Kinetics and Mechanism of Anation Reactions of $[M(NH_3)_5(H_2O)]^{3+}$ by $H_3PO_n/H_2PO_n^-$ Systems (M = Cr^{III}, $n = 3$; M = Co^{III}, $n = 2$)

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The kinetics of anation of $[Cr(NH_3)_5(H_2O)]^{3+}$ with $H_3PO_3/H_2PO_3^-$ and of $[Co(NH_3)_5(H_2O)]^{3+}$ with $H_3PO_2/H_2PO_2^-$ has been studied at different temperatures and at $I = 1.0$ mol dm^{-3} ($LiClO_4$). The results are interpreted in terms of an I_a (near the I_a/I_d border) anation mechanism for the chromium complex and an I_d one for the cobalt complex. Comparison of the anation rate constants with those of other anating systems and the same transition-metal complexes confirms this assignment. A comparison of all the anation reactions $[M(NH_3)_5(H_2O)]^{3+} + H_3PO_n/H_2PO_n^-$ (M = Co^{III} or Cr^{III}; n = 2—4) is made, and two unexpected facts are examined: (*a*) for M = Cr^{III}, first-order rate constants for the neutral (k_1) and anionic (k_2) species of the series $H_3PO_n/H_2PO_n^-$ (n = 2—4) are the same ($k_1 = k_2$); and (*b*) for M = Co^{III}, even though the $H_2PO_n^-$ species are always reactive, the conjugated species, H_3PO_n, are not reactive, except for $n = 2$.

While the substitution reactions of penta-ammine complexes of Co^{III} are fairly well understood, those of the analogous chromium(III) complexes are less straightforward.[1] For cobalt(III) complexes an I_d mechanistic assignment has been made on the basis of thorough studies on aquation reactions of $[Co(NH_3)_5X]^{2+}$. Furthermore, aquation reactions of $[Co(RNH_2)_5X]^{2+}$ (R = alkyl)[2] have also been studied and acceleration effects due to the increase in steric hindrance of the alkyl groups are in agreement with the previous I_d assignment. The same sort of studies on aquation reactions of $[Cr(NH_3)_5X]^{2+}$ and $[Cr(RNH_2)_5X]^{2+}$ led to an I_a assignment for the substitution mechanism, although less strongly supported than for the case of the $[Cr(H_2O)_6]^{3+}$ complex;[1,2] moreover, a borderline mechanism has often been proposed. Recently, the different behaviours of aquation reactions of $[M(RNH_2)_5X]^{2+}$ (M = Cr^{III} or Co^{III}) on increasing the size of the alkyl group has also been related to ground-state effects, namely π-basic bonding between the metal centre and the chloro ligand.[3]

On the other hand, anation reactions of the corresponding $[M(NH_3)_5(H_2O)]^{3+}$ (M = Cr^{III} or Co^{III}) complexes have been less studied. It seems clear that the I_a/I_d and I_d assignments are correct, respectively.[4,5] Recent results from this laboratory on anation reactions of $[M(RNH_2)_5(H_2O)]^{3+}$ (M = Cr^{III} or Co^{III}, R = CH_3)[6] agree with this assignment.

Some anation reactions of the type (1) (M = Cr^{III}, n = 2

$$[M(NH_3)_5(H_2O)]^{3+} + H_3PO_n/H_2PO_n^- \longrightarrow [M(NH_3)_5(H_2PO_n)]^{2+} + H_3O^+/H_2O \quad (1)$$

or 4, M = Co^{III}, n = 3 or 4) have previously been studied by some of us.[4–8] We report in this paper a kinetic study of reaction (1) for M = Cr^{III}, $n = 3$, and M = Co^{III}, $n = 2$, in order to complete the study of this type of anation reactions and provide an explanation to two unexpected facts: (*a*) H_3PO_n and $H_2PO_n^-$ species are equally reactive for M = Cr^{III}; and (*b*) with Co^{III} the reactivity of the H_3PO_n species compared with their conjugated bases ($H_2PO_n^-$) is negligible except when $n = 2$.

