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Kinetics of the Anation of Aquopentaamminecobalt(III) by Phosphoric Acid Dihydrogenphosphate

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The kinetics of the anation reaction of $[Co(NH_3)_5H_2O]^{3+}$ *by* $H_2PO_4^-/H_3PO_4$ *in aqueous solution has been studied at 50, 60 and 70 °C and I = 1.0 (*$LiClO_4$*). The results indicate a rate law of the form* $k_{obs} = k_f[H_2PO_4^-]$*, with no (or small) contribution from* H_3PO_4*. No kinetic evidence of ion-pair formation has been observed in contrast to the analogous chromium(III) study. Values of* $k_f \times 10^5$ *(*M^{-1} s^{-1}*) are: 4.50 ± 0.07, 15.4 ± 0.2, and 53.9 ± 0.8 at 50, 60 and 70 °C respectively; the corresponding activation parameters are* $\Delta H^{\ddagger} = 26.9 \pm 0.8$ *Kcal mol*$^{-1}$ *and* $\Delta S^{\ddagger} = 4.2 \pm 2.4$ *cal K*$^{-1}$ *mol*$^{-1}$.

Introduction

The anation kinetics of $[Cr(NH_3)_5H_2O]^{3+}$ by $H_2PO_4^-/H_3PO_4$ has been reported recently [1]. On the other hand the analogous study of the reaction of $[Co(NH_3)_5H_2O]^{3+}$ with $H_2PO_4^-/H_3PO_4$ has been only briefly investigated at 25 °C. Following our interest [1, 3, 4] in complexes containing phosphorus oxoanions we report a more complete study of the latter reaction at 50, 60 and 70 °C.

Experimental

Materials

Aquopentaamminecobalt(III) perchlorate, $[Co(NH_3)_5H_2O](ClO_4)_3$ was prepared from carbonatopentaamminecobalt(III) nitrate, $[Co(NH_3)_5CO_3]NO_3{\cdot}\frac{1}{2}H_2O$ [5] and recrystallized twice [6]. The spectrum of aquo complex in 0.10 *M* $HClO_4$, λ_{max} 491 nm (ϵ = 42.7 M^{-1} cm^{-1}), λ_{min} 402 nm (ϵ = 7.7 M^{-1} cm^{-1}), λ_{max} 346 nm (ϵ = 44.4 M^{-1} cm^{-1}) was in agreement with literature values [7]. A solution of dihydrogenphosphatopentaamminecobalt(III) was made according to Schmidt and Taube [2]. Maxima and intensity ratio, λ_{max} 515 nm, λ_{max} 357 nm, ϵ_1/ϵ_2 = 0.70 were also in accord with literature values [2]. The $LiClO_4$ was prepared from Li_2CO_3 and 60% analytical reagent $HClO_4$ and recrystallized three times. A solution was made up and standardized by passing aliquots through Amberlite IR 120 (H) and titrating the eluted protons with sodium hydroxide. A solution of LiH_2PO_4 was prepared by mixing equivalent amounts of solutions of H_3PO_4 and LiOH and its molarity checked gravimetrically [8].

Kinetic Runs

The progress of the reaction was monitored at 530 nm where maximum difference between the extinction coefficient of aquo and phosphato complexes occurs, on a Beckman DU 2 spectrophotometer equipped with a thermospacer set connected to a Heto 01 E 623 thermostat (±0.1 °C). Kinetic runs were carried out in excess of total phosphate, $[PO_4]_T$, with regard to initial aquo-complex (9.87 × 10^{-3} *M*). Values of k_{obs} were determined from the plots of $-\ln (A_\infty - A_t)$ against time which were linear to more than 80% reaction. Final absorbance values (A_∞) were calculated from the spectrum of $[Co(NH_3)_5H_2PO_4]^{2+}$. Successive scans (70 °C, $[PO_4]_T$ = 0.3 *M*, $[H^+]$ = 2.5 × 10^{-3} *M*) on a Beckman UV 5230 spectrophotometer gave retention of isosbestic points at 477, 345 and 404 nm in agreement with those calculated (477, 346 and 403 nm). A run without added phosphate (60 °C, $[H^+]$ = 0.001 *M*, I = 1.0) gave no change in spectrum over a 5 h period. Values of $[H^+]$, $H_2PO_4]$, and $[H_3PO_4]$ were calculated from added $HClO_4$, LiH_2PO_4, and previously determined acidity constants of H_3PO_4 in the same medium [1]. Errors quoted are standard deviations. Straight lines are least-squares fits with each point weighted as the inverse of its standard deviation.

