ABSTRACT

Ag(I), Hg (II), Tl(III), Fe(III) and other metal ions assisted aquation reactions of Cr(III), Co(III) and Rh(III) complexes are reviewed.

Studies on ultraviolet spectra and the aquation rates in the presence of silver ions show that four complexes are formed between the iodopenta-amminerhodium(III) cation and silver ions according to equations (i) and (ii)

$$2\ Rh(NH_3)_5I^{2+} + Ag^+ \overset{\beta_{21}}{\rightleftharpoons} [Rh(NH_3)_5I]_2Ag^{5+} \qquad (i)$$

$$Rh(NH_3)_5I^{2+} + nAg^+ \overset{\beta_n}{\rightleftharpoons} [Rh(NH_3)_5IAg_n]^{(2+n)+} \qquad (ii)$$

where n = 1, 2 and 3.

The stability constants obtained potentiometrically for $Rh(NH_3)_5IAg^{3+}$ and $[Rh(NH_3)_5I]_2Ag^{5+}$ are respectively $10^{3.07}$ and $10^{6.05}$ at 25°C and 0.10 mol ℓ^{-1} ionic strength. The enthalpy and entropy of formation of $Rh(NH_3)_5IAg^{3+}$ are -40.18 kJ mol^{-1} and -79.8 JK^{-1} mol^{-1} respectively.

From computer fitting of rate data, the pseudo-first order rate constants, k, for the silver ion assisted aquation of $Rh(NH_3)_5I^{2+}$ at 48.63°C and 1.0 mol ℓ^{-1} ionic strength are reproduced by equation (iii)

$$k/s^{-1} = \frac{2.0 \times 10^{-7} + 5.73 \times 10^{-3}\,[Ag] + 0.604[Ag]^2 + 3.53[Ag]^3}{1 + 77.3[Ag] + 86.7[Ag]^2 + 33.6[Ag]^3} \qquad (iii)$$

up to [Ag] of 1.0 mol ℓ^{-1}.

The overall formation constants, β^{C}_{n}, at zero ionic strength and 48.63°C of the complexes n = 1 to 3 in equation (ii) are respectively 16.6 $\ell\ mol^{-1}$, 1.56 $\ell^2\ mol^{-2}$ and 0.02 $\ell^3\ mol^{-3}$. The corresponding spontaneous aquation rate constants are $7.42 \times 10^{-5}\ s^{-1}$, $6.97 \times 10^{-3}\ s^{-1}$ and $0.105\ s^{-1}$, respectively.

At 76.41°C kinetic studies show that the silver ion assisted aquation of $Rh(NH_3)_5I^{2+}$ at low silver ion concentrations proceeds via the $Rh(NH_3)_5IAg^{3+}$ ion. The rate constants, k_2°, for the induced aquation at zero ionic strength are given by equation (iv)

$$k_2^{\circ} / \ell\ mol^{-1}\ s^{-1} = 3.44 \times 10^7 \exp - (63{,}798/RT) \qquad (iv)$$

with activation energy of 63.80 kJ mol^{-1}.

Analysis of previous work at 42.04°C [22] combined with the present results at 48.63°C give Arrhenius equations for the spontaneous aquation of the complexes as follows:-

$\underline{Rh(NH_3)_5IAg^{3+}}$

$$k = 7{\cdot}7 \times 10^{22} \exp - (16_6 \times 10^3/RT) \qquad (v)$$

$\underline{Rh(NH_3)_5IAg_2^{4+}}$

$$k = 4{\cdot}5 \times 10^{22} \exp - (15_3 \times 10^3/RT) \qquad (vi)$$

$\underline{Rh(NH_3)_5IAg_3^{5+}}$

$$k = 3{\cdot}7 \times 10^{20} \exp - (13_3 \times 10^3/RT) \qquad (vii)$$

where R is in Joules.

For the interactions of silver ions with isothiocyanatopenta-ammine complexes of Cr(III), Co(III) and Rh(III), the stability constants for the formation of 1:1 complexes, determined potentiometrically, are $10^{2.97}$, $10^{3.35}$ and $10^{3.38}$, respectively at 25°C and 0.10 mol ℓ^{-1} ionic strength. Adducts which analyse for $[Cr(NH_3)_5NCSAg](ClO_4)_3$, $[Cr(NH_3)_5NCSAg_2](NO_3)_4$, $[Co(NH_3)_5NCSAg](ClO_4)_3$ and $[Co(NH_3)_5NCSAg_2](NO_3)_4$ have been isolated as solids and their infrared spectra studied.

The silver ion assisted aquation of $Cr(NH_3)_5NCS^{2+}$ at 76.41°C and 0.10 mol ℓ^{-1} proceeds via the $Cr(NH_3)_5NCSAg^{3+}$ ion. The spontaneous aquation rate constants of the ions are 2.77×10^{-5} s^{-1} and 5.57×10^{-4} s^{-1} respectively.

Preliminary results on the kinetics of formation of silver ion containing complexes by stopped-flow spectrophotometry are reported. The formation of $Co(NH_3)_5NCSAg_3^{2+}$, in a stepwise manner from $Co(NH_3)_5NCSAg_2^{4+}$ with rate constant 0.158 s^{-1} at 25°C, is indicated. The overall formation constant for $Co(NH_3)_5NCSAg_2^{4+}$ from these kinetic data is 5.21×10^4 $\ell^2 mol^{-2}$ at 25°C and 0.10 mol ℓ^{-1} ionic strength.

Formation of an outersphere complex with rate constant 673 ℓ mol^{-1} s^{-1} is indicated for the $Rh(NH_3)_5I^{2+}$ - Ag^+ interaction at 25°C and 0.10 mol ℓ^{-1} ionic strength. This is followed by rearrangement and/or further reaction with silver ions prior to the aquation reaction.