Experimental

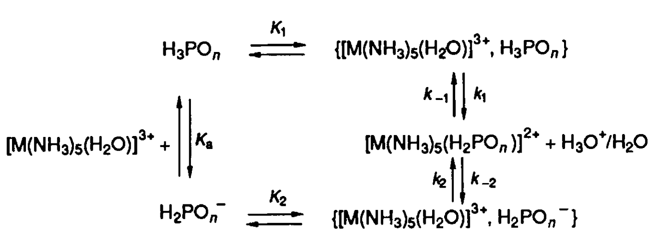
Reagents.—Chromium and cobalt aqua complexes, $[Cr(NH_3)_5(H_2O)][ClO_4]_3$[9] and $[Co(NH_3)_5(H_2O)][ClO_4]_3$,[10] were prepared according to well known procedures. Phosphinato and phosphonato complexes were obtained from a mixture of the aqua complex and the appropriate phosphorus oxoacid.[11–13] All complexes were characterized, and their solutions standardized. by their electronic spectra: $[Cr(NH_3)_5(H_2O)]^{3+}$ ($\lambda_{max.}$ = 358 and 477 nm, ε = 29.6 and 34.2 dm^3 mol^{-1} cm^{-1}), $[Co(NH_3)_5(H_2O)]^{3+}$ ($\lambda_{max.}$ = 345 and 491 nm, ε = 44.3 and 47.2 dm^3 mol^{-1} cm^{-1}), $[Cr(NH_3)_5(H_2PO_3)]^{2+}$ ($\lambda_{max.}$ = 368 and 500 nm, ε = 30.3 and 46.0 dm^3 mol^{-1} cm^{-1}), and $[Cr(NH_3)_5(H_2PO_2)]^{2+}$ ($\lambda_{max.}$ = 354 and 518 nm, ε = 49.5 and 61.7 dm^3 mol^{-1} cm^{-1}).

Solutions of lithium phosphite and lithium hypophosphite were prepared by mixing equivalent volumes of LiOH and H_3PO_3 or H_3PO_2 solutions.[5] Lithium perchlorate was prepared from lithium carbonate and 72% perchloric acid, and recrystallized three times. Solutions were standardized by passing aliquots down an Amberlite IR 120(H) column and titrating the liberated H^+ with NaOH. Phosphorus was also determined as quinolinium phosphomolybdate, after oxidation to P^V.[14]

All chemicals used were reagent-grade commercial materials.

Kinetics.—U.v.–visible spectra were recorded on a UV 5230 Beckman instrument equipped with a thermostatted cell compartment and interfaced to an Apple computer. Reactions were followed spectrophotometrically at 515 nm for the chromium complex and at 518 nm for the cobalt complex. The aqua complexes were checked for decomposition for approximately 8 h at the highest temperature and lowest acidity used without observing significant changes.

All kinetic runs were performed under pseudo-first-order conditions, the total phosphorus concentration being at least 10 times that of the aqua complex. Observed rate constants were obtained from linear and exponential unweighted least-squares methods.[15] When decomposition of the final product was observed, the time-scale was set as to monitor only the initial anation step and infinity absorbance readings were determined by standard unknown-final-reading methods[16] (the number of half-lives taken was always between two and three). In all cases errors in $k_{obs.}$ values were within the range of 3—10% of the actual value, depending on the stability of the final absorbance reading. Solutions for the kinetic runs were prepared by mixing calculated amounts of stock solutions of LiH_2PO_3 (or LiH_2PO_2), $HClO_4$, $[Cr(NH_3)_5(H_2O)][ClO_4]_3$ {or $[Co(NH_3)_5$-



Scheme 1. M = Cr^{III}, $n = 3$; M = Co^{III}, $n = 2$

Table 1. First-order rate constants, $k_{obs.}$, for the anation of $[Cr(NH_3)_5(H_2O)]^{3+}$ (1.4×10^{-2} mol dm^{-3}) by the $H_3PO_3/H_2PO_3^-$ system, $I = 1.0$ mol dm^{-3} ($LiClO_4$)

T/°C	$[H^+]$/mol dm^{-3}	$[P]_T$/mol dm^{-3}	$10^5k_{obs.}$/s^{-1}
40.0	0.01	0.20	0.94
		0.40	1.56
		0.80	2.36
	0.10	0.40	0.87
		0.60	1.11
		0.80	1.47
	0.15	0.40	0.73
		0.60	0.92
		0.70	1.20
50.0	0.01	0.20	3.52
		0.40	5.73
		0.60	7.21
		0.80	8.54
	0.05	0.20	2.41
		0.40	3.95
		0.60	5.46
		0.80	7.13
	0.10	0.20	1.93
		0.40	3.50
		0.48	3.93
		0.60	4.69
		0.70	5.09
	0.15	0.20	1.65
		0.40	2.92
		0.60	3.90
		0.70	4.71
	0.40	0.20	1.26
		0.30	1.90
		0.40	2.41
		0.50	2.63
60.0	0.01	0.20	8.53
		0.40	19.7
		0.60	25.8
		0.80	27.0
	0.05	0.20	6.82
		0.40	15.4
		0.60	20.3
		0.80	22.7
	0.10	0.20	6.63
		0.40	11.1
		0.60	14.2
		0.80	19.1
	0.15	0.20	6.78
		0.40	10.1
		0.60	15.6
		0.70	16.9
	0.40	0.20	3.62
		0.30	5.42
		0.40	6.93
		0.50	8.36

