

- (8) A. E. Dwight, to be submitted for publication in *J. Less-Common Met.*
 (9) A. F. Wells, "Structural Inorganic Chemistry", Clarendon Press, Oxford, England, 1975.
 (10) C. E. Lundin, F. E. Lynch, and C. B. Magee, *J. Less-Common Met.*, **56**, 19 (1977).
 (11) E. S. Machlin, private communication.

- (12) A. C. Switendick, Report No. SAND 78-0250, Sandia Laboratories, April 1978.
 (13) D. M. Gruen, M. H. Mendelsohn, and I. Sheft, *Sol. Energy*, **21**, 153 (1978).
 (14) F. A. Kuijpers and H. H. van Mal, *J. Less-Common Met.*, **23**, 395 (1971).

Contribution from the Department of Inorganic and Structural Chemistry, The University, Leeds LS2 9JT, England

Kinetics and Mechanism of the Reaction of Phosphate (H_3PO_4 and H_2PO_4^-) with Aquopentaamminechromium(III)

MIGUEL FERRER and A. GEOFFREY SYKES*

Received May 8, 1979

The reaction of phosphate with $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ (pH 1–2) yields the phosphato complex $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{PO}_4^{2+}$ which is stable to further reaction (including NH_3 loss) at the temperatures 40–60 °C investigated. From the kinetics ($I = 1.00 \text{ M}$ (LiClO_4)) evidence was obtained for outer-sphere association of H_3PO_4 ($K_1 = 0.32 \text{ M}^{-1}$) and H_2PO_4^- ($K_2 = 1.8 \text{ M}^{-1}$) with $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$, where K_1 and K_2 show little or no dependence on temperature. Rate constants for interchange leading to formation of the phosphato complex are as far as could be ascertained identical ($k_1 = k_2$), with $k(50 \text{ °C}) = 1.45 \times 10^{-4} \text{ s}^{-1}$, $\Delta H^\ddagger = 25.0 \text{ kcal mol}^{-1}$, and $\Delta S^\ddagger = 1.1 \text{ cal K}^{-1} \text{ mol}^{-1}$. Comparisons are made with other studies involving $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ as well as $\text{Cr}(\text{H}_2\text{O})_6^{3+}$. Reactivity patterns for $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ are intermediate between those for $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ on the one hand (I_a assignment) and $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ and other 2+ aquo ions on the other (I_d). The previously determined volume of activation for H_2O exchange on $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ has been interpreted in terms of an I_a assignment. This is consistent with reactivity patterns only if it is accepted that plots of $\log k_{\text{aq}}$ against $\log (K_{15}K_{\text{OS}})$ yield slopes of 1.0 for an I_d mechanism and <1.0 for an I_a mechanism.

Whereas substitution reactions of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ are believed to proceed by an associative interchange (I_a) mechanism,¹ reactions of $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ (replacement of H_2O) and Cr^{III} -amine complexes remain controversial with no firm consensus.^{2–6} It is now recognized that nonparticipating ligands are relevant in determining the course of a substitution process, and this is particularly well illustrated in the case of cobalt(III) by the assignment of a D mechanism for reactions of $\text{Co}(\text{CN})_5\text{H}_2\text{O}^{2-}$ ⁷ and I_d for $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ ⁸ and with a suggestion of associative character (I_a) for the reactions of $\text{Co}(\text{H}_2\text{O})_6^{3+}$ ⁹

We here report a study of the reaction of phosphate with $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$, which provides further information and helps clarify some aspects of the substitution behavior of this complex.

