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The Kinetics of Aquation of Amminepentaaquachromium(III) Ion. A Comparison with Unsaturated Amine Ligands

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The aquation of amminepentaaquachromium(III) ion was studied as a function of acidity and temperature at $\mu = 1.0$ M ($HClO_4 + NaClO_4$). The rate law is of the form $-\mathrm{dln}\,[Cr(H_2O)_5(NH_3)^{3+}]/\mathrm{dt} = k_0 + k_{-1}/[H^+]$. The enthalpy (kcal mol^{-1}) and entropy (cal mol^{-1} K^{-1}) of activation for the acid-independent path are 27.8 and —5.3, and for the acid-inverse path 34.8 and 7.0. The corresponding specific rates extrapolated to 25 °C are 1.8×10^{-9} s^{-1} and 7.0×10^{-12} M s^{-1}. $Cr(H_2O)_5(NH_3)^{3+}$ aquates significantly faster than expected on the basis of the linear correlation between $-\log k_0$ and pK_a of the free ligands established for the analogous complexes with a series of substituted pyridine ligands. Implications of this observation are discussed.

INTRODUCTION

The aquation kinetics of a series of ligandpentaaquachromium(III) complexes were recently reported where the ligands were substituted pyridines[1]. A linear correlation was observed between the logarithm of the aquation rates and the logarithm of the conjugate acid dissociation constant of the free ligands. The degree of sensitivity of the aquation rates to the basicity of the free pyridine ligands was compared with the one observed for the analogous monosubstituted chromium(III) complexes with a series of uninegative ligands[2] and possible mechanistic implications were discussed. The complexes of the series[1], studied in aqueous perchlorate medium, contained electronically unsaturated amine ligands and an extension of the series to include the saturated ammine ligand seemed appropriate. The available kinetic data on the aquation of the $Cr(H_2O)_5NH_3{}^{3+}$ ion in nitrate medium[3] could not be used since it was shown that nitrate ion catalyzed aquation of this chromium(III) complex[4].

Here we report the rate and activation parameters for both acid-independent and acid-dependent paths of the aquation of the $Cr(H_2O)_5NH_3{}^{3+}$ ion in perchlorate medium. Since the completion of this work kinetic data on the aquation by the acid-independent path have appeared in the literature[5,6].

EXPERIMENTAL

Materials

The aqueous solution of $Cr(H_2O)_5NH_3{}^{3+}$ was prepared by the literature method[7]. It was purified on a Dowex 50w — x8 ion-exchange column using 1 M and 3 M $HClO_4$. Chromium(III) was determined as Cr(VI) after oxidation with alkaline hydrogen peroxide[8]. The absorption spectrum of $Cr(H_2O)_5NH_3{}^{3+}$ obtained on a Cary 17 spectrophotometer agreed with that previously reported[6] (λ_{max} 546 (ε 19.8) and 396 nm (ε 18.4)). The other chemicals, all analytical grade »Merck«, were used without further purification. Double-distilled water was used throughout.

Kinetic Measurements

The technique using ampoules was employed as previously described[9], and the progress of the reaction was followed spectrophotometrically using a Cary 17 instrument. The decrease in absorbance was measured at 200 nm, where the $Cr(H_2O)_5(NH_3)^{3+}$ and $Cr(H_2O)_6^{3+}$ ions have molar absortivities 809 and 219 cm^{-1} mol^{-1}, dm^3, respectively. First-order rate constants were calculated from the slopes of the straight lines obtained by plotting log $(E_t - E_\infty)$ *vs.* time, where E_t and E_∞ are the absorbances at time *t* and after 10 half-lives of the reaction. Linearity of the plots was preserved for at least three half-lives of the reaction. E_∞ agreed with the absorption for the product ions.

RESULTS

The aquation reaction

$$Cr(H_2O)_5(NH_3)^{3+} \xrightarrow[H_2O]{H^+} Cr(H_2O)_6^{3+} + NH_4^+$$

was studied at 80.2 to 99.9 °C and the ionic strength 1.0 M adjusted by $NaClO_4$. At particular hydrogen ion concentration and amminechromium(III) concentration in the range of 3×10^{-4} to 2×10^{-3} M the aquation rate is given by

$$-d[Cr(H_2O)_5(NH_3)^{3+}]/dt = k_{obsd}\,[Cr(H_2O)_5(NH_3)^{3+}]$$

and the first-order rate constants, k_{obsd}, observed at different temperatures are presented in Table I. At a constant temperature k_{obsd} is linearly dependent upon $(H^+)^{-1}$ and given by

$$k_{obsd} = k_o + k_{-1}\,[H^+]^{-1} \qquad (1)$$

as it is usually found for monosubstituted chromium(III) complexes when the coordinated ligand has low or no residual basicity[10]. This behavior is consistent with the reaction proceeding by two paths:

$$\text{Rate} = k_o\,[Cr(H_2O)_5\,(NH_3)^{3+}] + k'_{-1}\,[Cr(H_2O)_4\,(OH)\,(NH_3)^{2+}]$$