$(H_2O)][ClO_4]_3\}$, and $LiClO_4$ ($I = 1.0$ mol dm^{-3}), in 1-cm optical path spectrophotometric cells. Acidity constants of H_3PO_n ($n = 2$ or 3) have been experimentally determined ($I = 1.0$ mol dm^{-3}, $LiNO_3$),[4,5] at the same temperatures as those used in the kinetic experiments: K_a (H_3PO_3) = 5.21×10^{-2}, 5.50×10^{-2}, and 5.68×10^{-2} mol dm^{-3} at 40, 50, and 60 °C; (H_3PO_2) = 5.85×10^{-2}, 4.72×10^{-2}, and 3.97×10^{-2} mol dm^{-3} at 60, 70, and 80 °C. These values were used to determine the value of $[H^+]$ at these temperatures.

Results

The processes studied in order to complete previous work with penta-ammine complexes of Cr^{III} and Co^{III} and phosphorus oxoanions as incoming ligands[4–8] are shown in Scheme 1. These reactions are the only ones which occur at this pH range and temperatures, as shown by a very good retention of isosbestic points during the reaction time (λ = 476, 418, and 369 nm, M = Cr^{III}, $n = 3$, $[H^+] = 0.10$, $[Cr] = 1.5 \times 10^{-2}$, $[P]_T = 1.0$ mol dm^{-3}, 55 °C; λ = 487, 403, and 350 nm, M = Co^{III}, $n = 2$, $[H^+] = 0.01$, $[Co] = 1.2 \times 10^{-2}$, $[P]_T = 1.0$ mol dm^{-3}, 80 °C). No redox reaction was observed for the system $[Co(NH_3)_5(H_2O)]^{3+} + H_3PO_2/H_2PO_2^-$ under the kinetic conditions used.[9] Nevertheless, low acidities were avoided so as to prevent any secondary reactions, especially at the higher temperatures. The possibility of a substitution reaction at the phosphorus oxoanion centre was ruled out by the much slower reaction of water exchange with these ligands.[17,18]

Tables 1 and 2 give the $k_{obs.}$ values of the reactions studied $\{[M(NH_3)_5(H_2O)]^{3+} + H_2PO_n^-/H_3PO_n$ with M = Cr, $n = 3$, and M = Co, $n = 2\}$ as a function of the total phosphorus concentration, acidity, and temperature. From the values for $[H_2PO_n^-]$ and $[H_3PO_n]$ calculated at the different acidities, using K_a values determined at $I = 1.0$ mol dm^{-3} ($LiClO_4$) for the two acids involved, it is clear that both the anionic and neutral species are reactive, both for the chromium and cobalt complexes. This has already been observed for the chromium complex and phosphate[7] or hypophosphite[4] as incoming ligands. However, these results do not agree with previous anation studies of the cobalt complex with $H_3PO_n/H_2PO_n^-$ (n = 3 or 4), where it had been found that the reactivity was due only to $H_2PO_n^-$.[5]

The rate law derived from the Scheme is as in equation (2)

$$\text{Rate} = k_1[\text{o.s.}_1] + k_2[\text{o.s.}_2] - k_{-1}[\text{MP}][H^+] - k_{-2}[\text{MP}] \quad (2)$$

where o.s.$_1$ and o.s.$_2$ denote the outer-sphere complexes and MP the anated complex. This expression can be converted[19] into (3)

$$\text{Rate} = \frac{(K_1k_1[H^+] + K_2K_ak_2)[P]_T}{[H^+] + K_a + (K_1[H^+] + K_2K_a)[P]_T} \cdot [M(NH_3)_5(H_2O)^{3+}] - (k_{-1}[H^+] + k_{-2})[\text{MP}] \quad (3)$$

with $[P]_T = [H_2PO_n^-] + [H_3PO_n]$. On integration ($[H^+]$ and $[P]_T$ remain effectively constant with time in a given kinetic run), expression (4) or (5) is obtained.