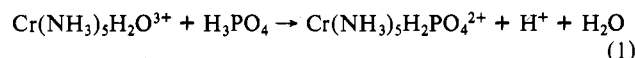
Experimental Section

Reactants. The nitrate salt of aquopentaamminechromium(III), $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}](\text{NO}_3)_3 \cdot \text{NH}_4\text{NO}_3$, was first prepared.¹⁰ For the conversion to the perchlorate salt 10 g of the latter was dissolved in 120 mL of water and 72% perchloric acid (60 mL) added.¹¹ The complex was recrystallized once by using the same procedure. Spectra in 0.10 M HClO_4 were in agreement with literature values λ_{max} 481 nm (ϵ 35.3 $\text{M}^{-1} \text{ cm}^{-1}$) and λ_{max} 361 nm (ϵ 30.5 $\text{M}^{-1} \text{ cm}^{-1}$).^{12,13} A sample of the dihydrogen phosphato complex $[\text{Cr}(\text{NH}_3)_5(\text{H}_2\text{PO}_4)](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ was prepared by the procedure in ref 14. The spectrum in 0.10 M HClO_4 gave λ_{max} 502 nm (ϵ 48.4 $\text{M}^{-1} \text{ cm}^{-1}$) and λ_{max} 370 nm (ϵ 29.3 $\text{M}^{-1} \text{ cm}^{-1}$) in agreement with published values.¹⁴ Solutions of phosphoric acid were prepared from AnalaR (sp gr 1.75, Hopkin and Williams) reagent. These were standardized by titration with NaOH to the methyl orange end point. Solutions of lithium dihydrogen phosphate were prepared by mixing equivalent volumes of H_3PO_4 and LiOH (BDH, laboratory reagent). Lithium perchlorate was prepared from Li_2CO_3 (BDH, laboratory reagent) and 72% HClO_4 (BDH, AnalaR) and was recrystallized three times. Solutions were standardized by passing down an Amberlite IR 120(H) resin column and titrating the liberated H^+ with NaOH.

Determination of Acid Dissociation Constant of H_3PO_4 . Solutions of 0.10 M H_3PO_4 , $I = 1.00 \text{ M}$ (LiClO_4), were titrated potentiometrically (pH meter Radiometer PHM 4d) with 1.0 M NaOH at three

different temperatures. Acid dissociation K_a values obtained were $10^2 K_a$ (M) = 2.05 ± 0.06 (25 °C), 1.72 ± 0.09 (40 °C), and 1.56 ± 0.06 (50 °C). From a graph of $\log K_a$ against reciprocal temperature (K) an extrapolated value $10^2 K_a = 1.41 \pm 0.07 \text{ M}$ (60 °C) was obtained. Values obtained were in good agreement with the literature.¹⁵

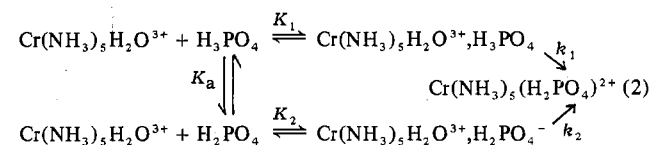
Kinetic Runs. Anation reactions (carried out in thermostated spectrophotometric cells) were monitored by conventional spectrophotometry at λ 520 nm (Unicam SP500) (Figure 1). Scan UV-visible spectra (Unicam SP8000) gave retention of isosbestic points at 368, 420, and 470 nm for a run at 60 °C ($[\text{H}^+] = 0.10 \text{ M}$, $I = 1.00 \text{ M}$ (LiClO_4)), over a 10-h period. Solutions of $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ and $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{PO}_4^{2+}$ in 0.10 M HClO_4 retained constant spectra for at least 8 h at 60 °C. There is thus no evidence for ammonia loss from the phosphato complex. On addition of an excess of H_3PO_4 to $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ and heating of the mixture (60 °C), an orange to red color change was observed and the spectrum of $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{PO}_4^{2+}$ was obtained. The reaction can be summarized therefore by (1).



First-order rate constants, k_{obsd} , were obtained from slopes ($\times 2.303$) of plots of absorbance changes $\log (A_\infty - A_t)$ against time (t), with total phosphate, $[\text{PO}_4]_{\text{T}}$, in at least 10-fold excess of $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}]$. The latter was generally ca. 0.014 M, repeat runs with the concentration decreased 4 \times giving identical k_{obsd} values. Values of the final absorbance, A_∞ , were calculated from the known spectrum of $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{PO}_4^{2+}$. Plots were linear to at least 85% completion. Variation of $[\text{H}^+]$ was achieved by mixing calculated amounts of LiH_2PO_4 , H_3PO_4 , and HClO_4 . The ionic strength was adjusted to 1.00 M (LiClO_4) in all cases.

