Kinetic study of formation of $[Co(H_2PO_4)(H_2O)_5]^{2+}$ at Various Acidities and Ionic Strengths *

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The reaction of $[Co(H_2O)_6]^{3+}$ with the system $H_3PO_4/H_2PO_4^-$ to yield the 1:1 complex $[Co(H_2PO_4)(H_2O)_5]^{2+}$ has been studied in aqueous solution at 25 °C and at different acidities and ionic strengths. The reactivity of this complex has been found to be *ca.* 4 orders of magnitude greater than that of $[Co(NH_3)_5(H_2O)]^{3+}$. The results are interpreted in terms of a dissociatively activated conjugate-base substitution with an enhanced rate due to a rapid low-spin $\longleftrightarrow$ high-spin equilibrium for the $[Co(H_2O)_6]^{3+}$ complex. As for other similar cobalt–phosphate systems, only substitution activity due to $H_2PO_4^-$ has been detected. The first acidity constant of $[Co(H_2O)_6]^{3+}$ has also been measured as a function of ionic strength.

Although cobalt(III) has played an important role in the development of the mechanisms of the reactions of metal complexes,[1] studies of the substitution reactions of its most simple form in aqueous solution, $[Co(H_2O)_6]^{3+}$, are very scarce.[2] This is due to several reasons: the difficulty of its preparation; the instability of the corresponding solutions;[3] the high acidity of $[Co(H_2O)_6]^{3+}$ acting as an 'aquacid' and its tendency to polymerize; and finally its strong oxidizing character $[E^\circ(Co^{3+}–Co^{2+}) = +1.84$ V] which precludes substitution studies with reducing species.[4] On the other hand, several authors have previously attempted to determine the acidity constant of $[Co(H_2O)_6]^{3+}$, but the errors involved are large.[5]

We present in this paper the first study of an anation reaction of $[Co(H_2O)_6]^{3+}$ with a non-reducing species, at variable ionic strength and acidity. The $H_2PO_4^-/H_3PO_4$ system was chosen for its acid–base characteristics which allow a careful $[H^+]$-dependence study of the reaction. We have also redetermined the acidity constant of $[Co(H_2O)_6]^{3+}$ in the same medium as that used in the kinetic study.

Experimental

Reagents.—The ion $[Co(H_2O)_6]^{3+}$ was prepared by anodic oxidation of $[Co(H_2O)_6]^{2+}$ at 0 °C and a current density between 2 and 6 mA cm^{-2} (electrode surface area, *ca.* 30 cm^2 shiny platinum). In order to improve yields and reproducibility the cobalt(II) concentration was chosen as 5.5×10^{-2}–6.5×10^{-2} mol dm^{-3} in 3–4 mol dm^{-3} $HClO_4$ and the electro-oxidation time was 18–22 h. No difference was observed when the oxidation was done under a nitrogen atmosphere.[6] The yield was 80–90% relative to the initial concentration of Co^{II}.

Solutions of $[Co(H_2O)_6]^{3+}$ were standardized spectrophotometrically (λ_{max} = 404 and 606 nm, ε = 40.8 and 35.5 dm^3 mol^{-1} cm^{-1}) and the absence of polymeric species checked by the complete absence of a strong absorbance at 332 nm (ratios A_{332}/A_{480} and A_{606}/A_{332} should be 1.4 and 6.0:1 respectively).[7]

Other materials. Solutions of lithium perchlorate were prepared and characterized as previously described.[8] Stock solutions of $HClO_4$ and H_3PO_4 were prepared from concentrated reagent-grade materials and standardized by $[H^+]$ titration.

Table 1 First acid dissociation constant for the $[Co(H_2O)_6]^{3+}$ complex at 25 °C and various ionic strengths ($LiClO_4$)

I/mol dm^{-3}	K_c/mol dm^{-3}
1.0	0.012 ± 0.002
2.0	0.009 ± 0.006
3.0	0.015 ± 0.005

All the $HClO_4$, H_3PO_4 and $LiClO_4$ solutions were electrolysed in the anodic compartment of an electrolytic cell at 4.0 V during 4–6 h in order to eliminate any reducing species in the reaction medium, which could later interfere with the anation reaction studied.

