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Kinetics of the Anation of Aquopentaamminechromium(III) by Hypophosphite

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The kinetics of the anation of $[CrH_2O(NH_3)_5]^{3+}$ *by* $H_3PO_2/H_2PO_2^-$ *in aqueous solution have been studied at 40, 50 and 60 °C* ($I = 1.0$, $LiClO_4$)*. From the analysis of the kinetic data the constants for outer sphere association of* $[CrH_2O(NH_3)_5]^{3+}$ *with* H_3PO_2 *and* $H_2PO_2^-$ *are obtained* ($10\ K_1 = 1.3 \pm 0.6\ M^{-1}$ *and* $10\ K_2 = 3.3 \pm 1.2\ M^{-1}$ *respectively). The interchange constants for both outer-sphere complexes are identical:* $10^4\ k_i(s^{-1}) = 1.39 \pm 0.50$, 3.44 ± 0.95 *and* 15.1 ± 2.9 *at 40, 50 and 60 °C respectively* ($\Delta H^{\ddagger} = 28.7 \pm 5.2$ *Kcal* mol^{-1}, $\Delta S^{\ddagger} = 14.8 \pm 4.6$ *cal* $K^{-1}\ mol^{-1}$)*. The values of* $k_i(s^{-1})$*, or* k_iK_1 *and* k_iK_2 ($M^{-1}\ s^{-1}$) *at a given temperature fall within the not too large span of other rate constants for anations of* $[CrH_2O(NH_3)_5]^{3+}$ *with different anions, consistent with the previous assignment of a* I_d–I_a *borderline mechanism.*

Introduction

A number of kinetic studies have appeared involving hypophosphite as a reducing agent [1]. Hypophosphite has also been examined as a ligand: Espenson and colleagues have reported the kinetics of formation of hypophosphito complexes from $[M(H_2O)_6]^{3+}$ (M = Cr, Fe) [2, 3]. Furthermore we have prepared and characterized two different salts of the cation $[CrH_2PO_2(NH_3)_5]^{2+}$ [4].

We report in this paper a study of the kinetics of formation of the above cation from the corresponding aquocomplex:

$$[CrH_2O(NH_3)_5]^{3+} + H_3PO_2/H_2PO_2^- \rightarrow [CrH_2PO_2(NH_3)_5]^{2+} + H_3O^+/H_2O \qquad (1)$$

in order to provide more data on the reactivity and mechanism of $[CrH_2O(NH_3)_5]^{3+}$.

Experimental

Materials

Aquopentaamminechromium(III) perchlorate [5] was prepared from $[(NH_3)_5Cr(OH)Cr(NH_3)_5]Cl_5$ [6] and characterized by chromium analysis and quantitative visible spectra [7]. $[CrH_2O(NH_3)_5](ClO_4)_3$ prepared in this fashion could be stored in the dark much longer than that prepared from $[CrH_2O(NH_3)_5](NO_3)_3$, probably due to the presence of nitrate impurities in the perchlorate salt [8]. A solution of LiH_2PO_2 (*ca.* 1.8 *M*) was prepared by slowly neutralizing a stirred solution of *ca.* 4.8 *M* H_3PO_2 (prepared by diluting 50% UCB H_3PO_2) kept in an ice-water bath, with an equivalent amount of *ca.* 3.7 *M* LiOH solution (prepared from Carlo Erba $LiOH \cdot H_2O$). The solutions were standardized gravimetrically (see below) and by acid–base titration. The final concentration of LiH_2PO_2 was checked both by oxidizing an aliquot with hot concentrated perchloric acid and determining the resulting phosphate as quinolinium phosphomolybdate [9], and by determining hypophosphite and phosphite iodometrically [10]. The content in phosphite and phosphate did not exceed 2%. $[CrH_2PO_2(NH_3)_5](ClO_4)_2 \cdot 3H_2O$ was prepared from aquopentaamminechromium(III) perchlorate and characterized by Cr, NH_3 and $H_2PO_2^-$ determinations, and quantitative visible spectra [4]. A stock solution of $LiClO_4$ was prepared and standardized as before [7]. $LiNO_3$ was prepared from lithium carbonate and nitric acid and standardized analogously to $LiClO_4$.