Results

First-order constants, k_{obsd} (Table I), gave a nonlinear dependence on total phosphate, $[\text{PO}_4]_{\text{T}}$, at each $[\text{H}^+]$ (Figure 2). A reaction scheme (2), which gives (3), is consistent with



$$k_{\text{obsd}} = \frac{K_1 k_1 [\text{H}^+][\text{PO}_4]_{\text{T}} + K_2 k_2 K_a [\text{PO}_4]_{\text{T}}}{[\text{H}^+] + K_a + K_1 [\text{H}^+][\text{PO}_4]_{\text{T}} + K_2 K_a [\text{PO}_4]_{\text{T}}} \quad (3)$$

data obtained. Equation 3 can be written as (4) where A and

$$\frac{1}{k_{\text{obsd}}} = \frac{[\text{H}^+] + K_a}{A} \left(\frac{1}{[\text{PO}_4]_{\text{T}}} \right) + \frac{B}{A} \quad (4)$$

B are as defined in (5) and (6). By inspection A and B will

$$A = K_1 k_1 [\text{H}^+] + K_2 k_2 K_a \quad (5)$$

$$B = K_1 [\text{H}^+] + K_2 K_a \quad (6)$$

be constant at constant $[\text{H}^+]$, so that (4) can be tested for by plotting $1/k_{\text{obsd}}$ against $[\text{PO}_4]_{\text{T}}^{-1}$ at each $[\text{H}^+]$ (Figure 3). Since the intercept (B/A) is as far as can be determined invariant with $[\text{H}^+]$, we conclude that $k_1 = k_2$ (Table II). Values of A from the slopes in Figure 3 have been graphed against $[\text{H}^+]$ (Figure 4) and yield outer-sphere complexing constants K_1 and K_2 (Table II). From the temperature variation of K_1 and K_2 it is concluded that the enthalpy terms ΔH_1 and ΔH_2 are around zero. To determine the corresponding entropy terms, we used average values of K_1 ($0.32 \pm 0.11 \text{ M}^{-1}$) and K_2 ($1.8 \pm 0.5 \text{ M}^{-1}$). The activation parameters ΔH^\ddagger ($25.0 \pm 0.4 \text{ kcal mol}^{-1}$) and ΔS^\ddagger ($1.1 \pm 1.1 \text{ cal K}^{-1} \text{ mol}^{-1}$) were obtained by a least-squares fit.

Discussion

The common intercept observed in Figure 3 carries the implication that k_1 and k_2 for the formation of $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{PO}_4^{2+}$ from outer-sphere complexes involving H_3PO_4 and H_2PO_4^- are as far as can be ascertained identical. Any differences in rate constants are relatively small and cannot be distinguished by the procedure employed. The same applies for the corresponding reactions of $\text{C}_2\text{O}_4\text{H}^-$ and $\text{C}_2\text{O}_4^{2-}$,¹⁶ where it has been concluded that within experimental error the rate constants for interchange are identical. These observations are consistent with an I_d or I_a process, since it is reasonable that $\text{O}=\text{P}(\text{OH})_3$ and $\text{O}=\text{P}(\text{OH})_2\text{O}^-$ should present the same "face" to the complex and therefore react at about the same rate once they are within the outer-coordination sphere. Activation parameters for the interchange with H_3PO_4 and H_2PO_4^- (Table II) are similar to those for $\text{C}_2\text{O}_4\text{H}^-$ and $\text{C}_2\text{O}_4^{2-}$ ($\Delta H^\ddagger = 26.4 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = 8.6 \text{ cal K}^{-1} \text{ mol}^{-1}$).

Anation rate constants k_{an} (Table III; k_1 and k_2 in this paper) are now known for a number of reactions in which it has been possible to determine K_{OS} (K_1 and K_2 in this paper).^{3,16,17} For the admittedly limited range of reactants the spread in k_{an} (and also $k_{\text{r}} = k_{\text{an}}K_{\text{OS}}$) is now close to an order of magnitude. This is in excess of the spread of ca. $5\times$ in k_{an} for reactions of Ni^{2+} and Co^{2+} with a wide range of nucleophiles, which is regarded as acceptable for an I_d assignment.¹⁸ Therefore these observations do not now provide as strong support for an I_d assignment for the reactions of $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ as previously indicated.³ It appears that H_2O dissociation from $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ in an interchange process involving an outer-sphere complex is not the only rate-controlling feature but that there is a dependence also on the nature and identity of the incoming ligand (i.e., some associative character). At the same time it must be reiterated that $k_{\text{NCS}}/k_{\text{Cl}}$ (ratio of k_{r} values) is 6 for $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ whereas for $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ it is 60.³ The dependence of the interchange process on incoming nucleophile is not therefore as great for $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ as for $\text{Cr}(\text{H}_2\text{O})_6^{3+}$.