Determination of the Acid Dissociation Constant of $[Co(H_2O)_6]^{3+}$.—Electronic spectra of solutions of $[Co(H_2O)_6]^{3+}$ (5×10^{-3}–6×10^{-3} mol dm^{-3}) at 25 °C, varying acidities, and constant ionic strength were recorded and the slope of a standard plot[9] of $[H_3O^+](\varepsilon_{obs} - \varepsilon_{Co^{III}})$ *versus* $(\varepsilon_{obs} - \varepsilon_{Co^{III}})$ for the equilibrium $[Co(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Co(H_2O)_5(OH)]^{2+} + H_3O^+$ gave the K_c values shown in Table 1. The study was confined to the 0.4–0.05 mol dm^{-3} $[Co(H_2O)_6]^{3+}$ range in order to prevent the appearance of polymeric forms of the aquaions.

Kinetics.—Reactions with $t_{\frac{1}{2}} < 30$ s were followed spectrophotometrically on a Durrum D-110 stopped-flow instrument and those with $t_{\frac{1}{2}} > 30$ s on a HP8452A diode-array instrument fitted with a SFA-11 rapid-mixing attachment. Runs were carried out under pseudo-first-order conditions and observed rate constants were derived from exponential or linear standard least-squares fits. Some runs were carried out with less than a 10-fold excess of H_3PO_4, and the standard second-order treatment was used.[10] Standard unknown-infinity reading methods had to be used for reactions at low acidities in order to prevent interference from secondary reactions.[11] The stability of the 'working' $[Co(H_2O)_6]^{3+}$ solutions was checked under the conditions of the runs (0.5–5 min, depending on the acidity), and no appreciable variation in the electronic spectrum (< 5%) was observed. Least-squares errors for the rate constants were always within 3–8% of the calculated values.

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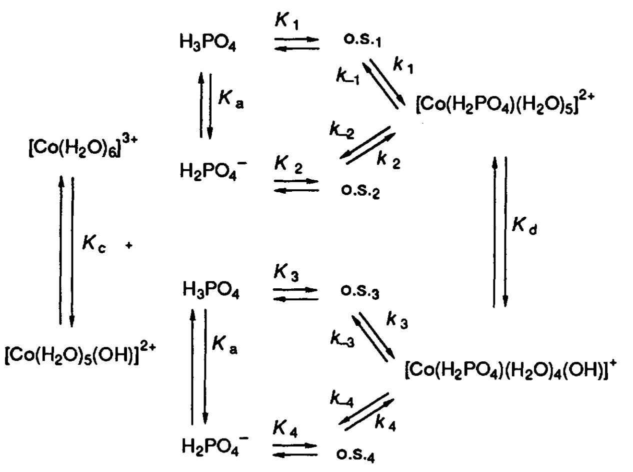
* *Supplementary data available* (No. SUP 56860, 4 pp.): primary kinetic data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.



Scheme 1 o.s. = outer-sphere complex

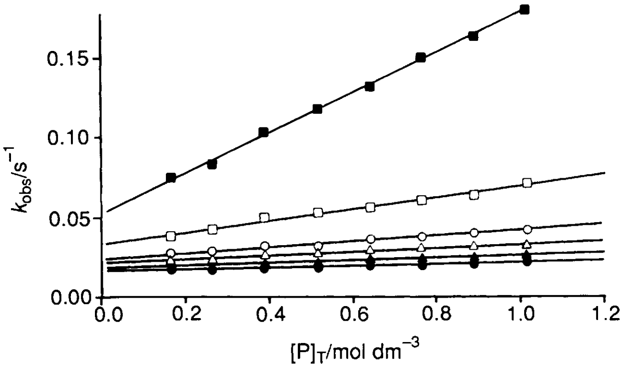


Fig. 1 Plot of k_{obs} *versus* total phosphate concentration for the reactions studied at 25 °C and I = 3.0 mol dm^{-3} ($LiClO_4$). $[H_3O^+]$ = 3.0 (●), 2.5 (▲), 2.0 (△), 1.5 (○), 1.0 (□) and 0.5 mol dm^{-3} (■)

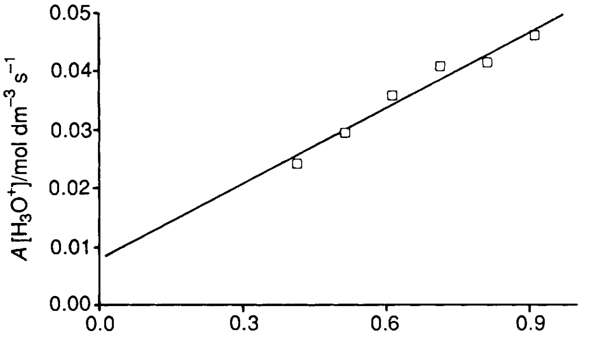


Fig. 2 Plot of $A[H_3O^+]$ *versus* $[H_3O^+]$ at I = 1.0 mol dm^{-3} ($LiClO_4$) and 25 °C for the reactions studied

All the plots of k_{obs} *versus* $[P]_T$ (total phosphate concentration) were fitted by an unweighted linear least-squares treatment and the errors obtained for the slope and intercept were always in the 10–15% range of the actual value.