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TABLE I. Observed Rate Constants for Anation of $[Co(NH_3)_5H_2O]^{3+}$ by Phosphate, I = 1.0 ($LiClO_4$), λ = 530 nm.

Temperature = 50.0 °C			Temperature = 60.0 °C			Temperature = 70.0 °C		
$[H^+]_{eq}$ (*M*)	$[PO_4]_T$ (*M*)	10^5 k_{obs} (s^{-1})	$[H^+]_{eq}$ (*M*)	$[PO_4]_T$ (*M*)	10^5 k_{obs} (s^{-1})	$[H^+]_{eq}$ (*M*)	$[PO_4]_T$ (*M*)	10^5 k_{obs} (s^{-1})
0.001	0.19	0.82	0.001	0.19	2.87	0.001	0.19	10.09
	0.28	1.26		0.28	4.05		0.28	14.58
	0.47	2.01		0.47	6.91		0.46	23.09
	0.75	3.07		0.56	7.70			
0.003	0.17	0.64	0.003	0.17	2.23	0.003	0.17	7.10
	0.26	0.96		0.25	3.10		0.25	10.55
	0.43	1.62		0.42	5.14		0.42	18.46
	0.52	1.80		0.51	6.17		0.67	27.30
	0.69	2.57		0.68	8.14			
0.0075	0.15	0.42	0.0075	0.15	1.60	0.008	0.14	4.78
	0.23	0.72		0.22	2.20		0.22	6.92
	0.38	1.06		0.37	4.13		0.36	11.14
	0.45	1.39		0.44	4.67		0.58	19.13
	0.61	1.87		0.59	5.71			
0.013	0.14	0.32	0.014	0.13	1.08	0.015	0.13	3.39
	0.20	0.49		0.20	1.69		0.19	5.29
	0.34	0.84		0.33	2.69		0.32	8.07
	0.40	1.15		0.39	3.27		0.51	12.64
	0.54	1.29		0.52	4.06			
0.023	0.12	0.23	0.025	0.12	0.87	0.029	0.11	2.25
	0.18	0.33		0.18	1.18		0.17	3.32
	0.30	0.58		0.29	1.92		0.28	5.53
	0.37	0.93		0.35	2.38		0.45	8.57
	0.49	1.00		0.47	3.03			

TABLE II. Observed Rate Constants with Same $[H_2PO_4^-]$ and Different $[H_3PO_4]$ for the Anation of Aquopentaamminecobalt(III) by Phosphate at 50 °C.

$[H_2PO_4^-]$, *M*	$[H_3PO_4]$, *M*	10^5 k_{obs}, s^{-1}
0.11	0.09	0.49
0.11	0.19	0.59
0.18	0.01	0.82
0.18	0.16	0.84
0.22	0.04	0.96
0.22	0.18	1.15
0.26	0.02	1.26
0.26	0.12	1.06

TABLE III. Values of k_f and Activation Parameters for the Anation of Aquopentaamminecobalt(III) by Phosphate.

Temp. (°C)	10^5 k_f, M^{-1}, s^{-1}
50.0	4.50 ± 0.07
60.0	15.4 ± 0.2
70.0	53.9 ± 0.8
$\Delta H^{\ddagger}$ = 26.9 ± 0.8 Kcal mol^{-1}	
$\Delta S^{\ddagger}$ = 4.2 ± 2.4 cal K^{-1} mol^{-1}	

Results and Discussion

The system $H_2PO_4^-/H_3PO_4$* reacts with $[Co(NH_3)_5H_2O]^{3+}$ to give $[Co(NH_3)_5H_2PO_4]^{2+}$ as the only product in agreement with the excellent retention of calculated isosbestic points (see Experimental). Values of k_{obs} as function of $[PO_4]_T$, and $[H^+]$ are given in Table I. Values of k_{obs} with same $[H_2PO_4^-]$ do not show any clear increasing dependence on $[H_3PO_4]$, as can be seen from Table II for example, suggesting that H_3PO_4 is non-reactive or much less so than $H_2PO_4^-$. Nonreactivity of a protonated anion in anation reactions has been previously reported by Swaddle *et al.* [9] in the system NO_3^-/HNO_3 + $[Co(NH_3)_5H_2O]^{3+}$.

The plots of k_{obs} against $[H_2PO_4^-]$ (Fig. 1) and against $[PO_4]_T$ (not shown) are linear without any curvature. The rate law has the form

*A calculation using the three acidity constants of H_3PO_4 showed that in the pH range used the only phosphorus containing species are H_3PO_4 and $H_2PO_4^-$.

TABLE IV. Second Order Rate Constants for the Anation of $[Co(NH_3)_5H_2O]^{3+}$ by Uninegative Anions at 60 °C.