One of the prime difficulties in assessing fully the behavior of $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ is the restriction of studies to a limited number of incoming nucleophiles due to the incidence of subsequent reactions involving rapid loss of coordinated NH_3 .¹⁹ Previously we have indicated that a linear free energy plot of

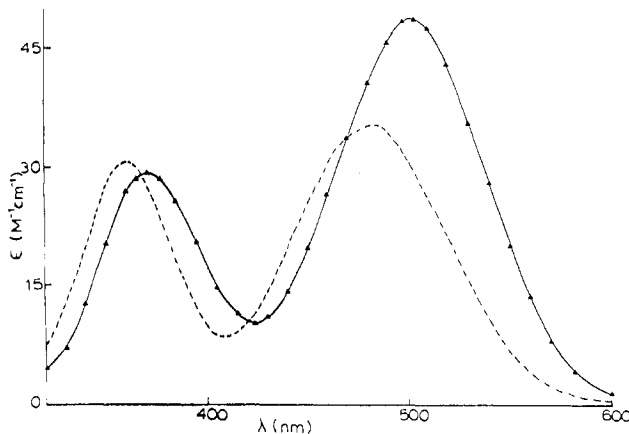


Figure 1. UV-visible spectra of $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ (---) and $\text{Cr}(\text{NH}_3)_5(\text{H}_2\text{PO}_4)^{2+}$ (\blacktriangle) in aqueous solution; $[\text{H}^+] = 0.10 \text{ M}$; $I = 1.00 \text{ M}$ (LiClO_4).

Table I. First-Order Rate Constants, k_{obsd} , for the Anation of $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ (0.014 M) with Phosphate^a

[H ⁺], M	[PO ₄] _T , M	10 ⁵ k _{obsd} , s ⁻¹		
		40.0 °C	50.0 °C	60.0 °C
0.010	0.143		2.15	
	0.20	0.77	2.90	10.8
	0.30	1.11	3.85	14.9
	0.50	1.56	5.8	19.4
	0.70		6.8	23.4
0.025	0.80	1.99	7.4	24.0
	0.143		1.65	
	0.20	0.57	2.14	7.0
	0.30	0.78	3.06	9.9
	0.50	1.09	4.5	14.1
0.050	0.70		6.0	19.4
	0.80	1.54	6.2	20.2
	0.143		1.19	4.0
	0.20	0.43	1.65	5.3
	0.30	0.67	2.22	7.8
0.075	0.50	0.93	3.32	11.9
	0.70		4.4	15.2
	0.80	1.26	4.7	15.8
	0.20	0.42	1.38	4.4
	0.30	0.61	1.89	6.0
0.100	0.50	0.86	2.96	9.1
	0.70		3.9	12.4
	0.80	1.31	4.2	13.1
	0.143			2.56
	0.20	0.38	1.19	3.61
	0.30	0.53	1.72	5.1
	0.40			6.9
	0.50	0.90	2.54	7.9
	0.60		2.99	
	0.70		3.22	10.0
	0.80	1.18		

^a Total phosphate, $[\text{PO}_4]_{\text{T}}$, in >10 -fold excess; $I = 1.00 \text{ M}$ (LiClO_4).

Table II. Summary of Outer-Sphere Formation Constants for H_2PO_4^- (K_1) and H_2PO_4^- (K_2) with $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ ^a

temp, °C	10 ⁵ k ₁ (=k ₂), s ⁻¹	K ₁ , M ⁻¹	K ₂ , M ⁻¹
40.0	3.9 ± 0.5	0.24 ± 0.09	2.0 ± 0.3
50.0	14.0 ± 2.0	0.48 ± 0.12	1.2 ± 0.5
60.0	46.0 ± 8.0	0.25 ± 0.13	2.2 ± 0.6
	$\Delta H^\ddagger = 25.0 \pm 0.4^b$	$\Delta H_1 \approx 0^b$	$\Delta H_2 \approx 0^b$
	$\Delta S^\ddagger = 1.1 \pm 1.1^c$	$\Delta S_1 = -2.3^c$	$\Delta S_2 = +1.2^c$