$$k_{obs.} = \frac{K_1k_1[H^+] + K_2K_ak_2}{[H^+] + K_a + (K_1[H^+] + K_2K_a)[P]_T} \cdot [P]_T + k_{-1}[H^+] + k_{-2} \quad (4)$$

or

$$k_{obs.} = \frac{A}{[H^+] + K_a + B[P]_T} \cdot [P]_T + C \quad (5)$$

$$A = K_1k_1[H^+] + K_2K_ak_2 \quad (6)$$

$$B = K_1[H^+] + K_2K_a \quad (7)$$

$$C = k_{-1}[H^+] + k_{-2} \quad (8)$$

Table 2. First-order rate constants, $k_{obs.}$, for the anation of $[Co(NH_3)_5(H_2O)]^{3+}$ (9.4×10^{-3} mol dm^{-3}) by the $H_3PO_2/H_2PO_2^-$ system, I = 1.0 mol dm^{-3} ($LiClO_4$)

T/°C	$[H^+]$/mol dm^{-3}	$[P]_T$/mol dm^{-3}	$10^5k_{obs.}$/s^{-1}
60.0	0.01	0.20	5.30
		0.30	6.00
		0.50	9.00
		0.70	10.8
		0.80	11.8
	0.05	0.10	5.00
		0.20	4.70
		0.30	6.20
		0.50	9.70
		0.70	11.3
	0.10	0.10	4.70
		0.20	6.80
		0.30	6.40
		0.50	9.50
		0.70	10.9
		0.80	13.4
	0.15	0.10	5.90
		0.30	6.90
		0.40	8.80
		0.50	8.60
	0.20	0.10	6.80
		0.20	4.70
		0.30	7.10
		0.40	7.00
		0.50	9.30
		0.60	9.90
	0.30	0.10	5.60
		0.20	5.60
		0.40	7.30
		0.50	7.90
		0.60	8.00
70.0	0.10	0.50	31.4
		0.60	34.5
		0.70	37.9
	0.15	0.30	25.0
		0.50	28.6
		0.60	32.7
		0.70	36.4
70.0	0.30	0.40	32.4
		0.50	37.6
		0.60	38.0
	0.40	0.10	29.1
		0.20	30.8
		0.30	32.4
		0.40	35.1
		0.50	40.4
80.0	0.05	0.10	56.8
		0.20	61.8
		0.30	71.3
		0.50	86.4
		0.70	104
		0.80	113
	0.10	0.10	60.8
		0.20	64.3
		0.30	69.9
		0.50	89.0
		0.60	91.7
		0.70	104
	0.15	0.10	66.2
		0.20	67.3
		0.30	77.3
		0.50	92.2
		0.60	92.7
		0.70	104
	0.20	0.10	84.6
		0.20	74.1
		0.30	80.7
		0.50	88.4
		0.60	112
		0.70	114
	0.30	0.20	87.2
		0.30	91.2
		0.40	114
		0.50	105
		0.60	110
	0.40	0.10	100
		0.20	104
		0.30	113
		0.50	126

For M = Cr and n = 3, plots of $k_{obs.}$ *versus* $[P]_T$ at constant acidity (Figure 1) are hyperbolic. The infinity absorbance readings are equal to the calculated values for a 100% conversion into the phosphonato complex, indicating that there is no back reaction (C = 0). Equation (5) can then be rewritten as (9). Plots of $1/k_{obs.}$ *versus* $1/[P]_T$ at constant acidity

$$1/k_{obs.} = \frac{[H^+] + K_a}{A} \cdot \frac{1}{[P]_T} + \frac{B}{A} \qquad (9)$$

(Figure 2) give good straight lines from which the values of A and B/A for each value of $[H^+]$ can be determined. Alternatively (60 °C), the hyperbolic plots of $k_{obs.}$ *versus* $[P]_T$ were fitted by equation (5) with C = 0, and A and B were calculated at each $[H^+]$. Plots of A *versus* $[H^+]$ give the values of $K_2K_ak_2$ (intercept) and K_1k_1 (slope) according to equation (6) (Figure 3) for each temperature. As shown in Figure 2, values of B/A are $[H^+]$ independent, as already found for anations of the same metal centre by the $H_3PO_n/H_2PO_n^-$ (n = 2 or 4) systems.[4,7] This implies that $k_1 = k_2 = A/B$, and K_1 and K_2 can then be calculated. The validity of this assumption was checked by comparison of the observed and theoretically calculated rate constants; differences were smaller than 8% of the observed values, and within the experimental error of the $k_{obs.}$ value. No reliable values of enthalpy change can be found for K_1 and K_2. Table 3 summarizes the inner- and outer-sphere constants, as well as the corresponding enthalpy and entropy terms, derived from Eyring plots, for this system.

