Synthesis, Characterization, and Kinetics of Formation of $[Cr(H_2PO_4)(H_2O)_5]^{2+}$†

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The complex $[Cr(H_2PO_4)(H_2O)_5]^{2+}$ has been prepared from the reaction between $[Co(PO_4)(NH_3)_4]$ and $[Cr(H_2O)_6]^{2+}$, and characterized. Its kinetics of formation from $[Cr(H_2O)_6]^{3+}$ and $H_2PO_4^-$–H_3PO_4 has been studied in aqueous solution at 50, 60, and 70 °C in the range $[H^+] = 0.04$—0.12 mol dm^{-3}, $I = 1.0$ mol dm^{-3} ($LiClO_4$). Only $H_2PO_4^-$ has been found to be reactive. The rate data were consistent with an I_a mechanism. Values for the interchange rate constant (10^4k_i) are 0.323, 1.87, and 7.71 s^{-1} at 50, 60, and 70 °C, respectively (mean value for outer-sphere complexation constant, $K = 1.82$ dm^3 mol^{-1}). A comparison is made with data for similar systems.

Although some reports have appeared on the complex formation between chromium(III) and phosphate,[1–4] the synthesis and full characterization of the 1:1 complex $[Cr(H_2PO_4)(H_2O)_5]^{2+}$ have not been described. We now report the synthesis, separation, and characterization of the 1:1 complex between $[Cr(H_2O)_6]^{3+}$ and phosphate (hereafter referred to as the phosphato complex) which we formulate in acidic media (see below) as $[Cr(H_2PO_4)(H_2O)_5]^{2+}$.

Experimental

Preparation of the Phosphato Complex.—This was prepared by the reaction between $[Co(PO_4)(NH_3)_4]$ and $[Cr(H_2O)_6]^{2+}$ in aqeuous solution. In a typical preparation, a 0.0822 mol dm^{-3} solution (15 cm^3) of $[Co(PO_4)(NH_3)_4]\cdot 3H_2O$ which was 0.81 mol dm^{-3} in $HClO_4$ (the amount necessary to protonate both the PO_4 ligand and the ammonia released, and to leave a slight excess of H^+) was degassed and mixed under anaerobic conditions with 0.274 mol dm^{-3} $Cr(ClO_4)_2$ (5 cm^3, 0.145 mol dm^{-3} in $HClO_4$). (These quantities correspond to a 10% molar excess of Cr^{II} over Co^{III}.) The resulting solution immediately turned green due to reaction (1). After a few minutes the flask was opened to the air and shaken vigorously. A 10 cm^3 portion of this solution was diluted to 100 cm^3 with water and loaded onto a column (length 5 cm, internal diameter 1 cm) of cation exchanger (Dowex 50W × 4, 100—200 mesh) in the H^+ form. The column was washed with water until neutral and then eluted with a solution 0.3 mol dm^{-3} in $LiClO_4$ and 0.01 mol dm^{-3} in $HClO_4$. Three bands separated: a dark green one at the top which barely moved at all and presumably contained the dimer $[(H_2O)_4Cr(OH)_2Cr(H_2O)_4]^{4+}$ (generated by the reaction of the excess of Cr^{II} and atmospheric oxygen[5]); an orange band in the middle; and a bright green band at the bottom. The last band moved faster and a concentrated fraction was collected. Determination of chromium and phosphate gave a molar ratio $Cr:PO_4$ of 0.97:1; furthermore, the behaviour on the cation exchanger indicates a 2+ charge for the complex, thus identifying this green fraction as the desired complex $[Cr(H_2PO_4)(H_2O)_5]^{2+}$ (see also Results and Discussion). The orange band (containing the Co^{2+}) was collected and analysed for Co. A 93% recovery was found with respect to the total cobalt loaded onto the column.

$$[Cr(H_2O)_6]^{2+} + [Co(PO_4)(NH_3)_4] + 6H^+ + 5H_2O \longrightarrow [Cr(H_2PO_4)(H_2O)_5]^{2+} + [Co(H_2O)_6]^{2+} + 4NH_4^+ \quad (1)$$