^a Prior to outer- and inner-sphere interchange process k_1 (=k₂) is as defined in eq 2; $I = 1.00 \text{ M}$ (LiClO_4). ^b kcal mol⁻¹. ^c cal K⁻¹ mol⁻¹.

log k_{aq} against log ($K_{15}K_{\text{OS}}$) for five X⁻ ligands gives a slope of 0.91 ± 0.05 .³ Since then, the value of $K_{15}K_{\text{OS}}$ (the overall

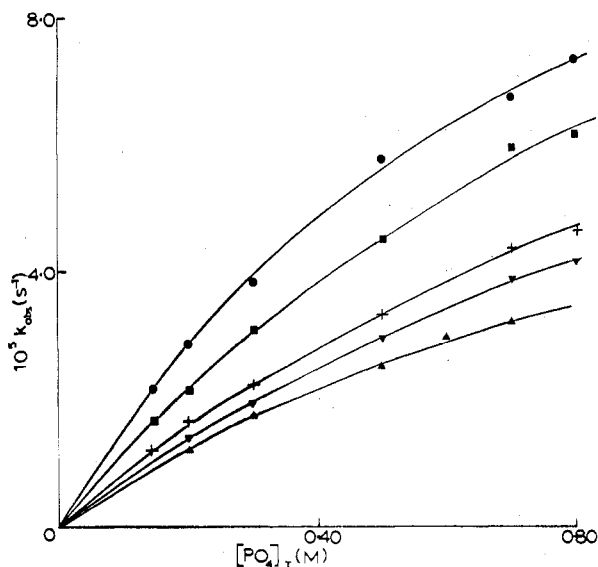


Figure 2. Variation of first-order rate constants, k_{obs} , for the reaction of $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ with total phosphate, $[\text{PO}_4]_{\text{T}}$, at 50 °C; $I = 1.00 \text{ M}$ (LiClO_4); $[\text{H}^+] = 0.010 \text{ M}$ (●), 0.025 M (■), 0.050 M (+), 0.075 M (▼), 0.10 M (▲).

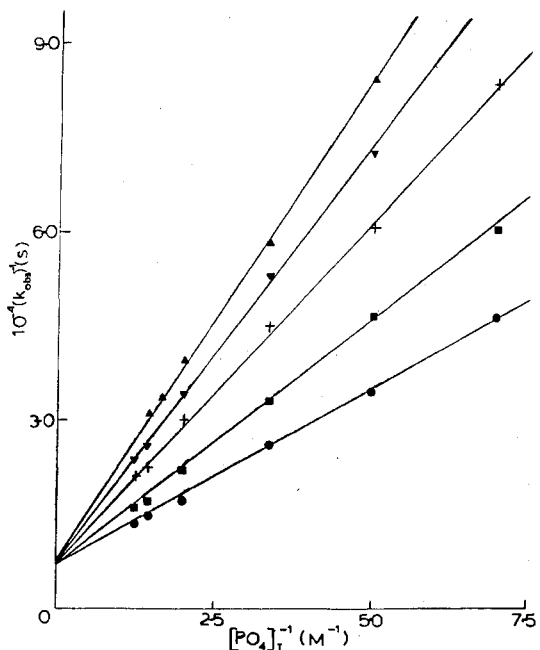


Figure 3. Dependence of first-order rate constants, k_{obs} , for the reaction of $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ on total phosphate concentration, $[\text{PO}_4]_{\text{T}}$, at 50 °C; $I = 1.00 \text{ M}$ (LiClO_4); $[\text{H}^+] = 0.01 \text{ M}$ (●), 0.025 M (■), 0.05 M (+), 0.075 M (▼), 0.10 M (▲).

equilibrium constant for formation of $\text{Cr}(\text{NH}_3)_5\text{X}^{2+}$ has been challenged for $\text{X}^- = \text{Br}^-$ and a new value 0.019 M^{-1} reported.²⁰ We have redetermined this quantity and find a value of $0.34 \pm 0.03 \text{ M}^{-1}$ in agreement with the earlier determination (0.30 M^{-1}), from formation and aquation rate constants.³ On present evidence (without opting for one or other of these determinations²¹) it can be concluded that the slope in Figure 5 is in the range 0.7–0.9. We do not think at this stage that it is profitable (or valid) to mark the point for H_2O exchange on this correlation,²⁰ which is exclusively for 1– reactants. A similar plot for $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ yields a slope of 0.56.²²

