Base Hydrolyses of Penta-ammineruthenium(III) Complexes of Organonitriles

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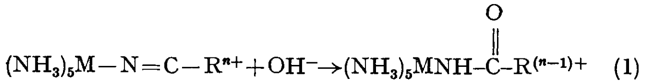
Summary Base hydrolysis of the $Ru(NH_3)_5^{3+}$ complex of acetonitrile to the corresponding complex of the acetamide anion occurs with a rate *ca.* 10^8 as fast as the free ligand, *ca.* 10^6 as fast as the analogous Ru^{II} complex, and more than 10^2 faster than the Rh^{III} analogue.

Co-ordination to cationic metal centres such as $Co(NH_3)_5^{3+}$ markedly enhances rates of base hydrolysis (1) of organonitriles to the corresponding co-ordinated amides;[1,2] however, reaction rates for other non-labile complexes have



$$(NH_3)_5M{-}N{=}C{-}R^{n+} + OH^- \rightarrow (NH_3)_5MNH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R^{(n-1)+} \quad (1)$$

not previously been reported. We have found that co-ordination to Ru^{III} results in a substantially greater rate enhancement. Moreover, homologous Ru^{III}, Rh^{III}, and Ru^{II} complexes show dramatic differences in the rate of hydrolysis which can be directly attributed to the metal ion electronic configurations and related metal–ligand interactions.

Reaction of the benzonitrile and acetonitrile complexes of $Ru(NH_3)_5^{3+}$ in weakly basic solution results in the corresponding benzamido and acetamido-complexes which have been characterized by their spectral and acid-base properties. Similarly, the Rh^{III} complex $Rh(NH_3)_5(MeCN)^{3+}$ hydrolyses in dilute NaOH solution to give $Rh(NH_3)_5(MeCONH)^{2+}$. Both acetamido-complexes have been isolated as the perchlorate salts and demonstrated to be identical to authentic complexes prepared by independent routes from acetamide and the aquopenta-ammine complexes by established procedures.[3,4] The authentic complexes were characterized by elemental analyses and spectral properties.

The Rh^{III} complex $Rh(NH_3)_5MeCN^{3+}$ hydrolyses in dilute aqueous NaOH according to the second-order rate law $\{v = k_{OH}\,[Rh(NH_3)_5(MeCN)^{3+}][OH^-]\}$ with $k_{OH} = 1{\cdot}0 \pm 0{\cdot}1$ l mol^{-1} s^{-1} (25°; μ 1·0M $NaClO_4$). The Ru^{III} analogues were sufficiently more reactive that HCO_3^-–CO_3^{2-} buffer solutions (pH 8—9) were used in order to follow the reactions by conventional spectral techniques. The reaction rate is a function of hydroxide and buffer concentrations, but extrapolation of observed rates to zero buffer concentration at different pH's allowed evaluation of k_{OH}. This was $2{\cdot}2 \times 10^2$ l mol^{-1} s^{-1} for the acetonitrile complex and $2{\cdot}0 \times 10^3$ l mol^{-1} s^{-1} for the benzonitrile complex, in both cases reactivity enhancements of more than 10^8 over the hydrolysis rates for the free ligands.[1,2] In contrast the Ru^{II} complex $Ru(NH_3)_5(MeCN)^{2+}$ is remarkably unreactive displaying only slow decomposition over a period of days in deaerated 0·1M aqueous NaOH. An upper limit of 6×10^{-5} l mol^{-1} s^{-1} can be assigned to k_{OH} under these conditions, an enhancement at most by a factor of 38 over the free ligand value ($1{\cdot}6 \times 10^{-6}$ l mol^{-1} s^{-1} at 25°).[2]

The reactivity of the $4d^6$ complex $Rh(NH_3)_5(MeCN)^{3+}$ toward hydrolysis is quite close to that of the homologous $3d^6$ Co^{III} ion $Co(NH_3)_5(MeCN)^{3+}$ ($k_{OH} = 3{\cdot}4$ l mol^{-1} s^{-1} at 25°)[2] under similar conditions. The much greater reactivity of the closely analogous $4d^5$ Ru^{III} complex must be attributed to the relative ability of Ru^{III} to act as a π-acceptor,[5] thus stabilizing the developing negative charge resulting from rate-determining hydroxide attack on the nitrile unit. Given that other 2+ metal ions have been shown to be effective in catalytic hydrolysis of organonitriles,[6] the remarkable unreactivity of the $4d^6$ Ru^{II} complex may reflect a kinetic effect of the demonstrated ability of the $Ru(NH_3)_5^{2+}$ unit's ability for π-backbonding into the nitrile ligand.[3,7]

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