Dinitrogen Complexes of Osmium(III) and Ruthenium(III) Ammines

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Summary Electrochemical oxidation of known dinitrogen complexes in aqueous solution has been shown to produce transient $[Os(NH_3)_5N_2]^{3+}$ and $[(NH_3)_5RuN_2Ru(NH_3)_5]^{5+}$ species with decomposition rate constants of 0·02 sec^{-1} and 0·10 sec^{-1}, respectively; no $[Ru(NH_3)_5N_2]^{3+}$ was detected.

WE have been studying the electrochemistry of the dinitrogen complexes of Os^{II} and Ru^{II} and our results are consistent with the following:

(1) $[Os(NH_3)_5N_2]^{2+} \xrightleftharpoons{\text{rev}} [Os(NH_3)_5N_2]^{3+} + e$

$$[Os(NH_3)_5N_2]^{3+} \xrightarrow{k\,=\,0{\cdot}02\ \mathrm{sec}^{-1}} [Os(NH_3)_5(H_2O)]^{3+} + N_2$$

(2) $[(NH_3)_5RuN_2Ru(NH_3)_5]^{4+} \xrightleftharpoons{\text{rev}} [(NH_3)_5RuN_2Ru(NH_3)_5]^{5+} + e$

$$[(NH_3)_5RuN_2Ru(NH_3)_5]^{5+} \xrightarrow{k\,=\,0{\cdot}1\ \mathrm{sec}^{-1}} [Ru(NH_3)_5N_2]^{2+} + Ru^{III}(NH_3)_5X\dagger$$

(3) $[Ru(NH_3)_5N_2]^{2+} \rightarrow Ru^{III}(NH_3)_5X\dagger + N_2 + e$

The starting materials were prepared according to published procedures.[1] All potentials reported are relative to a saturated calomel reference. The work was carried out at 25·0°.

For $[Os(NH_3)_5N_2]^{2+}$, controlled-potential oxidation in a 0·08 M-$MeSO_3H$ electrolyte on Pt at +0·32 V consumed 1·0 faraday per mole and gave a solution with a u.v.

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† $X = SO_4^{2-}$ or HSO_4^- in sulphate electrolyte.

spectrum[2] consistent with that of $[Os(NH_3)_5(H_2O)]^{3+}$. Cyclic voltammetry on the $[Os(NH_3)_5N_2]^{2+}$ was carried out in a H_2SO_4–K_2SO_4 electrolyte (pH 1·1, μ = 0·31) at a Pt disc electrode. The forward scan gave an anodic peak (E_p = + 0·315 v) and the reverse scan a cathodic peak (E_p = + 0·255 v). The voltammograms were entirely consistent with the requirements for a reversible one-electron charge-transfer followed by a break up of the product.[3,4] Decomposition of the $[Os(NH_3)_5N_2]^{3+}$ was observed only at slow scan rates: the ratio of peak currents, $(i.p.)_c/(i.p.)_a$, was significantly less than 1. The rate constant for the decomposition was determined from the voltammograms[3] using scan rates of 10, 20, and 50 mv sec^{-1} and switching potentials of +0·375 to +0·475 v. The results were also confirmed by double-potential step chronoamperometry[5] using pulses of 2·5 to 10 sec duration. A rate constant for the decomposition of 2×10^{-2} sec^{-1} was consistently obtained.

Controlled-potential oxidation of the dimeric $[(NH_3)_5RuN_2Ru(NH_3)_5]^{4+}$ in a H_2SO_4–K_2SO_4 electrolyte (pH 2·3, μ = 0·30) on Pt at +0·50 v consumed 1·0 faraday per mole. The products were $[Ru(NH_3)_5N_2]^{2+}$ and $Ru^{III}(NH_3)_5X$ in a 1 : 1 mole ratio as determined by the u.v. spectrum and polarography, respectively.[6] Cyclic voltammetry in a 0·28 M-H_2SO_4 electrolyte at a Pt disc electrode gave an anodic peak (E_p = + 0·495 v) on the forward scan and a cathodic peak (E_p = + 0·435 v) on a reverse scan. The criteria used before were again consistent with a reversible one-electron charge-transfer followed by break up of the product. The rate constant for the decomposition was a consistent 1×10^{-1} sec^{-1} (scan rates 10 to 200 mv sec^{-1} for switching potential of +0·600 v; 5 sec pulses).

Controlled-potential oxidation of the $[Ru(NH_3)_5N_2]^{2+}$ in the H_2SO_4–K_2SO_4 electrolyte (pH 2·3, μ = 0·30) on Pt at +0·72 v consumed 1·0 faraday per mole and gave a solution with the u.v. spectrum[6] characteristic of $Ru^{III}(NH_3)_5X$. However, in this case, cyclic voltammetry did not give evidence for the formation of $[Ru(NH_3)_5N_2]^{3+}$ even at scan rates up to 100 v sec^{-1}. Rather, the forward scan on a graphite electrode gave an anodic peak (E_p = + 0·81 v) while the reverse scan gave a well displaced cathodic peak (E_p = − 0·33v at 100 mv sec^{-1}). This latter peak is characteristic of $Ru^{III}(NH_3)_5X$ in the sulphate electrolyte.

The existence of N_2 complexes of Os^{III} was first suggested by Chatt *et al.*[7] While we have not prepared a solid complex, our results substantiate their findings. The fact that we are unable to detect a monomeric Ru^{III}–N_2 complex may be attributed to a lack of stabilizing π back bonding. However the dimeric Ru^{III}–N_2–Ru^{II} complex is relatively stable, presumably due to the π back bonding from Ru^{II}.

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