One-electron Reduction of Cobalt(III) Hexa-ammine Ion by Hydroxymethyl Radicals in Aqueous Solution

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Summary The reaction of $\cdot CH_2OH$ radicals with $[Co(NH_3)_6]^{3+}$, despite having an overall E° of *ca.* 1 V, generates less than one-tenth of the stoicheiometric amount of Co^{2+} in acidic solution; in neutral solution Co^{2+} and CH_2O are quantitatively produced.

THE hydroxymethyl radical, $\cdot CO_2OH$, is a powerful reducing agent[1] and it reacts rapidly[2] with $[Co(NH_3)_6]^{3+}$ generating Co^{2+} and CH_2O in neutral solution.[3] It has been assumed[2] that this electron-transfer reaction proceeds *via* an outer-sphere mechanism so that the reaction rate constant is directly related to the overall free energy change of the reaction.[4]

We have found that $\cdot CH_2OH$ radicals, generated in the continuous ^{60}Co γ-radiolysis of deoxygenated aqueous solutions containing 1M-MeOH, 5—10 × 10^{-4}M phosphate buffer, and saturated with N_2O, do not appreciably reduce 5 × 10^{-4}M $[Co(NH_3)_6]^{3+}$ (as the ClO_4^- or $CF_3SO_3^-$ salt) to Co^{2+} in acidic ($HClO_4$ or CF_3SO_3H) solution but do so quantitatively in neutral solution. Specifically, under these experimental conditions in acidic or neutral solution, the only effective radical in the system is $\cdot CH_2OH$ (G 6·2). At pH > 5·0, $G(Co^{2+}) = 6{\cdot}2$ and $G(CH_2O) = 6{\cdot}1$ indicating quantitative reduction of the complex and oxidation of the radical. At pH < 3, $G(Co^{2+}) < 0{\cdot}5$ and $G(CH_2O) = 1{\cdot}2$; in the absence of the complex at pH 1, $G(CH_2O) = 1{\cdot}0$

demonstrating that in acidic solution, in the presence or absence of the complex, the radical disappears *via* the same bimolecular combination or disproportionation reactions.[5] Between pH 3 and 5, $G(Co^{2+})$ increases smoothly showing an apparent pK_a of *ca.* 4·2. There is no spectral evidence for aquation or any other modification of the complex upon irradiation in acidic solution.

Neither the complex[6] nor the radical show changes in structure due to protonation–deprotonation in the pH range between acidic and neutral solution; the spectrum and the bimolecular decay kinetics of $\cdot CH_2OH$ are independent of pH in the range 1—6[5] and the electron-transfer properties of the radical are the same at pH 3[7] as at pH 7.[8] Because the reactive species maintain their integrity over that pH range, no change in the energetics nor the nature of the primary mechanistic step would be expected to occur. If the reaction were truly a simple outer-sphere electron-transfer reaction, it would have to occur rapidly and quantitatively in a pH-independent manner. The failure of the reaction of $\cdot CH_2OH$ with $[Co(NH_3)_6]^{3+}$ to generate more than token quantities of Co^{2+} in acidic solution leads to the conclusion that such lack of reactivity arises from kinetic and mechanistic, and not thermodynamic, factors. The results demonstrate that the reaction cannot occur *via* a strictly outer-sphere mechanism as has been previously proposed.[2] Rather, we propose that the interaction of $\cdot CH_2OH$ with $[Co(NH_3)_6]^{3+}$ involves an associative mechanism, such that the transfer of an electron from the associated radical to the $e_g{}^*$ acceptor orbital of the metal, requiring reorganization of the inner co-ordination sphere and excitation of the electron, occurs at a low intramolecular rate with an accompanying activation barrier when the associated radical remains protonated in acidic solution. Deprotonation of the associated radical with a pK_a value lower (say, 4·2) than that of the free radical (10·7)[9] would generate the more strongly reducing $\cdot CH_2O^-$ radical and intramolecular electron transfer would become rapid compared to the lifetime of the associated complex-radical system (estimated to be in the order of μs). Intramolecular electron transfer from a co-ordinated radical to a Co^{III} centre has been shown to be relatively slow.[10]

A lack of correlation between the reaction rate constant and the free energy function[4] for the reaction of this simple radical, and others such as $CO_2{}^-$, with simple ammine complexes has been noted.[2,11,12] Since this reaction apparently does not occur *via* a simple outer-sphere mechanism, the basis for this attempted correlation has been removed. These results also demonstrate that a thermodynamically spontaneous electron-transfer reaction involving a free radical may be kinetically inefficient, a feature which must be considered when evaluating the redox potentials of radicals, for example.[8]

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