Other Materials.—A 0.866 mol dm^{-3} solution of $Cr(ClO_4)_3$ in 0.454 mol dm^{-3} $HClO_4$ was prepared by reaction of a 1.2 mol dm^{-3} solution of CrO_3 (1 dm^3) in 4.5 mol dm^{-3} $HClO_4$ with 30% H_2O_2 (350 cm^3). The excess of hydrogen peroxide was eliminated with platinum black.[6] The spectrum in 0.1 mol dm^{-3} $HClO_4$, $\lambda_{max.}$ 573 nm (13.1), 407 (15.3), and $\lambda_{min.}$ 479 ($\varepsilon = 3.2$ dm^3 mol^{-1} cm^{-1}) was in agreement with the literature.[7] A stock solution of 0.274 mol dm^{-3} $[Cr(H_2O)_6]^{2+}$ in 0.145 mol dm^{-3} $HClO_4$ was prepared by reaction of the above $[Cr(H_2O)_6]^{3+}$ solution, diluted ten-fold, with amalgamated zinc.[8] The complex $[Co(PO_4)(NH_3)_4]$ was prepared by a modification of the von Siebert method.[9] Stock solutions of LiH_2PO_4 and H_3PO_4 were prepared as previously described.[10]

Other Techniques.—All operations involving Cr^{II} were carried out under oxygen-free nitrogen using serum caps and syringe techniques. Total chromium was determined spectrophotometrically at 372 nm after oxidation of the samples with $NaOH + H_2O_2$.[11] Phosphates were determined gravimetrically as quinolinium molybdophosphate[12] $[C_9H_8N]_3[PMo_{12}O_{40}]$, after removing the Cr^{III} by oxidation to $[Cr_2O_7]^{2-}$ with hot 60% perchloric acid. Chromium(II) was determined spectrophotometrically at 715 nm ($\varepsilon = 4.82$ dm^3 mol^{-1} cm^{-1}). The column loading and elution process was speeded up by using a nitrogen cylinder; the column was provided with a jacket through which ice-cold water always circulated. Visible spectra were recorded on a Beckman UV 5230 spectrophotometer.

Kinetics.—The progress of the reaction was followed on a Beckman DU.2 spectrophotometer, equipped with a thermospacer (50, 60, 70 °C, ±0.1 °C), at 625 nm where the maximum difference exists between the absorption coefficients of the hexa-aqua and phosphato complexes. The ionic strength was adjusted to unity with $LiClO_4$. The total phosphate concentration was always in great excess with regard to that of chromium which was the same in all runs, 2.53×10^{-2} mol dm^{-3}, thus ensuring pseudo-first-order conditions. In the acidity range used, $[H^+] = 0.04$—0.12 mol dm^{-3}, the only species present in appreciable amounts are $[Cr(H_2O)_6]^{3+}$, H_3PO_4, and $H_2PO_4^-$. The lower end of the acidity range was set at 0.04 mol dm^{-3} since at lower acidities (0.020 mol dm^{-3}) a more complex behaviour was observed (see below). Equilibrium values of $[H_3PO_4]$, $[H_2PO_4^-]$, and $[H^+]$ in each run were determined from the amounts of the stock solutions of LiH_2PO_4, and $HClO_4$ added and using the previously determined values of the first acidity constant of H_3PO_4 at the same temperatures and ionic strength.[13]

The stability of $[Cr(H_2O)_6]^{3+}$ under the kinetic conditions was tested by observing its spectrum after 2.3 h at 70 °C {$[H^+]$

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† *Non-S.I. unit employed:* cal = 4.184 J.

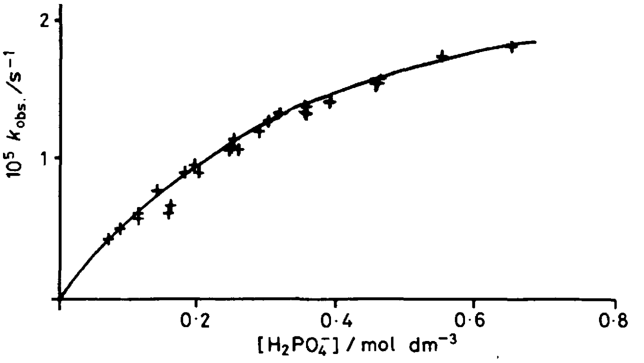

Figure 1. Variation of $k_{obs.}$ with $[H_2PO_4^-]$ at 50 °C for the reaction of $[Cr(H_2O)_6]^{3+}$ with phosphate, I = 1.0 mol dm^{-3} ($LiClO_4$)

= 0.040 mol dm^{-3}; I = 1.0 mol dm^{-3} ($LiClO_4$)}. Successive scans of a 3.46 × 10^{-2} mol dm^{-3} solution of $[Cr(H_2O)_6]^{3+}$, 0.1 mol dm^{-3} in $HClO_4$, and 0.88 mol dm^{-3} in total phosphate gave a retention of isosbestic points at 564, 501, and 408 nm during the first 70% of reaction, in excellent agreement with those determined (566, 500, and 408 nm) from the known spectra of the hexa-aqua and phosphato complexes.