Instances in which associative characteristics of substitution on $\text{Cr}(\text{NH}_3)_5\text{X}^{2+}$ appear to be emphasized are the reactions in which NH_3 loss is observed.¹⁹ Interestingly no NH_3 loss is observed from the complex $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{PO}_4^{2+}$, and it has

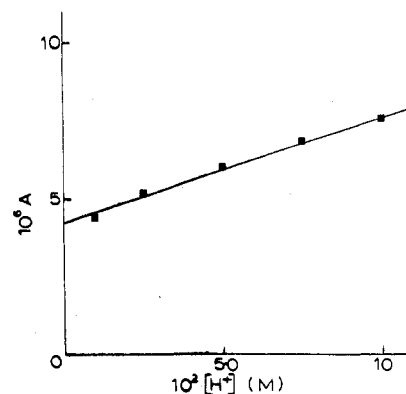


Figure 4. Dependence of the constant A , defined in eq 5, on $[\text{H}^+]$, for the reaction of $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ with phosphate at 50 °C; $I = 1.00 \text{ M}$ (LiClO_4).

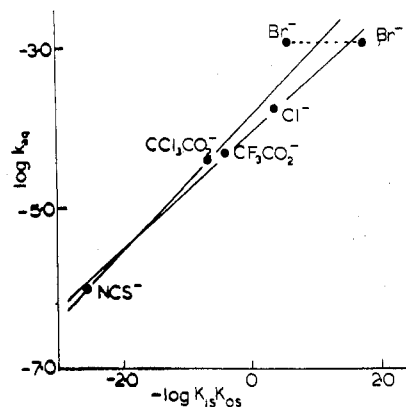


Figure 5. Linear free energy plot of $\log k_{\text{aq}}$ against $-\log (K_{1s}K_{\text{OS}})$ for acidopentaamminechromium(III) complexes at 50 °C; $I = 1.00 \text{ M}$ (LiClO_4).

Table III. Comparison of Anation Rate Constants, Outer-Sphere Association Constants (from Kinetics), and Formation Rate Constants ($k_{\text{f}} = k_{\text{an}}K_{\text{OS}}$) for Reactions of $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ ^a

	$10^4 k_{\text{an}},^b$ s^{-1}	$K_{\text{OS}},^c$ M^{-1}	$10^4 k_{\text{f}},$ $\text{M}^{-1} \text{s}^{-1}$	ref
H_3PO_4	1.45	0.32	0.46	this work
H_2PO_4^-	1.45	1.79	2.59	this work
NCS^-		<i>d</i>	4.16	3
Cl^-			0.69	3
HC_2O_4^-	6.2 ^e	1.16	6.45	16
$\text{C}_2\text{O}_4^{2-}$	6.2 ^e	4.5	29.1	16
$\text{NH}_3^+\text{CH}_2\text{CO}_2^-$	14.2	0.55	7.82	17
H_2O	13.7			22

^a At 50 °C; $I = 1.00 \text{ M}$ (LiClO_4). ^b k_1 and k_2 in this paper. ^c K_1 and K_2 in this paper. ^d K_{OS} is smaller than the value (0.68 M^{-1}) previously reported in ref 3 [R. van Eldik (personal communication) and T. Ramasami (unpublished work)]. ^e Rate constants k_{an} for the reactions of HC_2O_4^- (5.86 s^{-1}) and $\text{C}_2\text{O}_4^{2-}$ (6.46 s^{-1}) are equal within experimental error.

likewise been concluded that with other large anionic ligands such as SeO_3^{2-} and IO_3^- no clear-cut NH_3 -labilizing effect is observed.⁸ With smaller oxyanions such as NO_2^- ,²³ NO_3^- ,²⁴ SO_4^{2-} ,¹⁹ SO_3^{2-} ,¹⁹ and CO_3^{2-} ,²⁵ as well as carboxylate ligands,^{17,26} NH_3 loss is apparent and is believed to occur with transient chelation of the oxy groups.