All concentrations for the runs were calculated from the dilution of stock solutions. The ratio $[H_3PO_4]/[H_2PO_4^-]$ had a maximum at 50:1 for the lowest acidity studied.

Electronic Spectra.—Spectra were recorded on an HP8452A or a Shimadzu UV-160A instrument in 1 cm optical path cells. The cell holders of both instruments were thermostatted at 25 ± 0.2 °C.

Results

The $[Co(H_2O)_6]^{3+}$ solutions prepared in 3–4 mol dm^{-3} $HClO_4$ medium, under the conditions described (which gave better results than those previously published), were found to be quite stable at −30 °C during 48 h. The criteria taken as a measure of the stability were the reproducibility of the kinetic results and the non-appearance of polymeric forms (shown by a strong absorbance at 332 nm). When the acidity is decreased, or the temperature raised, degradation of these solutions occurs rather quickly, but always on a longer time-scale than that of the kinetics of anation.

As for the stoichiometry of the complex formed under the conditions of this work, it was shown to be 1:1 (total mole fraction of ligand = 0.53) ($Co^{III}:H_2PO_4^-$) by Job's method.[12] For $[P]_T:[Co^{III}]$ values greater than 65:1 the 1:1 stoichiometry does not hold and such excesses were avoided. On the other hand, experiments run under second-order conditions ($[P]_T:[Co^{III}]$ = 5:1), gave rate constants in excellent agreement with the values expected from extrapolation of the plots of k_{obs} *versus* $[P]_T$ obtained under first-order conditions.

The reaction was followed at 354 nm, where the increase in absorbance was large enough and the spectral changes due to possible polymerization were at a minimum. No isosbestic points were observed as in other previous work.[2] The span of $[H^+]$ values used was determined by the ionic strength as well as by the lowest value acceptable for the non-existence of polymeric forms. Different cobalt(II) contents of the cobalt(III) solutions do not affect the observed rate constants. The observed rate constants for the reactions studied as a function of acidity, total phosphorus concentration, and ionic strength have been deposited as SUP 56860.

The results are consistent with Scheme 1. The associated rate equation (1) can be written, where $[P]_T = [H_3PO_4] +$

$$k_{obs} = \frac{A[P]_T}{B + C[P]_T} + D \qquad (1)$$

$[H_2PO_4^-]$, $A = k_1K_1[H_3O^+] + k_2K_2K_a + k_3K_3K_c + k_4K_4(K_aK_c/[H_3O^+])$, $B = [H_3O^+] + K_a + K_c + K_aK_c/[H_3O^+]$, $C = K_1[H_3O^+] + K_2K_a + K_3K_c + K_4K_aK_c/[H_3O^+]$, and $D = \{[H_3O^+]/(K_d + [H_3O^+])\}\{k_{-1}[H_3O^+] + k_{-2} + k_{-3}K_d + k_{-4}K_d/[H_3O^+]\}$. The first dissociation constants of H_3PO_4 and $[Co(H_2O)_6]^{3+}$, K_a and K_c, have been determined in this and previous work under the same conditions.[8,13] Fig. 1 shows some of the plots of k_{obs} *versus* $[P]_T$ obtained. From these, it is clear that the C term is negligible and D and A/B values can be derived directly from the intercepts and slopes of the plots. From K_a and K_c, B can be calculated at each acidity and a plot of $A[H_3O^+]$ *versus* $[H_3O^+]$ should give k_1K_1, $k_2K_2 + k_3K_3$, and k_4K_4. Fig. 2 shows one of these plots; again it is clear that a very good linearity exists, indicating that the second-order term (k_1K_1) is negligible under these conditions. On the other hand, a plot of $D(K_d + [H_3O^+])$ *versus* $[H_3O^+]$ (K_d being iteratively estimated as $\frac{1}{2}K_c$ in order to keep the best fit) also gives an excellent linearity, indicating that, for both the forward and reverse reactions, path 1 in Scheme 1 is negligible, in agreement with the principle of microreversibility. Table 2 gives the kinetic and equilibrium constants obtained, as a function of the ionic strength. Paths 2 and 3 in Scheme 1 are kinetically indistinguishable, and so the two contributions (one being a conjugate-base and the other a simple substitution mechanism) cannot be separated.