For M = Co^{III} and n = 2 the plots of $k_{obs.}$ *versus* $[P]_T$ at different acidities are linear and show a non-zero ($[H^+]$-dependent) intercept, indicating an equilibrium reaction. The absence of curvature in these plots implies that the B term in equations (5) and (7) represents a negligible value compared to the ($[H^+] + K_a$) term. From these plots the values of A and C were calculated at each acidity, and when plotted *versus* $[H^+]$, as in Figures 4 and 5, the values of k_{-1}, k_{-2}, k_1K_1, and k_2K_2 can be calculated. Table 4 shows the kinetic parameters for this system. The product of the inner- and outer-sphere constants cannot be resolved in its components, as has been found for other systems.[5,8] Interestingly, and as stated above, previous studies on the anation of the related systems,[5,8] $[Co(NH_3)_5(H_2O)]^{3+} + H_2PO_n^-/H_3PO_n$ (n = 3 or 4), showed no reactivity for the neutral, H_3PO_n, species.

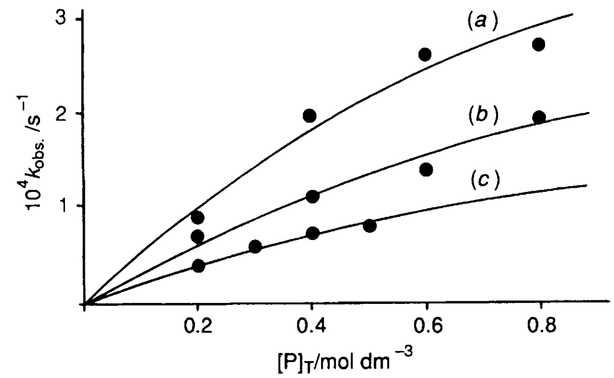


Figure 1. Plots of $k_{obs.}$ *versus* $[P]_T$ for the anation reaction of $[Cr(NH_3)_5(H_2O)]^{3+}$ by the $H_3PO_3/H_2PO_3^-$ system at different acidities [60 °C, I = 1.0 mol dm^{-3} ($LiClO_4$)]: $[H^+]$ = 0.01 (*a*), 0.1 (*b*), or 0.4 mol dm^{-3} (*c*)

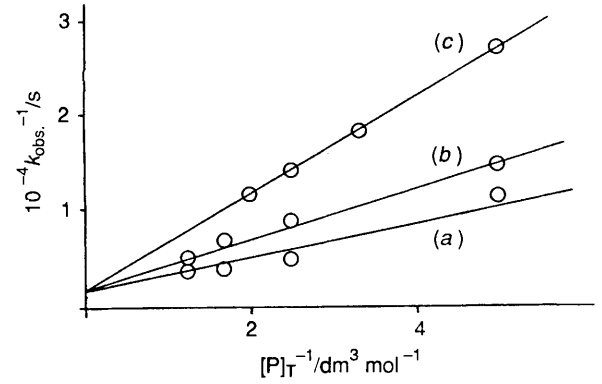


Figure 2. Plots of $1/k_{obs.}$ *versus* $1/[P]_T$ for the anation reaction of $[Cr(NH_3)_5(H_2O)]^{3+}$ by the $H_3PO_3/H_2PO_3^-$ system at different acidities (see Figure 1)

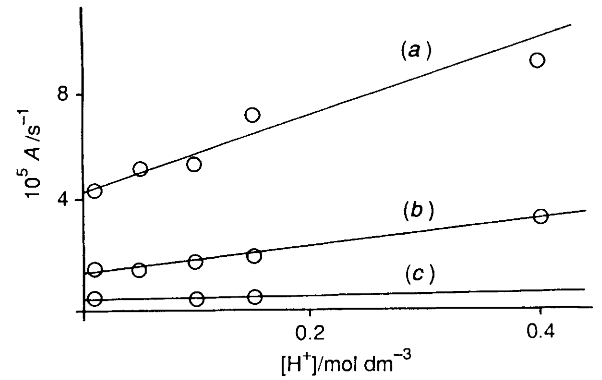


Figure 3. Plots of A [equations (5) and (6)] *versus* $[H^+]$ for the $[Cr(NH_3)_5(H_2O)]^{3+}$ + $H_3PO_3/H_2PO_3^-$ anation reaction at different temperatures [I = 1.0 mol dm^{-3} ($LiClO_4$)]: (*a*) 60, (*b*), 50, and (*c*) 40 °C