Determination of Acidity Constants of Hypophosphorous Acid

The acidity constants of H_3PO_2 could not be determined by conventional potentiometric titration with NaOH at 25, 40 and 50 °C, due to oxidation or decomposition of the acid, probably by the high local concentration of NaOH. The constants were determined by measuring the pH (on a Radiometer PHM 64 Research pH meter) of solutions of different concentrations of H_3PO_2 at $I = 1.0$ and comparing with calibration curves of $[H^+](HNO_3)$ *versus* pH in the same medium and at the same temperature. A perchlorate medium gave erratic measurements in agreement with Espenson [3], and the determinations were carried out in a $LiNO_3$ medium. The results are given in Table I.

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TABLE I. Acidity Constants (K_a) of Hypophosphorous Acid at Different Temperatures (I = 1.0, $LiNO_3$).

Temp. (°C)	25.0	40.0	50.0	60.0
K_a (*M*)	0.142	0.0827	0.0801	0.0688[a]

[a]Value determined by extrapolation.

Kinetic Runs

The kinetic runs were carried out in the thermostatted (±0.1 °C) compartment of a Beckman DU.2 spectrophotometer at 520 nm. The ionic strength was adjusted to 1.0 with $LiClO_4$. The concentration of hypophosphite was in great excess with regard to that of the aquocomplex (0.015 *M*). First order rate constants, k_{obs}, were obtained from the slopes of plots of $-\ln(A_\infty - A_t)$ *versus* time which were linear to at least 70% completion. The value of A_∞ was determined from the spectrum of a sample of $[CrH_2PO_2(NH_3)_5](ClO_4)_2$. The equilibrium values of $[H^+]$, $[H_2PO_2^-]$ and $[H_3PO_2]$ were calculated from added $HClO_4$, H_3PO_2, LiH_2PO_2 and the acidity constants of H_3PO_2 at the three temperatures. Slopes, intercepts of straight lines and their errors were obtained by linear least-squares fits on a HP65 programmable calculator. Errors quoted are standard deviations.

Results

Successive scans on a Beckman UV 5230 spectrophotometer ($[H^+] = 0.01$ *M*, $[H_2PO_2^-]_T = 0.8$ *M*, 60 °C) gave an excellent retention of isosbestic points at 367, 417 and 474 nm (isosbestic points calculated from known spectra of aquo and hypophosphito complexes 364, 416 and 472 nm). Thus, the only reaction occurring is (1). The plots of k_{obs} (y) against $[H_2PO_2^-]_T$ (x) at each $[H^+]$ are given in Figure 1 and Table II. To decide whether these plots were curved (y = a/(b + cx)) or straight lines (y = d + ex), a residual variance analysis using Gauss–Seidel's method [11] was carried out. Results showed a better fit for y = a/(b + cx) indicating outer-sphere complexation. The following mechanism was found to be consistent with the rate data:

$$[CrH_2O(NH_3)_5]^{3+} +$$

$$\begin{tikzcd}
H_3PO_2 \arrow[r, shift left, "K_1"] \arrow[dd, shift left, "K_a"] & OSC_1 \arrow[l, shift left] \arrow[dr, "k_1"] & \\
 & & {[CrH_2PO_2(NH_3)_5]^{2+} +} \\
H_2PO_2^- \arrow[r, shift left, "K_2"] \arrow[uu, shift left] & OSC_2 \arrow[l, shift left] \arrow[ur, "k_2"'] &
\end{tikzcd}$$

$$+ H_3O^+/H_2O \qquad (2)$$

where $OSC_1 = \{[CrH_2O(NH_3)_5]^{3+}, H_3PO_2\}$ and $OSC_2 = \{[CrH_2O(NH_3)_5]^{3+}, H_2PO_2^-\}$,