Values of $k_{obs.}$ were obtained from the slopes of plots of $-\ln(A_\infty - A)$ where (A = absorbance) against time, and using only A *vs.* t data corresponding to the first 60% completion of reaction wherein the isosbestic points and linearity were retained. The value of A_∞ was calculated from the known spectrum of $[Cr(H_2PO_4)(H_2O)_5]^{2+}$.

Results and Discussion

We assign the formulation $[Cr(H_2PO_4)(H_2O)_5]^{2+}$ to the phosphato complex on the basis of the following: (1) chemical analyses (see Experimental section); (2) other reactions of the same type, $[CoX(NH_3)_5]^{z+}$ + Cr^{II}, afford $[CrX(H_2O)_5]^{z+}$ complexes and some have been used in a preparative way;[14] (3) that the residue $Cr(H_2O)_5^{3+}$ will enhance the acidity of the protons bound to the phosphate ligand to a similar degree as[15] $Cr(NH_3)_5^{3+}$ or[16] $Co(NH_3)_5^{3+}$; furthermore, the column elution behaviour also supports a 2+ charge for the complex;[17] (4) we believe that the phosphate group in the complex acts as a unidentate group due to the reluctance of PO_4 (which behaves similarly to SO_4[18]) to act as a bidentate ligand for Cr^{III}. The spectrum of the phosphato complex in 0.1 mol dm^{-3} $HClO_4$ ($\lambda_{max.}$ 593, ε = 16.6; 418 nm, ε = 17.1 dm^3 mol^{-1} cm^{-1}) is similar to that suggested previously.[16]

The plots of $-\ln(A_\infty - A)$ *vs.* time are linear (under the conditions noted above), thereby leading to equation (2). Table 1 gives the value of $k_{obs.}$ as a function of $[H^+]$, phosphate concentration, and temperature. The values of $k_{obs.}$ for virtually the same $[H_2PO_4^-]$ but different $[H_3PO_4]$ are approximately the same, indicating that H_3PO_4 is non-reactive or much less so than $H_2PO_4^-$. Plots of $k_{obs.}$ against $[H_2PO_4^-]$ at each temperature are curved (Figure 1) indicating ion-pair formation. A reaction scheme compatible with these observations is shown in (3) and the associated rate equation is (4), which is in accord with the plots in Figure 1. Equation (4) can be rearranged to (5) and from plots of $1/k_{obs.}$ against $1/[H_2PO_4^-]$ which are linear (Figure 2) the values of k_i and K can be obtained. These are given along with the corresponding activation parameters in Table 2.

$$-d[Cr(H_2O)_6]^{3+}/dt = k_{obs.}[Cr(H_2O)_6{}^{3+}] \tag{2}$$

$$H_2PO_4^- + [Cr(H_2O)_6]^{3+} \overset{K}{\rightleftharpoons} \{H_2PO_4^-, [Cr(H_2O)_6]^{3+}\} \xrightarrow{k_i} [Cr(H_2PO_4)(H_2O)_5]^{2+} + H_2O \tag{3}$$

$$k_{obs.} = \frac{k_i K[H_2PO_4^-]}{1 + K[H_2PO_4^-]} \tag{4}$$

$$\frac{1}{k_{obs.}} = \frac{1}{k_i K}\cdot\frac{1}{[H_2PO_4^-]} + \frac{1}{k_i} \tag{5}$$