Discussion

Tables 5 and 6 show the different rate constants (first- and second-order) for the anation reactions of $[Cr(NH_3)_5(H_2O)]^{3+}$ and $[Co(NH_3)_5(H_2O)]^{3+}$ complexes with various incoming ligands. As has already been stated, the mechanism of substitution reactions of chromium(III) penta-ammine complexes is considered to be I_a. This is based mainly on a value of -5.8 cm^3 mol^{-1} for the activation volume of the water-exchange reaction.[20] However, if we look at the span of k_1 values we see that it is much smaller than that of the hexa-aquachromium(III) anations,[21] and nearly as small as that of those of cobalt(III)-penta-ammine complexes. This, together with the fact that the activation volume is smaller than that of $[Cr(H_2O)_6]^{3+}$, lead us to regard the mechanism as less associatively activated than is usually considered (near the I_a/I_d border).

Table 3. Summary of kinetic data for the anation reaction of $[Cr(NH_3)_5(H_2O)]^{3+}$ by the $H_3PO_3/H_2PO_3^-$ system, I = 1.0 mol dm^{-3} ($LiClO_4$). Errors indicate standard deviations of least-squares fitted values

T/°C	$10^4k_1(=10^4k_2)$/ s^{-1}	$10^5k_1K_1$/ dm^3 mol^{-1} s^{-1}	$10^4k_2K_2$/ dm^3 mol^{-1} s^{-1}
40.0	0.430 ± 0.032	0.557 ± 0.044	0.687 ± 0.009
50.0	1.50 ± 0.14	4.73 ± 0.53	2.37 ± 0.31
60.0	5.94 ± 0.25	11.8 ± 1.7	7.84 ± 0.57

$\Delta H^‡$ = 110 ± 9 kJ mol^{-1}, $\Delta S^‡$ = 24.7 ± 1.7 J K^{-1} mol^{-1}, $\bar{K}_1$ = 0.21 dm^3 mol^{-1}, $\bar{K}_2$ = 1.4 dm^3 mol^{-1} where $\bar{K}_1$ and $\bar{K}_2$, are the average values over the three temperature values.

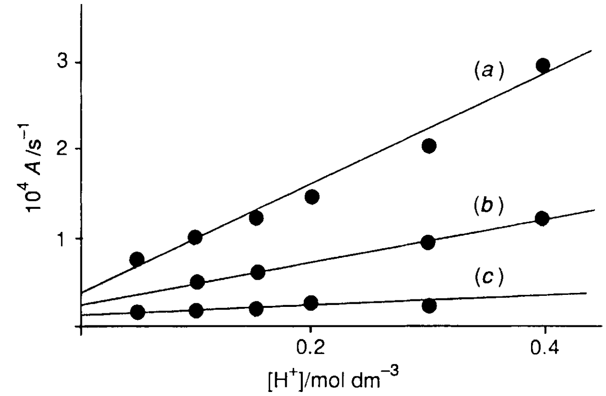


Figure 4. Plots of A [equations (5) and (6)] *versus* $[H^+]$ for the $[Co(NH_3)_5(H_2O)]^{3+}$ + $H_3PO_2/H_2PO_2^-$ anation reaction at different temperatures [I = 1.0 mol dm^{-3} ($LiClO_4$)]: (*a*) 80, (*b*) 70, and (*c*) 60 °C

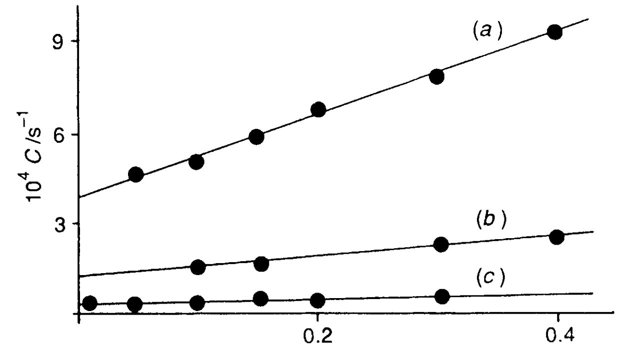


Figure 5. Plots of C [equations (5) and (8)] *versus* $[H^+]$ for the $[Co(NH_3)_5(H_2O)]^{3+}$ + $H_3PO_2/H_2PO_2^-$ anation reaction at different temperatures (see Figure 4)

