THE ACID DISSOCIATION CONSTANTS OF AQUOPENTAMMINECOBALT(III) AND AQUOPENTAMMINECHROMIUM(III) CATIONS IN WATER, DEUTERIUM OXIDE, AND AQUEOUS DIOXAN*

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In connection with our recent investigations on nucleophilic octahedral substitutions, it is necessary to compare the acid-strengths of metal complexes in various solvents measured under identical conditions. The information required for such comparison was apparently not available and the present work was therefore initiated to determine the acid dissociation constants of aquopentamminecobalt(III) and aquopentamminechromium(III) cations in water, deuterium oxide, and aqueous dioxan (20% w/w) at 20° and ionic strength of 0·1M.

$$[M(NH_3)_5OH_2]^{3+} \overset{K_a}{\rightleftharpoons} [M(NH_3)_5OH]^{2+} + H^+ \qquad (M = Co \text{ and } Cr)$$

These complexes were supplied as the nitrates and the ionic strength of the solution was controlled by means of sodium nitrate. The data obtained are collected in Table 1.

Table 1

ACID DISSOCIATION CONSTANTS OF $[M(NH_3)_5OH_2]^{3+}$ CATIONS AT 20° AND IONIC STRENGTH OF 0·1M IN VARIOUS SOLVENTS

Metal	Solvent	pK_a (obs.)	pK_a (corr.)*	K_a (mole/l.)
Co	water	6·18	6·18	$6·61 \times 10^{-7}$
Co	deuterium oxide	6·35	6·67	$2·14 \times 10^{-7}$
Co	aqueous dioxan (20% w/w)	6·33	6·30	$5·01 \times 10^{-7}$
Cr	water	5·10	5·10	$7·94 \times 10^{-6}$
Cr	deuterium oxide	5·26	5·58	$2·63 \times 10^{-6}$
Cr	aqueous dioxan (20% w/w)	5·28	5·25	$5·62 \times 10^{-6}$

* See Experimental.

On changing the solvent from water to deuterium oxide, the dissociation constant of the cobalt(III) acid is reduced by a factor of 3·09, while the corresponding factor for the chromium(III) acid is very similar (3·02). This has a direct bearing on the mechanisms which have been put forward for explaining the deuterium isotope effect on octahedral base hydrolysis. In general, any mechanism which invokes a large difference between the cobalt(III) and the chromium(III) cases with respect to

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deuterium isotope effect on acidities would therefore appear to be remote from the truth. The present results find their counterpart in observations among organic weak acids, e.g., acetic acid,[1] which is known to be less dissociated in deuterium oxide. In view of the rapid deuterium exchange of these complexes, it is assumed that the observed data refer to the dissociation of a deuteron from the deuterated cation in deuterium oxide, i.e.

$$[M(ND_3)_5OD_2]^{3+} \overset{K_a}{\rightleftharpoons} [M(ND_3)_5OD]^{2+} + D^+ \qquad (M = Co \text{ and } Cr)$$

and that the amount of protium oxide so formed is negligibly small.

On adding dioxan to water, the dielectric constant of the latter is reduced. A decrease in dielectric constant of solvent generally makes separation of ions more difficult and hence reduces the dissociation constants of acids. This effect is rather marked for most organic acids because they are neutral. For example, the dissociation constants of acetic acid[2] in water and 20% w/w aqueous dioxan at 20° are respectively $1 \cdot 75 \times 10^{-5}$ and $5 \cdot 09 \times 10^{-6}$, i.e. a reduction factor of 3·44. However, for cationic acids, electrostatic repulsion will tend to favour separation of the proton. The two effects act in opposition and so the overall effect is small, as shown by the present data, where the corresponding reduction factors are 1·32 (Co) and 1·41 (Cr) respectively.

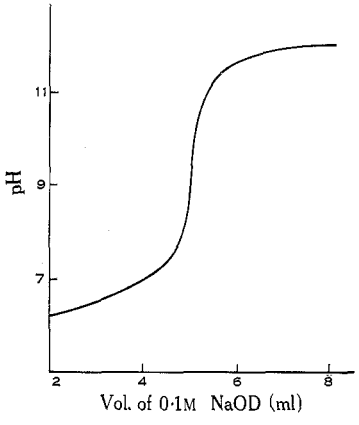

Fig. 1—pH titration curve for the addition of sodium deuteroxide solution to a solution of $[Co(ND_3)_5OD_2](NO_3)_3$ in deuterium oxide at 20° and ionic strength of 0·1M.

Experimental

Aquopentamminecobalt(III) nitrate was prepared from carbonatopentamminecobalt(III) nitrate by the method of Basolo and Murmann.[3] The crude product was purified by dissolving in the minimum amount of water, filtering, and adding cold nitric acid (1 : 1). The crystals obtained on cooling were filtered off, washed with alcohol and ether, and then air-dried (Found: equiv. wt., 116. Calc. for $[Co(NH_3)_5OH_2](NO_3)_3$: equiv. wt., 116).

[1] Gary, R., Bates, R. G., and Robinson, R. A., *J. phys. Chem.*, 1965, **69**, 2750.
[2] Harned, H. S., and Owen, B. B., "The Physical Chemistry of Electrolytic Solutions." 3rd Edn, p. 756. (Reinhold: New York 1958.)
[3] Basolo, F., and Murmann, R. K., *Inorg. Synth.*, 1953, **4**, 171.

Aquopentamminechromium(III) nitrate was prepared from its ammonium nitrate double salt by the method of Mori.[4] The product was purified by dissolving in the minimum amount of water, filtering, and adding cold concentrated nitric acid. The crystals were filtered off, washed with alcohol and ether, and then air-dried (Found: equiv. wt., 114. Calc. for $[Cr(NH_3)_5OH_2](NO_3)_3$: equiv. wt., 114).

The equivalent weight of these complexes was determined by passing a solution containing a known amount of the salt through a cation-exchange resin column (Amberlite IR 120; H^+ form) and titrating the acid in the effluent and washings with standard alkali.

The pK_a values of these complexes in water, deuterium oxide, and aqueous dioxan (20% w/w) were determined by titrating the aquo cations with standard sodium hydroxide or sodium deuteroxide using a glass electrode as indicator and a Pye Dynacap pH-meter. A typical titration curve (for the cobalt complex in deuterium oxide) is shown in Figure 1. The pH-meter was standardized on buffer solutions in water only, but corrections were made to the observed pK_a values in deuterium oxide ($+0\cdot32$) and aqueous dioxan ($-0\cdot03$) by carrying out the measurements on acetic acid in these solvents and comparing the results with literature values.[1,2]

The water used was freed from dissolved carbon dioxide by boiling, and then cooling under an atmosphere of nitrogen. The deuterium oxide supplied had a purity of not less than 99·7% and was used without further purification. Dioxan was refluxed over sodium and fractionally distilled (b.p. 101·5°/760 mm). Sodium deuteroxide solution was prepared by dissolving cleaned dried metallic sodium in deuterium oxide and standardized with acid.

Acknowledgments

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[4] Mori, M., *Inorg. Synth.*, 1957, **5**, 131.