Anion	10^4 k_f, M^{-1} s^{-1}	I	Ref.
Cl^-	1.70	2.0 ($LiClO_4$)	10
AcO^-	2.5	1.0 (KNO_3)	12
N_3^-	2.24	0.51 ($NaClO_4$)	9
Hox^-	3.2	1.0 (KNO_3)	13
$HCOO^-$	1.68	1.0 (KNO_3)	14
$Hsucc^-$	5.20	0.3 ($NaClO_4$)	15
$H_2PO_4^-$	1.54	1.0 ($LiClO_4$)	This work

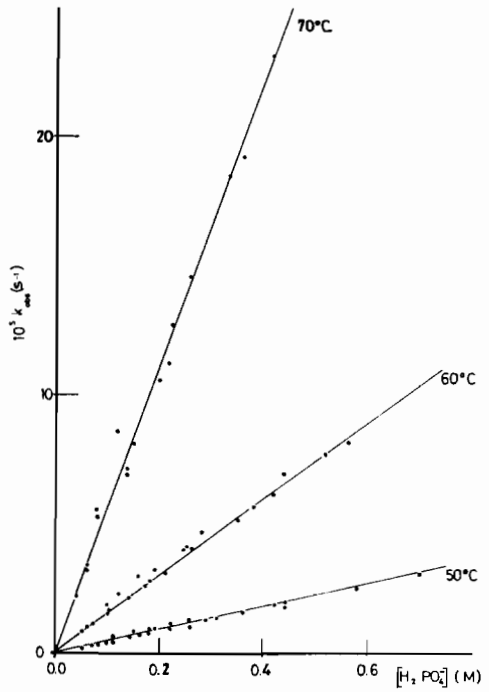

Fig. 1. The dependence of k_{obs} on $[H_2PO_4^-]$ for the anation of aquopentaamminecobalt(III) by phosphate.

$$k_{obs} = k_f[H_2PO_4^-]$$

Values of k_f and activation parameters are given in Table III. The value of k_f extrapolated to 25 °C (1.23×10^{-6} M^{-1} s^{-1}) is fairly similar to that found by Taube *et al.* (2.0×10^{-6} M^{-1} s^{-1}) in the equilibrium study of the same system at 25 °C [2].

Our results are in accordance with those of Kelm *et al.* [10]; they studied the anation reaction of $[Co(NH_3)_5H_2O]^{3+}$ and chloride sulphate (probably a mixture of SO_4^{2-} and HSO_4^-) and did not find any curvature in the plots of k_{obs} against [anion] concluding that K_{OS} should be less than 0.1 M^{-1}. All this does not agree with previously determined K_{OS} (25 °C) for $[Co(NH_3)_5H_2O]^{3+}/X^{n-}$ (X^{n-} = $H_2PO_4^-$, SO_4^{2-}) of 2.9 M^{-1} [2] and 11.2 M^{-1} [11] respectively; with such values some curvature should show up in the plots.

The analogous chromium system $[Cr(NH_3)_5H_2O]^{3+} + H_2PO_4^-/H_3PO_4$ has been recently kinetically investigated under similar conditions [1]. It behaves differently since the plots of k_{obs} against $[PO_4]_T$ show marked curvature. Equilibrium constants for outer-sphere complex formation

$$[Cr(NH_3)_5H_2O]^{3+} + H_3PO_4 \rightleftharpoons$$

$$[Cr(NH_3)_5H_2O]^{3+}, H_3PO_4 \qquad K_1 = 0.32\ M^{-1}$$

$$[Cr(NH_3)_5H_2O]^{3+} + H_2PO_4^- \rightleftharpoons$$

$$[Cr(NH_3)_5H_2O]^{3+}, H_2PO_4^- \qquad K_2 = 1.8\ M^{-1}$$

could be determined. One can speculate on how the variation of electronic configuration for the metallic centre (d^3 to d^6) can decrease the value of K_2 from 1.8 M^{-1} to less than *ca.* 0.1 M^{-1}. Certainly the type of information obtained in these studies is invaluable in assessing the whole nature of outer sphere coordination which on the basis of the present studies is not solely determined by overall charge (and size) of reactants.

Finally it is of interest to compare our value of k_f for example at 60 °C, 1.54×10^{-4} M^{-1} s^{-1}, with those found by other authors for anation reactions of the same complex with different mononegative anions. Table IV indicates that our value of k_f is similar to those of the other mononegative anions, in accord with a mechanism with dissociative activation. The spread of rate constant is less than that now observed for $[Cr(NH_3)_5H_2O]^{3+}$ which in turn is less than that observed for $[Cr(H_2O)_6]^{3+}$ which displays associative characteristics.

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