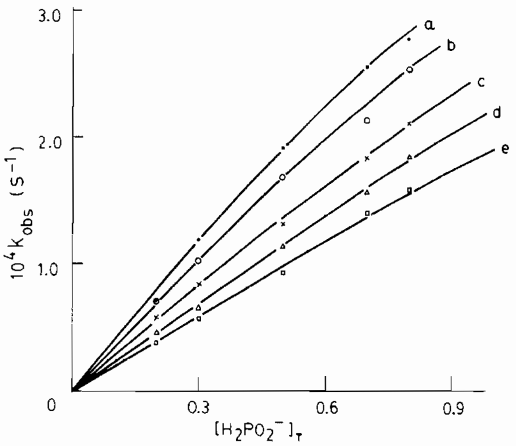

Fig. 1. Plots of k_{obs} against total hypophosphite, $[H_2PO_2^-]_T$, for the reaction of $[CrH_2O(NH_3)_5]^{3+} + H_3PO_2/H_2PO_2^-$ at 60 °C. $[H^+] = 0.01$ *M* (●, a), 0.05 *M* (○, b), 0.1 *M* (×, c), 0.2 *M* (△, d), 0.4 *M* (□, e).

TABLE II. First Order Rate Constant, k_{obs}^a, for Anation of $[CrH_2O(NH_3)_5]^{3+}$ by $H_3PO_2/H_2PO_2^-$, I = 1.0 ($LiClO_4$).

$[H^+]$, *M*	$[H_2PO_2^-]_T$, *M*	$10^5 k_{obs}$, s^{-1}		
		40.0 °C	50.0 °C	60.0 °C
0.010	0.20	0.68	2.17	7.11
	0.30	0.99	3.09	11.9
	0.50	1.55	4.70	19.1
	0.70	2.26	6.26	25.5
	0.80	2.45	7.49	27.8
0.050	0.20	0.58	2.08	7.03
	0.30	0.80	3.17	10.3
	0.50	1.31	4.61	16.9
	0.70	1.78	6.79	21.4
	0.80	2.09	7.17	25.4
0.10	0.20	0.52	1.71	5.82
	0.30	0.82	2.67	8.49
	0.50	1.35	4.25	13.3
	0.70	1.83	5.25	18.4
	0.80	2.06	6.50	21.1
0.20	0.20	0.50	1.51	4.53
	0.30	0.77	2.30	6.52
	0.50	1.23	3.93	11.3
	0.70	1.67	5.05	15.7
	0.80	2.00	6.14	18.4
0.40	0.20	0.47	1.33	3.81
	0.30	0.62	2.17	5.78
	0.50	1.12	3.06	9.35
	0.70	1.52	4.75	14.0
	0.80	1.73	6.03	15.8

[a]Standard deviations were in the range 1.2–1.9%.

giving for k_{obs}

$$k_{obs} = [H_2PO_2^-]_T \frac{k_1K_1[H^+] + k_2K_2K_a}{[H^+] + K_a + [H_2PO_2^-]_T(K_1[H^+] + K_2K_a)} \tag{3}$$

The reaction scheme (2) is the same as that applied to the anation reaction of $[CrH_2O(NH_3)_5]^{3+}$ by $H_3PO_4/H_2PO_4^-$ [7]. This is not surprising given the similarity of both phosphorous oxoanions. Equation (3) may be rearranged to:

$$\frac{1}{k_{obs}} = \frac{[H^+] + K_a}{A} \frac{1}{[H_2PO_2^-]_T} + \frac{B}{A} \tag{4}$$

with

$$A = k_1K_1[H^+] + k_2K_2K_a \tag{5}$$

$$B = K_1[H^+] + K_2K_a \tag{6}$$

By plotting $1/k_{obs}$ *versus* $1/[H_2PO_2^-]_T$ at each acidity, straight lines are obtained (Fig. 2) and from the slope and intercept A and B may be determined. The intercepts of eqn. (4) are found not to be dependent on the acidity (Fig. 2), indicating that $k_1 = k_2$ (hereafter k_i) and $A/B = k_1 = k_2$. K_1 and K_2 are determined by plotting A against $[H^+]$ (Fig. 3). The values of K_1, K_2 and k_i at the three temperatures and the activation parameters are given in Table III.

