active intermediate *must* be protonated and must lose the proton; (2) Co(III) has filled t_{2g} orbitals capable of donating electrons to the π system associated with the bridging oxygen.

The Co–O bond system contains filled π-antibonding orbitals which enhance its donor properties *vis a vis* Cr(VI) making the

$$-\overset{\backslash/}{\underset{/|}{\text{Co}}}-\overset{\text{H}}{\text{O}}-\overset{\backslash/}{\underset{/|}{\text{Cr}}}$$
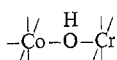
intermediate more likely to be strongly bonded than

$$\overset{\backslash}{\underset{/}{\text{P}}}-\text{O}-\overset{|/}{\underset{|\backslash}{\text{Cr}}}$$
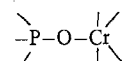
for instance.

It must be noted that if Co–OH_2 is assumed the attacking ligand, $k_f = 0.8$ which compares with $k_f = 2$ for $HOCrO_3^-$ of nearly identical acidity. The acid-independent term thus fits previous patterns regardless of choice of protonated form of the

$$-\overset{|/}{\underset{/|}{\text{Co}}}-\overset{/}{\underset{\backslash}{\text{O}}}$$

ligand. The inverse acid term must, on the other hand, involve a different mechanism than either of the two paths previously recognized.

Registry No. $Co(NH_3)_5H_2O^{3+}$, 14403-82-8; $HCrO_4^-$, 15596-54-0.

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Diamond Cell Study of Pressure-Induced Coordination Changes for Nickel(II) in Liquid Chloride Solvents

Sir:

We wish to report some impressively simple effects of pressure on a 4 ⇌ 6 coordination number equilibrium involving the transition metal ion Ni(II) and chloride ion ligands in a molten salt medium. The equilibrium has been investigated using a diamond anvil optical cell[1] operating under hydrostatic pressure conditions, in combination with a novel method of determining the pressure acting on the sample. Since the method is internal and allows the pressure on the sample to be defined to ±0.2 kbar at pressures up to 10 kbars, we believe we may be reporting the first really quantitative application of the diamond cell to a physicochemical problem.

The above equilibrium, which has been observed and studied in many dilute solutions of Ni(II) in molten chloride media at 1 atm pressure,[2-9] has been interpreted in terms of differences in site stabilization energies calculated from ligand field theory.[2,3] We have been concerned that the influence of the solvent, in particular the packing of the chloride ions under the influence of solvent ion forces, may not have been adequately taken into account in considering the position of the equilibrium in individual cases. This concern has motivated the present study of the effect of pressure on the state of equilibrium at constant temperature.

To simplify the experimental problem we have sought systems in which the equilibrium could be studied near room temperature, rather than at the higher temperatures common to previous, constant-pressure, studies. We achieved this by use of salts with large (weak field) organic cations for the chloride solvents. These salts also readily supercool and pass into the glassy state, a property which is vital to our pressure calibration method.

We have studied the spectrum of Ni(II) (present in ~2 mol % concentrations) in two different such solvents. Both solvents are binary solutions in order to minimize the danger of solvent crystallization during the experiment. These solutions were (A) α-picolinium (α-$CH_3C_5H_4NH^+$) chloride (59.9 mol %) + ethanolaminium ($OHCH_2CH_2NH_3^+$) chloride (40.1 mol %), chosen because the O ⇌ T coordination equilibrium can be shifted by change of temperature alone, and (B) α-picolinium chloride (60.5 mol %) + ethylaminium ($CH_3CH_2NH_3^+$) chloride (39.5 mol %), chosen for contrast with solvent A. Scale models (Courtold's) of the organic cations show these cations do not depart excessively from spherical symmetry; furthermore, their sizes are intermediate between those of chloride ion and the ($NiCl_4$) coordination group.

Contamination with potential ligand H_2O molecules is a problem since α-picolinium chloride is very hygroscopic. Our carefully sublimed preparation melted at 88–90° (well above the Beilstein-quoted value of 80°), and we performed all manipulations in a low dew point drybox. Our solutions nevertheless proved to contain up to 0.25 wt % (1.5 mol %) of H_2O according to Karl Fischer analysis of the stock solutions subsequent to all experiments.

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