Induced Electron Transfer in the Reaction of Hydroxyl Radicals with Pyridinepenta-amminecobalt(III) Ion in Aqueous Solution

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Summary The reaction of OH radicals with $(NH_3)_5Co^{III}$-py^{3+} ($k = 6{\cdot}5 \times 10^8$ M^{-1} s^{-1}) at pH 5·2 yields Co^{2+}; the OH-adduct to the pyridine ligand, detected by pulse radiolysis, undergoes slow first-order decay ($k = 6{\cdot}0$ s^{-1}).

THE reaction of hydroxyl radicals, generated in the pulse radiolysis of N_2O-saturated solutions, with $[(NH_3)_5Co^{III}$-py$](ClO_4)_3$ (5×10^{-4} M) at pH 5·2 revealed the formation of a transient absorption ($k = 6{\cdot}5 \times 10^8$ M^{-1} s^{-1}) with λ_{max} 320 nm (ϵ 1800 M^{-1} cm^{-1}) that was virtually identical to that obtained from the addition of OH radicals to free py or pyH^+.[1] The transient absorption decayed *via* dose-independent first-order kinetics with $k = 6{\cdot}0\ s^{-1}$ to yield a permanent product that showed a rising absorption at $\lambda < 320$ nm. Continuous ^{60}Co γ-radiolysis of N_2O-saturated solutions of 5—10 × 10^{-4} M $(NH_3)_5Co^{III}py^{3+}$ at pH 5—7 (buffered with 1 mM phosphate) generated Co^{2+} with $G(Co^{2+}) = 4{\cdot}4 \pm 0{\cdot}4$. The extent of reaction did not exceed 10%.

The reaction of OH radicals with $(NH_3)_5Co^{III}py^{3+}$ can be postulated as generating, in the first instance, a ligand radical co-ordinated to the Co^{III} centre through the addition of OH to the aromatic system: $(NH_3)_5Co^{III}(\dot{p}y\text{-}OH)^{3+}$. This intermediate decays in a first-order manner, unlike the OH-adducts to py/pyH^+[1] and $(NH_3)_5Co^{III}O_2CPh^{2+}$,[2] placing an upper limit of *ca.* $10^4\ M^{-1}\ s^{-1}$ for the rate constant of bimolecular processes. Although the +3 charge of the intermediate would cause the bimolecular specific rate to be less than that exhibited by the $(NH_3)_5Co^{III}O_2CP\dot{h}\text{-}OH^{2+}$ species ($2k = 9{\cdot}3 \times 10^7\ M^{-1}\ s^{-1}$),[2] the magnitude of the effect appears to be in excess of that expected on strictly electrostatic grounds.

Under conditions of continuous radiolysis, *ca.* 75% of e^-_{aq} ($G = 2{\cdot}0$) react with N_2O to yield OH in addition to the OH radicals ($G = 2{\cdot}8$) produced in the primary radiolytic step; *ca.* 25% of e^-_{aq} ($G = 0{\cdot}8$) react directly with the Co^{III} complex to form Co^{2+}. Thus, the observed yield of Co^{2+} cannot arise exclusively from the direct action of e^-_{aq}; we have also shown that the reaction of H atoms with the complex does not produce Co^{2+}. The observed yield of Co^{2+} can only arise if the OH-adduct to the pyridine ligand undergoes intramolecular electron transfer to reduce the metal centre; no Co^{2+} is formed from the reaction of OH with $(NH_3)_5Co^{III}O_2CPh^{2+}$.[3] The long lifetime of the radical intermediate makes the species highly susceptible to secondary reactions, such as with adventitious O_2, competing with its unimolecular decay.

Co-ordinated radical intermediates have been proposed for induced electron transfer processes in a number of cases.[4] Our results demonstrate that the OH radical, a very powerful one-electron oxidizing agent, can induce the reduction of the metal centre of a complex through the intermediacy of a co-ordinated ligand radical. We are currently examining in detail the characteristics of this and other co-ordinated radical species.

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[1] B. Cercek and M. Ebert, *Trans. Faraday Soc.*, 1967, **63**, 1687.

[2] M. Z. Hoffman and M. Simic, *J. Amer. Chem. Soc.*, 1970, **92**, 5533.

[3] H. Cohen and D. Meyerstein, *J. Amer. Chem. Soc.*, 1971, **93**, 4179.

[4] H. Taube, 'Electron Transfer Reactions of Complex Ions in Solution,' Academic Press, New York, 1970; P. Saffir and H. Taube, *J. Amer. Chem. Soc.*, 1960, **82**, 13; R. T. M. Fraser and H. Taube, *ibid.*, 1960, **82**, 4152; J. P. Candlin and J. Halpern, *ibid.*, 1963, **85**, 2518; R. Robson and H. Taube, *ibid.*, 1967, **89**, 6487; J. E. French and H. Taube, *ibid.*, 1969, **91**, 6951.