Discussion

The values of k_1 and k_2 are equal within the experimental error indicating that once the outer-sphere complexes have been formed, both have the same probability that an interchange event leads to the inner-sphere complex; the systems $[CrH_2O(NH_3)_5]^{3+} + H_2PO_4^-/H_3PO_4$ [7] and $[CrH_2O(NH_3)_5]^{3+} + ox^{2-}/Hox^-$ [12] have been shown to behave similarly. The equilibrium constants for formation of the 3+, 1− and 3+, 0 outer-sphere complexes are somewhat smaller than those found for other systems with the same charges. Apparently hypophosphite binds less tightly to aquopentaamminechromium(III) than other anions. This is in agreement with a kinetic study of the reaction $[Cr(H_2O)_6]^{3+} + H_2PO_2^-$ [2] where no evidence for ion-pair formation could be found (*i.e.* the values of K were too small to be detected kinetically).

The question of whether the mechanism of substitution reactions of $[CrH_2O(NH_3)_5]^{3+}$ is I_a or I_d remains unsettled. The following three criteria have been helpful in assigning an I_d (as opposed to I_a) mechanism to the substitution reactions of $[CoH_2O(NH_3)_5]^{3+}$: a) k_i does not change appreciably on changing the nature of the entering ligand (or if k_i is not known, k should not change on changing

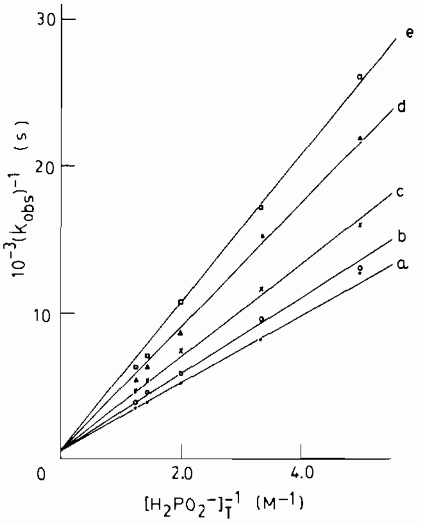

Fig. 2. Plots of $1/k_{obs}$ against $1/[H_2PO_2^-]_T$ for the reaction of $[CrH_2O(NH_3)_5]^{3+} + H_3PO_2/H_2PO_2^-$ at 60 °C; I = 1.0 ($LiClO_4$). $[H^+]$ = 0.01 *M* (●, a), 0.05 *M* (○, b), 0.1 *M* (X, c), 0.2 *M* (△, d), 0.4 *M* (□, e).

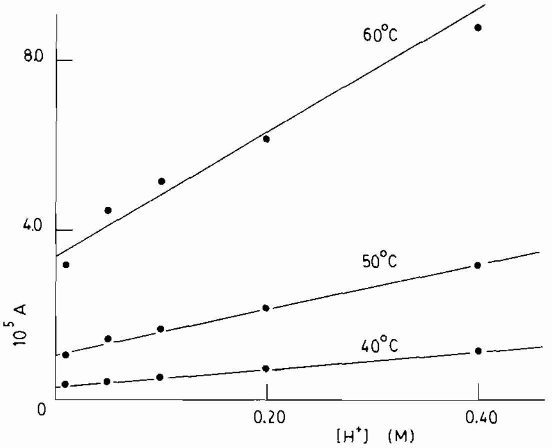

Fig. 3. Plots of A as defined in eqn. (5) against $[H^+]$ for the reaction of $[CrH_2O(NH_3)_5]^{3+} + H_3PO_2/H_2PO_2^-$; I = 1.0 ($LiClO_4$).