TABLE I

The first-order rate constants observed for the aquation of amminepentaaquachromium(III) ion at $\mu = 1.00$ M ($NaClO_4 + HClO_4$)[a]

T, °C	10^2 $HClO_4$, M	$10^5\,k_{obsd}{}^b$, s^{-1}	T, °C	10^2 $HClO_4$, M	$10^5\,k_{obsd}{}^b$, s^{-1}
99.9	100	2.85	89.8	1.63	3.00
99.9	3.14	6.72	80.2	100	0.329
99.9	1.63	10.1	80.2	3.14	0.593
89.8	100	1.01	80.2	1.63	0.828
89.8	3.14	1.96			

[a] $[Cr(H_2O)_5(NH_3)^{3+}] = 3 \times 10^{-4}$ to 2×10^{-3} M. [b] The average of two runs for a set of the conditions.

where $k'_{-1} = k_{-1}/K_h$, $1 \gg K_h (H^+)^{-1}$, and K_h is the equilibrium constant for the acid dissociation reaction (2),

$$Cr(H_2O)_5\,NH_3^{3+} \leftrightharpoons Cr(H_2O)_4\,(OH)NH_3^{2+} + H^+ \tag{2}$$

the value of which is not known.

The activation parameters were simultaneously computed for the both reaction paths given by (1) using a non-linear least squares program as described previously[1]. The values obtained are $\Delta H_o^{\ddagger} = 27.8 \pm 0.4$ kcal mol^{-1}, $\Delta S_o^{\ddagger} = -5.3 \pm 1.2$ cal mol^{-1} K^{-1}, $\Delta H_{-1}^{\ddagger} = 34.8 \pm 0.6$ kcal mol^{-1}, and $\Delta S_{-1}^{\ddagger} = 7.0 \pm 1.7$ cal mol^{-1} K^{-1}. The uncertainties quoted are standard deviations. The fitted values of k_{obsd} agreed with the experimental ones with an average deviation of 1.4% and the largest individual deviation of 3.0%. The specific rates extrapolated to 25 °C are $k_o = 1.8 \times 10^{-9}$ s^{-1} and $k_{-1} = 7.0 \times 10^{-12}$ M^{-1} s^{-1}.

Our $\Delta H_o^{\ddagger}$ value agrees well with the Arrhenius activation energy of 28.7 ± 0.3 kcal mol^{-1} reported by Mønsted and Mønsted[6], once the latter is diminished for RT (0.6 kcal mol^{-1}). The activation parameters for the acid-independent path reported by Guastalla and Swaddle differ more significantly[5].

DISCUSSION

The rate constants and the activation parameters for the aquation of 3+ charged aminepentaaquachromium(III) ions thus far studied are collected in Table II. The rate constants for the both paths decrease with the increase in pK_a of the free ligands. A linear dependence between $-\log k_o$ or $-\log k_{-1}$ upon pK_a for the pyridine-type ligands was graphically shown previously[1]. At 70 °C, a common temperature which requires the least extrapolation of the rate data, an excellent linearity is given by

$$-\log k_o = 0.457\ pK_a + 2.92 \tag{3}$$

$$-\log k_{-1} = 0.424\ pK_a + 4.31 \tag{4}$$

TABLE II

The specific rates and activation parameters for the aquation of aminepentaaquachromium(III) ions at ionic strength 1.0 M ($NaClO_4 + HClO_4$)

Amine	pK_a (free ligand)	70 °C		$\Delta H_o^{\ddagger}$ kcal mol^{-1}	$\Delta S_o^{\ddagger}$ cal mol^{-1} K^{-1}	$\Delta H_{-1}^{\ddagger}$ kcal mol^{-1}	$\Delta S_{-1}^{\ddagger}$ *cal* mol^{-1} K^{-1}
		$10^5\ k_o$ s^{-1}	$10^6\ k_{-1}$ M s^{-1}				
3-Cyanopyridine[a]	1.35[e]	29	14	23.9	—5.2	31.7	11.3
3-Chloropyridine[a]	2.81[e]	6.2	3.1	26.3	—1.6	33.5	13.7
4-Amidopyridine	3.61[f]	4.3[h]	—	—	—	—	—
Pyridine[b]	5.21[e]	0.55	0.3	27.2	—3.5	35.6	15.2
3-Methylpyridine[c]	5.67[e]	0.25	0.22	31.3	6.9	34.7	11.8
Ammine[d]	9.47[g]	0.097	0.019	27.8	—5.3	34.8	7.0