On the above evidence it would appear that $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ remains an other than clear-cut case for either an I_d or I_a assignment. Volumes of activation (ΔV^\ddagger) are also believed to be a reliable criterion for mechanism, at least for solvent-exchange reactions.¹ Thus if bond breaking is the step which sets the exchange process in motion, then an expansion must occur in going to the transition state and ΔV^\ddagger is positive. If

bond making is the critical step, then there is a collapse of the encounter complex and ΔV^\ddagger will be negative. The actual magnitude of ΔV^\ddagger is often more difficult to interpret. For $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ ΔV^\ddagger is $+1.2 \text{ cm}^3 \text{ mol}^{-1}$, consistent with an I_d assignment,²⁷ whereas for $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ it is $-9.3 \text{ cm}^3 \text{ mol}^{-1}$, consistent with an I_a process.²⁸ For the complex $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ a value of $-5.8 \text{ cm}^3 \text{ mol}^{-1}$ is observed, which is also believed to be diagnostic of an I_a mechanism.²⁹ The magnitude of the latter as compared to the other two values has been discussed by Swaddle and Stranks.²⁹

To summarize, one can accept implicitly that the sign of the volume of activation for solvent exchange is indeed diagnostic of mechanism. It then has to be accepted that for an I_d process a plot of $\log k_{\text{aq}}$ against $\log (K_{15}K_{\text{OS}})$ must yield a slope of 1.0 and that slopes <1.0 are indicative of some associative contribution and are therefore I_a . For an I_a assignment Swaddle¹ has indicated that slopes can vary over a wide range (from 0 to 1.0) and that for any one complex with a sufficiently wide range of nucleophiles such a plot should be curved. Thus the different slopes for $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ and $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ could be explained in terms of different regions of such curves being effective. The weakness in this approach is that as yet there are no known cases of substitution at a metal ion in which curvature has in fact been observed, and it is indeed surprising that for $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, where a fairly wide range of nucleophiles have been tested, no such feature is apparent. The alternative (and at this stage possibly less acceptable) approach is to say that the sign of ΔV^\ddagger for solvent exchange on $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ is itself somewhat misleading and/or does not necessarily apply to anation reactions, in which case the reactivity pattern displayed by $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ might best be described as intermediate between the I_a and I_d extremes. This would be consistent with our previous stance³ that " $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ exhibits more dissociative character than $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ in the substitution of H_2O ". Such discussion unfortunately reduces to semantics and how one defines an I_a process. Is it to be when there is some associative contribution or when the associated character is dominant?

Finally values of K_{OS} (Table III) for outer-sphere association with $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ merit some comment. High anion concentrations, and therefore ionic strengths, are necessary in these studies and thus have the effect of decreasing K_{OS} . Values previously reported for hexaaquo ions are as follows: for Cr^{3+} with NCS^- , $K_{\text{OS}} \approx 1.0 \text{ M}^{-1}$ ($I = 0.6 \text{ M}$);³⁰ for Cr^{3+} with Cl^- , $K_{\text{OS}} = 1.5 \text{ M}^{-1}$ ($I = 1.0 \text{ M}$);³¹ for Fe^{3+} with Br^- , $K_{\text{OS}} = 0.3 \text{ M}^{-1}$ ($I = 1.0 \text{ M}$);³² for Fe^{3+} with Cl^- , $K_{\text{OS}} \approx 1.5 \text{ M}^{-1}$ ($I = 0.6 \text{ M}$).³³ The K_{OS} values in Table III are closely similar for 1-oxyanions, somewhat greater for 2- ions, and less for zero-charged species. In other words an acceptable pattern emerges with (in the light of the K_{OS} for H_2PO_4^-) the zwitterion $\text{NH}_3^+\text{CH}_2\text{CO}_2^-$ exhibiting behavior intermediate between 1- ions and zero-charged species. All the partners in Table III

for which K_{OS} has been evaluated are oxy species capable of H bonding to ligands on the $\text{Cr}(\text{III})$ complex. For anions, e.g., Cl^- and Br^- , K_{OS} values are smaller, and these could not be evaluated from the kinetics studies.³

Acknowledgment. This paper has benefited from discussions and correspondence with Professor T. W. Swaddle, whose comments we gratefully acknowledge. M.F. (from the University of Barcelona) is also grateful to the British Council for a scholarship.

Registry No. $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$, 15975-47-0; H_3PO_4 , 7664-38-2; H_2PO_4^- , 14066-20-7; $\text{Cr}(\text{NH}_3)_5(\text{H}_2\text{PO}_4)^{2+}$, 71500-50-0.

