Exchange Rate of Co-ordinated Water Molecules at Acidoaquo Complexes

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Summary The rate of water exchange at an acidoaquo complex ML, $k^{-\mathrm{H_2O}}_{\mathrm{ML}}$, is related to the electron donating ability (E_n) of the ligand L, by equation (1); the proportionality constant γ is estimated for chromium(III), cobalt(II), iron(III), nickel(II), and oxovanadium(IV), and is correlated with the softness parameter σ using equation (2).

$$\log(k^{-\mathrm{H_2O}}_{\mathrm{ML}}/k^{-\mathrm{H_2O}}_{\mathrm{M}}) = \gamma E_n \qquad (1)$$

$$\gamma = -\,5{\cdot}5\sigma + 5{\cdot}5 \qquad (2)$$

It has been demonstrated[1] that the logarithmic rate constant of the water exchange at some acidoaquonickel(II) complexes, $\log(k^{-\mathrm{H_2O}}_{\mathrm{ML}})$, is linearly related to the electron donating ability (E_n) of the co-ordinated ligand L,[2] according to equation (1), where $k^{-\mathrm{H_2O}}_{\mathrm{ML}}$ is the rate constant of exchange of a water molecule H_2O^* at an acidoaquometal complex $ML(OH_2)_{h-1}{}^*OH_2$; [equation (3)] and h is the

$$ML(OH_2)_{h-1}{}^*OH_2 + H_2O \xrightarrow{k^{-\mathrm{H_2O}}_{\mathrm{ML}}} ML(OH_2)_h + H_2O^* \quad (3)$$

number of water molecules attached to ML. E_n has been proposed by Edwards[2] as a measure of the electron donating ability, and is defined by $E_n = E^0 + 2{\cdot}60$, where E^0 is the standard oxidation potential for the process: $2L^- \rightleftharpoons L_2 + 2e^-$. Equation (1) has been derived from mechanistic considerations of the formation constant of metal complexes.[3] The parameter γ is important in understanding not only the solvent exchange but also ligand substitution reactions in which the dissociation of a water molecule from ML is rate-determining. Equation (1) is similar to the Hammett equation;[4] γ is a constant characteristic of a metal ion and may be regarded as a reaction constant for the solvent exchange at acidoaquo complexes, while E_n is regarded as a substituent constant.

TABLE

Metal ions	Cr^{3+}	Co^{2+}	Fe^{3+}	Ni^{2+}	VO^{2+}
γ	2·2	0·47	1·2	0·40	1·3
σ	0·65	0·92	0·78	0·94	0·71

The left-hand side of equation (1) has been plotted against the electron donating ability of L for chromium(III),[5] cobalt(II),[6] iron(III),[7] nickel(II),[1,8] and oxovanadium(IV)[9] complexes (see Figure). The values of γ for these metal ions are determined from the slope of these plots and are given in the Table together with the softness parameter σ estimated previously.[10]

Interestingly γ is correlated with the softness parameter of the metal ion[10] using equation (2). The harder the metal ion, the more sensitive is the water exchange rate to the electron donating ability of the ligand(s) already attached. This seems reasonable because soft metal ions form bonds with more covalent character, *via* extensive back-donation, than hard metal ions.

The value of σ is known for 26 metal ions,[10] so γ may be predicted using equation (2) for these metal ions, providing the equation remains valid for all cases.

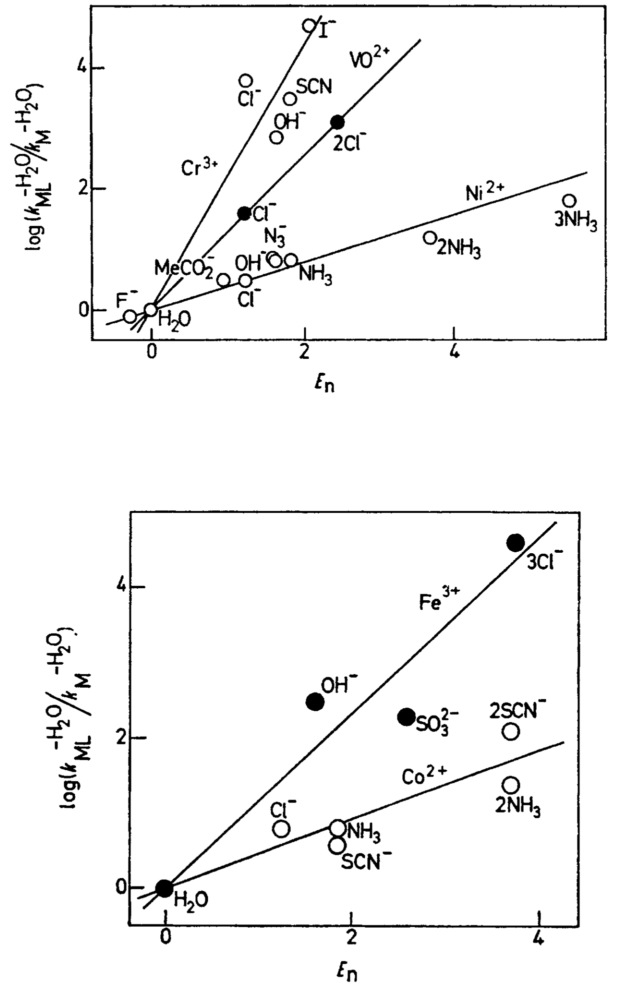

FIGURE. Plots of $\log(k^{-\mathrm{H_2O}}_{\mathrm{ML}}/k^{-\mathrm{H_2O}}_{\mathrm{ML}})$ *vs* E_n for Cr^{3+}, Co^{2+}, Fe^{3+}, Ni^{2+}, and VO^{2+} metal ions. Data sources: Cr^{3+}, ref. 5(a)(H_2O, hydroxide), ref. 5(b) (thiocyanate, chloride and iodide); Co^{2+}, ref. 6(a) (H_2O and chloride), ref. 6(b) H_2O and ammines), ref. 6(c) (H_2O and thiocyanates); Fe^{3+}, ref. 7(a) ($SO_3{}^{2-}$), ref. 7(b) (H_2O and hydroxide), ref. 7(c) (chloride); Ni^{2+}, ref. 1 (H_2O, hydroxide, azide, acetate and fluoride), ref. 8(a) (H_2O and ammines), ref. 8(b) (chloride); for VO^{2+} ref. 9 (H_2O and chlorides).

(*Received, 2nd December* 1975; *Com.* 1341.)

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