The Use of the Cyanide Ion as an Electron Mediator in an Activated Bridge Electron-transfer Reaction

By JOHN L. BURMEISTER* and DAVID SUTHERLAND

(*William Albert Noyes Chemistry Laboratory, University of Illinois, Urbana, Illinois*)

ALTHOUGH a considerable number of ligands have been used[1–3] as the bridging ligands, X, in reaction 1,

$$[Co(NH_3)_5X]^{2+} + [Co(CN)_5]^{3-} \xrightarrow{H_2O} [(H_3N)_5Co^{III}\text{–}X\text{–}Co^{II}(CN)_5]^{-} \longrightarrow [Co(CN)_5X]^{3-} + [Co(OH_2)_6]^{2+} + 5NH_3 \qquad (1)$$

the cyanide ion has not been included, since, until recently,[4,5] the oxidant $[Co(NH_3)_5CN]^{2+}$ had not been prepared.

Haim and Wilmarth[6] used the cyanide ion as an electron mediator by employing $[Fe(CN)_6]^{3-}$ as the oxidant in reaction 1, resulting in the formation of the binuclear ion $[(NC)_5Fe^{II}\text{–}CN\text{–}Co^{III}(CN)_5]^{6-}$. There has been no report of a case in which the

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* Present address, University of Delaware, Newark, Delaware.

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cyanide ion acts as an electron mediator in an oxidation–reduction reaction proceeding *via* the activated bridge electron-transfer mechanism and is then transferred to the co-ordination sphere of the oxidized reductant. We now report such a case.

To a solution of potassium cyanide (0·59 g., 9 mmoles) in water (3 ml.) was added $[Co(NH_3)_5CN]SO_4$ (0·048 g., 1·8 mmoles), prepared according to the method of Siebert.[2] No noticeable evolution of ammonia occurred until a crystal of $Co(C_2H_3O_2)_2,4H_2O$ was added, whereupon the $[Co(NH_3)_5CN]SO_4$ immediately dissolved, with evolution of ammonia. The suphate ion was precipitated as barium salt by the addition of a stoicheiometric amount of $Ba(C_2H_3O_2)_2$, and removed by filtration through a fritted-glass filter, the filtrate passing directly into ethanol (15 ml.) at 0°. The addition of ethanol (15 ml.) at 0° to the yellow solution resulted in the precipitation of an off-white solid which was isolated by filtration, washed with ethanol and ether, and dried *in vacuo* ($CaCl_2$). The yield was 0·42 g. (70% of theory).

Support for the formulation of the product as $K_3[Co(CN)_6]$ was found in the microanalytical results and the infrared spectrum of the complex (Nujol mull), which was identical to that of $K_3[Co(CN)_6]$ prepared according to Schlessinger's method.[7] Both spectra, however, differed from that reported[8] for the complex. In addition to the reported C–N stretching frequencies of 2143, 2129, and 2126 cm.$^{-1}$, weak bands at 2106 and 2089 cm.$^{-1}$ were found, under high resolution.

Formulation of the bridged intermediate or activated complex as $[(H_3N)_5Co^{III}–CN–Co^{II}(CN)_5]^-$ leads to the intriguing possibility that the initial product of the reaction is the linkage-isomeric form $[Co(CN)_5NC]^{3-}$. However, if such an isomer is initially formed, its rearrangement, possibly catalyzed by $[Co(CN)_5]^{3-}$ in a sequence similar to reaction 1, is so rapid as to prevent its isolation, even when the reaction was carried out in acetone at the temperature of solid carbon dioxide–acetone. The significance of this work does not lie in the synthesis of the well-known $K_3[Co(CN)_6]$, but rather in the means whereby it was accomplished.

Preliminary results of tracer experiments using ^{14}C-labelled cyanide in the $Co(NH_3)_5CN^{2+}$ oxidant and an excess (over the ratio $[CN^-]/[Co(NH_3)_5CN^{2+}] = 5$) of unlabelled cyanide in solution indicate[2,4] that the reaction is indeed proceeding predominantly *via* the inner-sphere activated-bridge mechanism discussed above. An outer-sphere electron-transfer reaction[2] between $Co(NH_3)_5CN^{2+}$ and $Co(CN)_6^{4-}$ (presumed[3] to co-exist in equilibrium with $Co(CN)_5^{3-}$ and cyanide) would, in this case, yield the same product, $Co(CN)_6^{3-}$, albeit containing no radioactive cyanide.

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