The more complicated behaviour observed at $[H^+]$ = 0.020 mol dm^{-3} (50 °C) was originally ascribed to the co-existence of the mechanism (6) at this acidity. Mechanism (6) together with (3) gives the overall reaction scheme (7). {A mechanism involving $[Cr(OH)(H_2O)_5]^{2+}$ and H_3PO_4 is possible, but has not been considered due to its kinetic indistinguishability from (3)}. The corresponding rate equation is (8) with $A = k_1K_1[H^+] + k_2K_2K_a$ and $B = K_1[H^+] + K_2K_a$. Equation (8) can be rearranged to (9), and from plots of $1/k_{obs.}$ *versus* $1/[H_2PO_4^-]$ the values of A and B can be determined at each acidity. From the slopes of plots of A and B *versus* $[H^+]$ the values of k_1 and K_1 can be determined. These (3.18 × 10^{-5} s^{-1} and 1.97 dm^3 mol^{-1} respectively) are in very good agreement with those determined assuming scheme (3). The same plots give a zero intercept within experimental error, which means that $(k_2)K_2 = 0$. This condition simplifies equation (9) to (10) which is virtually the same as (5) since $(1 + k_a/[H^+]) \approx 1$, and, of

$$[Cr(OH)(H_2O)_5]^{2+} + H_2PO_4^- \longrightarrow \{[Cr(OH)(H_2O)_5]^{2+},H_2PO_4^-\} \longrightarrow [Cr(H_2PO_4)(H_2O)_5]^{2+} + OH^- \tag{6}$$

$$\begin{tikzcd}
{[Cr(H_2O)_6]^{3+}} \arrow[dd, leftrightarrow, "K_a"'] & & \text{Ion pair 1} \arrow[dr, "k_1"] & \\
& + H_2PO_4^- \arrow[ur, leftrightarrow, "K_1"] \arrow[dr, leftrightarrow, "K_2"'] & & {[Cr(H_2PO_4)(H_2O)_5]^{2+} + H_2O/OH^-} \\
{[Cr(OH)(H_2O)_5]^{2+}} & & \text{Ion pair 2} \arrow[ur, "k_2"'] &
\end{tikzcd} \tag{7}$$

$$k_{obs.} = [H_2PO_4^-]\cdot\frac{A}{[H_2PO_4^-]B + [H^+] + K_a} \tag{8}$$

$$\frac{1}{k_{obs.}} = \frac{B}{A} + \frac{[H^+] + K_a}{A}\cdot\frac{1}{[H_2PO_4^-]} \tag{9}$$

$$\frac{1}{k_{obs.}} = \frac{1}{k_1} + \frac{1}{k_1K_1}\left(1 + \frac{K_a}{[H^+]}\right)\frac{1}{[H_2PO_4^-]} \tag{10}$$

Table 1. Values of the observed first-order rate constants, $k_{obs.}$, for the anation of $[Cr(H_2O)_6]^{3+}$ (2.53×10^{-2} mol dm^{-3}) by phosphate, I = 1.0 mol dm^{-3} ($LiClO_4$)

Temp. (°C)	$[H^+]$	$[H_3PO_4]$ mol dm^{-3}	$[H_2PO_4^-]$	$10^5k_{obs.}$ s^{-1}
50	0.020	0.283	0.222	1.28
		0.440	0.343	1.69
		0.596	0.465	2.14
		0.752	0.587	2.44
		0.909	0.708	2.66
		1.06	0.830	2.75
	0.045	0.469	0.163	0.66
		0.750	0.260	1.06
		1.03	0.358	1.31
		1.31	0.455	1.56
		1.59	0.553	1.73
		1.87	0.650	1.81
	0.070	0.517	0.115	0.56
		0.826	0.184	0.89
		1.13	0.254	1.14
		1.44	0.322	1.32
		1.75	0.391	1.41
		2.06	0.460	1.54
	0.095	0.543	0.089	0.49
		0.867	0.143	0.77
		1.19	0.196	0.95
		1.51	0.249	1.08
		1.84	0.303	1.26
		2.17	0.356	1.36
50	0.120	0.559	0.073	0.41
		0.894	0.116	0.60
		1.22	0.160	0.72
		1.56	0.203	0.90
		1.90	0.247	1.06
		2.23	0.291	1.19
60	0.045	1.63	0.512	7.72
		1.78	0.558	8.34
		1.92	0.603	8.66
		2.07	0.650	8.96
	0.070	1.34	0.422	7.10
		2.33	0.470	7.40
	0.095	1.05	0.331	5.95
		2.59	0.385	6.57
	0.120	2.41	0.248	5.37
70	0.045	1.76	0.505	3.87
		1.93	0.556	4.15
		2.11	0.606	4.37
		2.29	0.657	4.45
	0.070	2.19	0.404	3.40
		2.46	0.455	3.60
	0.095	2.23	0.303	2.92
		2.60	0.354	3.25
	0.120	2.34	0.253	2.65

