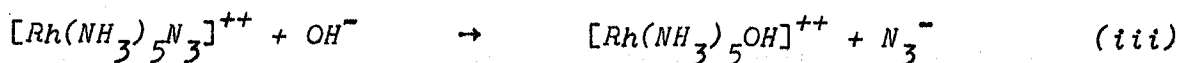
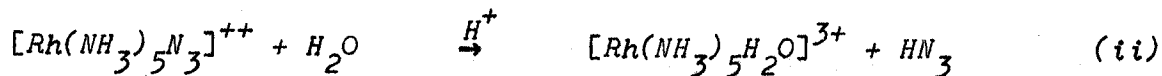
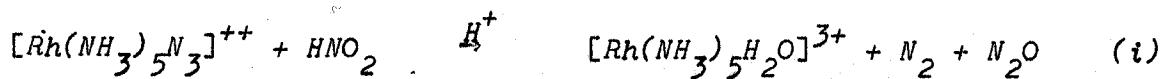


A B S T R A C T

The kinetics and mechanisms of the reactions of acidopentammine complexes are reviewed. The kinetics of the following reactions of azidopentamminerhodium(III) perchlorate were studied spectrophotometrically by measuring the rate of disappearance of the complex ion.



At 25°C the rate law for reaction (i) is

$$-\frac{d[\text{Complex}]}{dt} = [402[\text{H}^+][\text{HNO}_2] + 2730[\text{HNO}_2]^2][\text{Complex}] \quad (\text{iv})$$

and is consistent with a mechanism involving concurrent reactions of the nitrous acidium ion and dinitrogen trioxide with the complex ion. Support for the mechanism was obtained from the increase of the rate constant for the acid catalysed reaction pathway with ionic strength.

Reaction (ii) is acid catalysed. At perchloric acid concentrations in the range 7-70 millimoles litre⁻¹, the measured pseudo-first-order rate constant varies according

to equation (v)

$$k = k_a + k_2^0 [H^+] 10^{4AI^{1/2}} (1 + I^{1/2}) \quad (v)$$

where I is the ionic strength, A is a Debye-Huckel parameter and k_a and k_2^0 are the rate constants for the spontaneous and acid catalysed reactions at zero ionic strength respectively. The rate constants vary with temperature according to equations (vi) and (vii).

$$k_a = 4.78 \times 10^{10} \exp(-28,400/RT) \quad (vi)$$

$$k_2^0 = 3.80 \times 10^9 \exp(-24,580/RT) \quad (vii)$$

At 87.45°C at high perchloric acid concentrations a limiting rate is reached at perchloric acid concentrations greater than $8M$ indicating that the complex is completely protonated under these conditions. Spectrophotometric evidence for protonation is also presented.

Reaction (iii) was studied at low ionic strengths in the temperature range $77-97^\circ\text{C}$. The results are in agreement with the Bronsted-Bjerrum theory of the primary salt effect. The temperature variation of the second order rate constants at zero ionic strength is given by equation (viii).

$$k_2^0 = 6.03 \times 10^{18} \exp(-34,460/RT) \quad (viii)$$

The kinetic data for these reactions of $[\text{Rh}(\text{NH}_3)_5\text{N}_3]^{++}$ have been compared with similar data for the analagous reactions of other acidopentammine complexes.