The principle of microreversibility and the latest data obtained for aquation reactions of $[Cr(CH_3NH_2)_5X]^{3+}$ confirm this assignment.[22] Despite this assignment, the k_i value for H_3PO_n (referred to as k_1) is the same, within experimental error, as k_i for $H_2PO_n^-$ (referred to as k_2) for all n values (n = 2—4). The same fact had been observed for the anation of $[Cr(NH_3)_5(H_2O)]^{3+}$ with $HC_2O_4^-/C_2O_4^{2-}$. Provided that an I_a mechanism is operative for the anation reactions of $[Cr(NH_3)_5(H_2O)]^{3+}$ with these ligands, the metal centre ought to be able to distinguish between the two species (H_3PO_n and

Table 4. Summary of kinetic data for the anation reaction of $[Co(NH_3)_5(H_2O)]^{3+}$ by the $H_3PO_2/H_2PO_2^-$ system, $I = 1.0$ mol dm^{-3} ($LiClO_4$). Errors indicate standard deviations of least-squares fitted values

T/°C	$10^5K_1k_1$/ dm^3 mol^{-1} s^{-1}	$10^5K_2k_2$/ dm^3 mol^{-1} s^{-1}	10^5k_{-1}/ dm^3 mol^{-1} s^{-1}	10^5k_{-2}/ s^{-1}
60.0	4.1 ± 1.5	17.9 ± 3.6	7.1 ± 0.6	2.9 ± 0.1
70.0	24.9 ± 1.9	44.8 ± 5.7	36.2 ± 2.4	11.0 ± 0.6
80.0	61.2 ± 4.6	86.5 ± 28	132 ± 6	39.1 ± 1.3
$\Delta H^‡$/kJ mol^{-1}	130 ± 23*	74.5 ± 5.8*	140 ± 9*	120 ± 81
$\Delta S^‡$/J K^{-1}mol^{-1}	60 ± 23*	−93 ± 15*	91 ± 7*	36 ± 1

* Calculated from the second-order rate constant.

Table 5. Summary of rate constants for the anation of $[Cr(NH_3)_5(H_2O)]^{3+}$ by different entering ligands at 50 °C, $I = 1.0$ mol dm^{-3} ($LiClO_4$).

Ligand	10^4k_1/s^{-1}	$10^4K_1k_1$/ dm^3 mol^{-1} s^{-1}	Ref.
NCS^-	6.12	4.16	*a*
Cl^-	—	0.69	*a*
Br^-	—	3.71	*a*
$CCl_3CO_2^-$	—	1.81	*a*
$CF_3CO_2^-$	—	1.37	*a*
$HC_2O_4^-$	6.2	6.45	*b*
$C_2O_4^{2-}$	6.2	29.1	*b*
$^+NH_3CH_2CO_2^-$	14.2	7.82	*c*
H_3PO_4	1.45	0.46	7
$H_2PO_4^-$	1.45	2.59	7
H_3PO_3	1.5	0.47	This work
$H_2PO_3^-$	1.5	2.37	This work
H_3PO_2	3.44	0.45	4
$H_2PO_2^-$	3.44	1.14	4
H_2O	13.7	—	*d*

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O. S. 1 O. S. 2

Scheme 2.

Table 6. Summary of rate constants for the anation of $[Co(NH_3)_5(H_2O)]^{3+}$ by different entering ligands at 60 °C, $I = 1.0$ mol dm^{-3} ($LiClO_4$).

Ligand	10^4k_1/s^{-1}	$10^4K_1k_1$/ dm^3 mol^{-1} s^{-1}	Ref.
Cl^-	—	1.70	*a*
SO_4^{2-}	—	5.66	*a*
N_3^-	—	2.24	*b*
CH_3CO_2H	—	0.17	*c*
$CH_3CO_2^-$	0.5	2.5	*c*
$H_2C_2O_4$	—	0.66	*d*
$HC_2O_4^-$	1.8	3.2	*d*
$C_2O_4^{2-}$	1.25	11.5	*d*
HCO_2H	—	0.42	*e*
HCO_2^-	1.98	1.68	*e*
H_2succ	—	0.21	*f*
Hsucc$^-$	0.52	5.20	*f*
succ^{2-}	0.76	22.8	*f*
$H_2PO_4^-$	—	1.54	8
$H_2PO_3^-$	0.29	0.62	5
H_3PO_2	—	0.41	This work
$H_2PO_2^-$	—	1.79	This work
H_2O	7.04	—	*c*