[a] Ref. 1. [b] Ref. 9. [c] Ref. 10. [d] This work. [e] The value at 25 °C: F. Fischer, W. J. Galloway, and J. Vaughan, *J. Chem. Soc.* (1964) 3591. [f] The value at 20 °C: H. H. G. Jellinek, and J. R. Urwin, *J. Phys. Chem.* 58 (1954) 548. [g] T. H. Wirth and N. Davidson, *J. Amer. Chem. Soc.* 86 (1964) 4325. [h] The value in 1 M $HClO_4$: F. Nordmayer and H. Taube, *J. Amer. Chem. Soc.* 90 (1968) 1162.

However, the aquation rates of Cr $(H_2O)_5$ $(NH_3)^{3+}$ obtained in this work do not conform to these expressions. The acid-independent rate constant k_o is 17 fold faster than expected by expression 3 and k_{-1} is four fold faster than expected by (4).

The likely reasons for this behaviour of Cr $(H_2O)_5$ $(NH_3)^{3+}$ are its departure from a monotonous change in the solvation effect on the rate and/or in the strength and nature of the chromium(III)-nitrogen bond with the change in pK_a along the series of the amine ligands. The activation parameters for the acid-independent path presented in Table II appear to offer some insight into the relative extent of these effects on the aquation rates of aminepentaaquachromium(III) species (the activation parameters presented for the acid-inverse path are composite values).

$\Delta S_o^{\ddagger}$ do not change regularly and have similar values along the series, with the exception of the 3-picoline complex. The extent of solvation of the activated state as compared to the initial state, usually associated with the entropy of activation, does not seem to change significantly along the series. The increased inertnes of the amine complexes with increasing pK_a of the free ligands is thus brought about primarily by increase in $\Delta H_o^{\ddagger}$, its value for Cr $(H_2O)_5$ $(NH_3)^{3+}$ being lower than expected on this basis. In a predominantly dissociative mode of activation, by which aquation of these complexes is believed to proceed[1], the increase in $\Delta H_o^{\ddagger}$ reflects an increase in the chromium(III)-nitrogen bond strength. pK_a of the free ligand may be considered as a sort of relative measure of the extent of σ bonding for the interaction between the hard chromium(III) center and the hard nitrogen atom of the ligands. The observation that the typical σ-bonding ammine ligand dissociates significantly faster than expected by the linear expression 3 established for the pyridine-type ligands and has lower $\Delta H_o^{\ddagger}$ strongly indicates to the additional π-bonding interaction between the latter series of ligands and the chromium(III) center.

Information on chromium(III)-unsaturated amine bonding have been very scarce. Recently, spectroscopic evidence was offered for π-back-bonding to pyridine in *trans*-diacidotetrapyridinechromium(III) complexes[11,12].

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SAŽETAK

Kinetika akvacije aminpentaakvokrom(III) iona. Usporedba s nezasićenim aminskim ligandima

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Studirana je akvacija aminpentaakvokrom(III) iona kao funkcija kiselosti i temperature u 1.0 M ionskoj jakosti ($HClO_4 + NaClO_4$). Zakon brzine reakcije ima oblik: $-d \ln [Cr(H_2O)_5(NH_3)^{3+}]/dt = k_o + k_{-1}/[H^+]$. Entalpija (kcal mol^{-1}) i entropija (cal mol^{-1} K^{-1}) aktivacije za put neovisan o kiselosti su 27.8 i —5.3, a za put obrnuto ovisan o kiselosti 34.8 i 7.0. Odgovarajuće konstante brzine reakcije ekstrapolirane na 25 °C su 1.8×10^{-9} s^{-1} i 7.0×10^{-12} M s^{-1}. $Cr(H_2O)_5(NH_3)^{3+}$ podliježe akvaciji znatno brže nego što bi se očekivalo na osnovu linearne korelacije između $-\log k_o$ i pK_a slobodnih liganada ustanovljene za analogne komplekse s nizom supstituiranih piridinskih liganada. Diskutirane su implikacije ovih zapažanja.

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