TABLE III. Summary of Kinetic Data for the Anation of $[CrH_2O(NH_3)_5]^{3+}$ by $H_3PO_2/H_2PO_2^-$ in Aqueous Solution (I = 1.0, $LiClO_4$).

Temp. (°C)	10^4 k_i^a (s^{-1})	10 K_1 (M^{-1})	10 K_2 (M^{-1})
40.0	1.39 ± 0.50	1.50 ± 0.58	2.51 ± 1.00
50.0	3.44 ± 0.95	1.54 ± 0.51	4.04 ± 1.34
60.0	15.1 ± 2.9	0.90 ± 0.72	3.29 ± 1.36

$\Delta H^{\ddagger}$ = 28.7 ± 5.2 kcal mol^{-1}
10 $\bar{K}_1^b$ = 1.3 ± 0.6 M^{-1}
$\Delta S^{\ddagger}$ = 1.48 ± 4.6 cal K^{-1} mol^{-1}
10 $\bar{K}_2^b$ = 3.3 ± 1.2 M^{-1}

[a] $k_i = k_1 = k_2$. [b] $\bar{K}_1$ and $\bar{K}_2$ are the mean values of K_1 and K_2 at the three temperatures.

TABLE IV. Summary of Rate Constants for Anations of $[CrH_2O(NH_3)_5]^{3+}$ (50 °C, I = 1.0 $LiClO_4$).

Anion	10^4 k_i (s^{-1})	10^4 k^a (M^{-1} s^{-1})	Reference
NCS^-	–	4.16	[17]
Cl^-	–	0.69	[17]
H_3PO_4	1.45	0.46	[7]
$H_2PO_4^-$	1.45	2.59	[7]
$HC_2O_4^-$	6.2	6.45	[12]
$C_2O_4^{2-}$	6.2	29.1	[12]
$NH_3CH_2COO^-$	14.2	7.82	[18]
H_3PO_2	3.44	0.45	This work
$H_2PO_2^-$	3.44	1.14	This work
H_2O	13.7	–	[19]

$^a k = k_i K_{OS}$; K_{OS} is the equilibrium constant for formation of the outer-sphere complex.

the nature of the entering ligand for ligands of the same charge); thus, the span of k_i (or k) values is only about half an order of magnitude for substitution reaction of $[CoH_2O(NH_3)_5]^{3+}$ [13]. b) k_i is never greater than k for solvent (water) exchange [14]; this argument is not conclusive since an associatively activated mechanism may have k_i values greater or smaller than k for solvent exchange; however the fact that no ligand has been found for which k_i is greater than k_{H_2O} is in favour of a dissociative mechanism. c) $\Delta V^{\ddagger}$ for solvent (water) exchange (the easiest $\Delta V^{\ddagger}$ to interpret [15]) is a positive value for $[CoH_2O(NH_3)_5]^{3+}$ [16]. Applying these criteria to substitution reactions of $[CrH_2O(NH_3)_5]^{3+}$ we have: a) Values of k_i (or k) span a little more than an order of magnitude (Table IV). b) For all the systems investigated (except for $[CrH_2O(NH_3)_5]^{3+}$ + $^+NH_3CH_2COO^-$) k_i is always smaller than the rate constant for water exchange of $[CrH_2O(NH_3)_5]^{3+}$ (Table IV). c) $\Delta V^{\ddagger}$ for water exchange of the last-named cation is a negative value [20]. Point c) favours an I_a mechanism but in point a) the span is not large enough to warrant an I_a mechanism (for substitution reaction at $[Cr(H_2O)_6]^{3+}$ where an I_a mechanism seems to be well established, the corresponding span is about three orders of magnitude [21]). Point b) would favour an I_d mechanism since *only one* ligand has been found for which k_i is greater than k_{H_2O}. In view of all this we may say that the chromiumpentaammine systems involve less dissociative character than their Co(III) analogues in their substitution reactions, and the mechanism is probably borderline between I_d and I_a.

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