Table 2. Summary of kinetic data for the anation of $[Cr(H_2O)_6]^{3+}$ by $H_2PO_4^-$, I = 1.0 mol dm^{-3} ($LiClO_4$)

Temp. (°C)	k_i/s^{-1}	K/dm^3 mol^{-1}
50.0	3.23×10^{-5}	2.02
60.0	1.87×10^{-4}	1.41
70.0	7.71×10^{-4}	2.03

$\Delta H^{\ddagger}$ = 33.5 kcal mol^{-1}, $\Delta S^{\ddagger}$ = 26.3 cal K^{-1} mol^{-1}

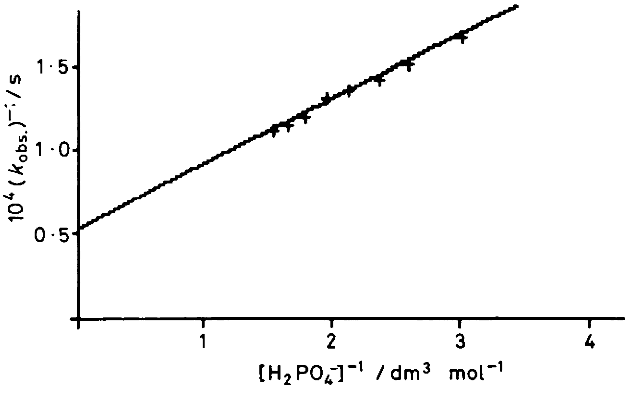

Figure 2. Plots of $1/k_{obs.}$ *vs.* $1/[H_2PO_4^-]$ at 60 °C for the reaction of $[Cr(H_2O)_6]^{3+}$ with phosphate, I = 1.0 mol dm^{-3} ($LiClO_4$)

course, it does not explain the behaviour at $[H^+]$ = 0.020 mol dm^{-3}. Accordingly the acidity range was reduced to 0.120—0.045 mol dm^{-3} and only $[Cr(H_2O)_6]^{3+}$ and $H_2PO_4^-$ were considered reactive. The more complicated behaviour at $[H^+]$ = 0.020 mol dm^{-3} is considered to be related to some mechanism more complicated than just the possibility of anation of the hydroxo species.

Table 3 gives values of second- (k) and first-order (k_i) rate constants for the anation of hexa-aquachromium(III) by dif-

Table 3. Summary of rate constants for anations of $[Cr(H_2O)_6]^{3+}$ by different entering ligands at 25 °C, I = 1.0 mol dm^{-3} ($LiClO_4$)

Ligand	10^8k_{an}/dm^3 mol^{-1} s^{-1}	k_i/s^{-1}	K_{IP}/dm^3 mol^{-1}	Ref.
SO_4^{2-}	1 100			18
Phthalate(2−)	51 400	7.31×10^{-5}	7.03	*a*
Cl^-	2.9			*b*
Br^-	0.9			*c*
I^-	0.08			*d*
F^-	2 000			*e*
NCS^-	180			*f*
SCN^-	0.4			*g*
NO_3^-	73			*h*
HSO_4^-	13			*i*
CH_3CO_2	103 000	9.87×10^{-5}	10.42	*j*
Salicylate	291 000	3.96×10^{-4}	7.35	*k*
Phthalate(1−)	18 400	7.00×10^{-5}	2.63	*a*
$H_2PO_4^-$	66.7	3.66×10^{-7}	1.82	*l*
HF	56			*m*
H_3PO_2	2 820			*n*
$H_2C_2O_4$	156			*o*
Glycine		3.26×10^{-5}		*p*
H_2O		25×10^{-7}		*q*
$HgCl^+$	0.13			*r*

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ferent anions, at 25 °C. The span of k (including the value found in this work) for uninegative anions (approximately seven orders of magnitude) clearly supports the already well known associative character of the substitution reactions of $[Cr(H_2O)_6]^{3+}$. The span of the few values known for k_i (three orders of magnitude) and also the fact that some of the values are larger than the rate constant for water exchange points to an I_a mechanism for the anation reactions. The span of values k or k_i for the anation reactions of $[Cr(H_2O)_6]^{3+}$ is much larger than that for the anation reactions of[19] $[Cr(NH_3)_5(H_2O)]^{3+}$, the last system having a more dissociative (or less associative) character. This fact is logical considering the effective radii of NH_3 and H_2O (1.69 and 1.38 respectively[20]); the ammonia molecules are larger and exert a greater steric crowding, favouring a dissociative mechanism.

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