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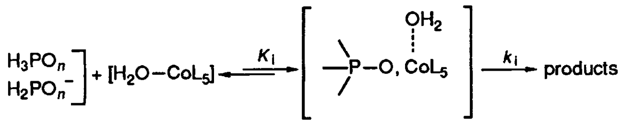
Table 7. Summary of kinetic data for the anation reactions of $[Cr(NH_3)_5(H_2O)]^{3+}$ by the $H_3PO_n/H_2PO_n^-$ systems [50°C, $I = 1.0$ mol dm^{-3} ($LiClO_4$)].

n	10^4k_1/ s^{-1}	$\bar{K}_1$*/ dm^3 mol^{-1}	$\bar{K}_2$*/ dm^3 mol^{-1}	Ref.
2	3.44	0.13	0.33	4
3	1.50	0.21	1.4	This work
4	1.45	0.32	1.8	6

* Average of values for 40, 50, and 60 °C.

$H_2PO_n^-$), and different values for k_1 and k_2 should be obtained for each n. The only way out of this apparent incongruity has already been suggested[7] for the anation reaction of $[Cr(NH_3)_5(H_2O)]^{3+}$ with $H_3PO_4/H_2PO_4^-$. That is, once the outer-sphere complex has been formed, with the correct orientation of the reacting species, the chromium cannot distinguish between the anionic and the neutral ligands for the interchange process, and the associative character of it is reflected by a 'tight' outer-sphere complex, as has recently been found for another type of reaction.[17,23] If this is correct, the k_i ($k_i = k_1 = k_2$) values for the different $H_3PO_n/H_2PO_n^-$ (n = 2—4) systems should be very similar. Table 7 shows that this is the case; an increase in the value of $k_1 = k_2$ is observed only for $n = 2$, probably due to an important decrease in the size of the anating species, together with an important electron enrichment of the oriented oxo-group when compared with that of the $n = 3$ and $n = 4$ species. Furthermore, if this associative tight outer-shere complex applies, the K_1 and K_2 values should reflect the difference in nature between the phosphorus oxoanions. Data in Table 7 support this point, K_2 increasing with n. A similar trend exists for K_1, but is less pronounced since the oxoanions are already fully protonated, with a zero overall charge.

As already discussed by many authors, and based mainly on the small span of k_iK_i values for anating species of the same charge, and on an activation volume of +1.2 cm^3 mol^{-1} for the water-exchange reaction,[24] an I_d mechanism seems clear for the anation reactions of $[Co(NH_3)_5(H_2O)]^{3+}$. Table 6 gives the values of the rate constants for the anation reactions of $[Co(NH_3)_5(H_2O)]^{3+}$ with the $H_3PO_n/H_2PO_n^-$ systems, including the values found in the present study. Surprisingly, even when the three anionic species ($H_2PO_n^-$) are reactive, the only neutral form (H_3PO_n) which is significantly reactive is the hypophosphorous acid, H_3PO_2. The different behaviour of H_3PO_2 can be explained by the following reasoning. The oxygen bound to the phosphorus atom (Scheme 3) has to 'wait' inside the outer-sphere complex for the Co–OH_2 bond to start breaking before starting to interact with the cobalt(III) centre (I_d definition).[25,26] If a proton migration to the already oriented oxo-group can occur during this time, this group will then become 'blocked,' preventing the anation reaction. This effect will show mainly for the H_3PO_n species; the $H_2PO_n^-$ counterpart already has a free oxo-group not directed towards



Scheme 3.

the cobalt centre that can be protonated without having any consequences on the overall anation rate. In this way, only a fraction of the outer-sphere complex, o.s.$_1$, will be reactive. The effect will then show a gradation according to the number of acidic protons present in the H_3PO_n species avilable to 'block' the oxo-group oriented towards the cobalt centre. Thus, the H_3PO_2 species, having only one acidic proton, will be more reactive than H_3PO_4 and, as Table 6 shows, is the only one presenting some reactivity.

Finally, it is interesting that, for the cobalt complexes, the product k_iK_i cannot be resolved into its components in most systems, due to the small value of K_i. This contrasts with the analogous chromium systems, where K_i are much greater (t_{2g}^3 *versus* t_{2g}^6 configuration).

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