As for the ionic strength dependence of the equilibrium and rate constants, Tables 1 and 2 show that, although the equilibrium constants do not seem to be affected by the changes in the I value at this level, the rate constants increase with increasing ionic strength.

Discussion

Comparison of the rate constants (Table 2) corresponding to paths 4 and 2 + 3 (kinetically indistinguishable) shows that a factor of 10^3–10^4 separates both paths. This difference is in the

Table 2 Kinetic constants obtained as a function of ionic strength ($LiClO_4$) at 25 °C

I/mol dm^{-3}	$k_2K_2K_a + k_3K_3K_c$/s^{-1}	$k_{-2} + k_{-3}K_d$/dm^3 mol^{-1} s^{-1}	k_4K_4/dm^3 mol^{-1} s^{-1}	k_{-4}/dm^3 mol^{-1} s^{-1}
1.0	0.043 ± 0.004	0.005 ± 0.001	29 ± 12	0.42 ± 0.14
2.0	0.0026 ± 0.0004	0.0116 ± 0.0008	88 ± 3	2.9 ± 0.2
3.0	0.0065 ± 0.0003	0.0043 ± 0.0006	145 ± 3	3.5 ± 0.1

range expected for a direct *versus* a conjugate-base mechanism in a dissociatively activated process,[14] indicating that path 3 could be considered negligible under the conditions studied. The differences in the k_4K_4/k_{-4} and $k_3K_3K_c/k_{-3}K_d$ values are attributed to medium effects on ion-pair formation, as already shown in other systems.[15] The fact that only the anionic species $H_2PO_4^-$ is reactive is not suprising, since for the analogous $[Co(NH_3)_5(H_2O)]^{3+} + H_3PO_4/H_2PO_4^-$ anation reaction only rate constants involving the anionic entering ligand have been reported.[16]

The series of complexes $[Co(NH_3)_x(H_2O)_{6-x}]^{3+}$ (x = 0–5) shows increasing anation rate constants on replacement of NH_3 by H_2O. This can be related to the availability of a high-spin complex for the dissociatively activated reaction.[17] Even so the 'jump' in the rate constant magnitude on going from $x = 2$ to 0 seems far too wide for a simple progression ($x = 5, k = 10^{-5}$; 4, 10^{-3}; 2, 10^{-2}; 0, 10^3 mol dm^{-3} s^{-1}), so $[Co(H_2O)_6]^{3+}$ has to have some special differentiating features when compared to the rest of the series.

The present kinetic study gives us the opportunity of comparing the reactivity of $[Co(H_2O)_6]^{3+}$ and $[Co(NH_3)_5(H_2O)]^{3+}$ towards the same anating species ($H_2PO_4^-/H_3PO_4$). The reactivity of the former is *ca.* 10^4 times greater than that of the latter. The explanation usually given[18] to account for the large rates observed for both substitution and redox reactions involves an equilibrium of the type $^1A_{1g} \longleftrightarrow {}^5T_{2g}$. The corresponding equilibrium constant, as measured by several techniques,[19] is very small (*ca.* 10^{-7}) and allows for only a very low concentration of the high-spin form. However, this is more than compensated for both by the fact that the equilibrium is established very rapidly [the energy difference $\Delta E(^1A_{1g} - {}^5T_{2g})$ has been estimated[20] and corresponds to a rate constant of *ca.* 10^5 s^{-1} for the process $^1A_{1g} \longrightarrow {}^5T_{2g}$], and by the high reactivity of this high-spin form. The high-spin form is very labile since it has two electrons in antibonding e_g orbitals, which increase the $Co-OH_2$ distance and favour a dissociatively activated mechanism. The presence of this $^5T_{2g}$ state as an 'intermediate step' in the rapid exchange of Co^{III} and Co^{II} has also been postulated, but in this case a H_2O-bridged intermediate also seems plausible.[21]

The possibility of a faster anation reaction *via* minor quantities of polymeric or μ-OH bridged species can be ruled out. Such species are known and characterized for Cr^{III} and Rh^{III},[22,23] and, although some acceleration exists, there is never a 10^8-fold difference in rate constants, their reactions having comparable rates to those of $[M(NH_3)_5(H_2O)]^{3+}$ and 'true' $[M(H_2O)_6]^{3+}$ complexes.

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