References and Notes

- (1) T. W. Swaddle, *Coord. Chem. Rev.*, **14**, 217 (1974).
- (2) N. V. Duffy and J. E. Earley, *J. Am. Chem. Soc.*, **89**, 272 (1967).
- (3) T. Ramasami and A. G. Sykes, *Inorg. Chem.*, **15**, 2885 (1976).
- (4) D. A. Palmer and H. Kelm, *Inorg. Chem.*, **16**, 3139 (1977).
- (5) B. S. Dawson and D. A. House, *Inorg. Chem.*, **16**, 1354 (1977).
- (6) L. Randolph and R. G. Linck, *Inorg. Chem.*, **16**, 2653 (1977).
- (7) A. Haim and W. K. Wilmarth, *Inorg. Chem.*, **1**, 573 (1962).
- (8) A. Haim, *Inorg. Chem.*, **9**, 426 (1970); C. H. Langford, *ibid.*, **4**, 265 (1964).
- (9) E.g.: Y. Sasaki and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1048 (1975), and references therein.
- (10) E. Kyuno, M. Kamada, and N. Tanaka, *Bull. Chem. Soc. Jpn.*, **40**, 1848 (1967).
- (11) R. Davies, G. B. Evans, and R. B. Jordan, *Inorg. Chem.*, **8**, 2025 (1969).
- (12) L. Mønsted and O. Mønsted, *Acta Chem. Scand., Ser. A*, **28**, 569 (1974).
- (13) N. A. Shatti, T. Ramasami, and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 74 (1977).
- (14) M. Ferrer, J. Casabo, and J. Coronas, *Inorg. Chim. Acta*, **16**, 47 (1976).
- (15) W. Schmidt and H. Taube, *Inorg. Chem.*, **2**, 698 (1963); *Chem. Soc., Spec. Publ.*, No. 17 (1964); No. 25 (1971).
- (16) O. Nor and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1232 (1973).
- (17) T. Ramasami, R. S. Taylor, and A. G. Sykes, *Inorg. Chem.*, **15**, 2318 (1976).
- (18) E.g.: F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2nd ed., Wiley, New York, 1967, p 156; R. G. Wilkins, *Acc. Chem. Res.*, **3**, 408 (1970).
- (19) T. Ramasami, R. K. Wharton, and A. G. Sykes, *Inorg. Chem.*, **14**, 359 (1975).
- (20) L. Mønsted, *Acta Chem. Scand., Ser. A*, **32**, 377 (1978).
- (21) The reporting of such divergent numbers is worrying and illustrates the difficulty in obtaining reliable values for this equilibrium constant. Mention should perhaps be made here of earlier work³ in which a value of $K_{15}K_{\text{OS}}$ for I^- was reported. Although perfectly acceptable in terms of a plot as in Figure 5, this was ignored because of uncertainties inherent in the determination of such a small quantity.
- (22) T. W. Swaddle and G. Guastalla, *Inorg. Chem.*, **7**, 1915 (1968).
- (23) T. C. Matts and P. Moore, *J. Chem. Soc. A*, 219 (1969).
- (24) G. Guastalla and T. W. Swaddle, *Can. J. Chem.*, **52**, 527 (1974).
- (25) J. E. Earley and W. Alexander, *J. Am. Chem. Soc.*, **92**, 2294 (1970).
- (26) E. Zinato, C. Furlani, G. Lanna, and R. Riccieri, *Inorg. Chem.*, **11**, 1746 (1972).
- (27) H. R. Hunt and H. Taube, *J. Am. Chem. Soc.*, **80**, 2642 (1958).
- (28) D. R. Stranks and T. W. Swaddle, *J. Am. Chem. Soc.*, **93**, 2783 (1971).
- (29) T. W. Swaddle and D. R. Stranks, *J. Am. Chem. Soc.*, **94**, 8357 (1972).
- (30) C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1208 (1955).
- (31) R. E. Connick and M. S. Tsao, Abstracts, 123rd National Meeting of the American Chemical Society, Atlantic City, N.J., 1955, No. 4 P.
- (32) D. W. Carlyle and J. H. Espenson, *Inorg. Chem.*, **8**, 575 (1969).
- (33) H. Wendt, quoted in H. Diebler, *Z. Phys. Chem. (Frankfurt am Main)*, **68**, 71 (1969).