The Cobalt(II) Intermediate in the Reactions of Vanadium(II) and Monosubstituted Pentacyanocobaltate(III) Ions†

By KEITH M. DAVIES and JAMES H. ESPENSON*

(*Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa* 50010)

REACTIONS of the type shown in equation (1) have not been

$$Co(CN)_5X^{3-} + V^{2+} + 5H^+ = Co^{2+} + V^{3+} + X^- + 5HCN \qquad (1)$$

studied previously. They have proved to be of especial interest since they have afforded a means of examining the reactions of the Co^{III} complex after its reduction. Although an ammine–cobalt(II) complex such as $Co(NH_3)_5^{2+}$ is probably the precursor of Co^{2+}_{aq} in the reaction of $Co(NH_3)_5X^{2+}$ and V^{2+}, for example, its presence has not been demonstrated. The energetics are frequently discussed in such terms, however, for both inner-sphere and outer-sphere reactions.[1] The choice of oxidizing agent in the present reactions permits experiments to demonstrate that $Co(CN)_5^{3-}$ is an intermediate, owing to its fairly slow decomposition to Co^{2+} and HCN in perchloric acid solution.[2]

Kinetic studies have been carried out in aqueous perchloric acid solution on the reactions given in eq. 1 for X = Cl^-, Br^-, I^-, $-SCN^-$, N_3^-, and H_2O. The reactions proceeded through a metastable intermediate, as shown by the maximum in the absorbance–time traces in the wavelength regions 260—350 nm., as illustrated in the Figure. The intermediate was shown to be $Co(CN)_5^{3-}$ by the absorbance changes[3] accompanying the initial reduction,[4] by comparison of the decay rates of the intermediate with those of $Co(CN)_5^{3-}$ under similar conditions,[2] and by use of $Co(NH_3)_5NCS^{2+}$ as a scavenger[6,7] for $Co(CN)_5^{3-}$ according to equation (2).

$$Co(CN)_5^{3-} + Co(NH_3)_5NCS^{2+} \rightarrow Co(CN)_5SCN^{3-} + Co^{2+} + 5NH_3 \qquad (2)$$

In accord with the scheme suggested, the rate of decomposition of the intermediate was independent of the initial Co^{III} concentration. The decay reaction followed the expected[2] first-order kinetics with a rate constant independent of which starting complex was used. There was a dependence on V^{2+} concentration, which was in considerable excess, presumably because of ion-pair formation (ion pairing is an important feature of the first reaction stage).[4] Rate constants for decay of the intermediate at 25·0° and 1·00M H^+ were 0·185 sec.$^{-1}$ (X = Br^-), 0·175 sec.$^{-1}$ (Cl^-), and 0·169 sec.$^{-1}$ (H_2O). Each of the values refers to 0·01M V^{2+} and an initial Co^{III} concentration of 3—7 × 10^{-5}M. The comparison with the known $Co(CN)_5^{3-}$ complex in the presence of vanadium(II) is illustrated by data at 0·50M H^+, 1·00M ionic strength at 25·0°, for which the rate constant for the intermediate is 0·112 sec.$^{-1}$ (X = Br^-, 0·01M V^{2+}) compared to 0·115 sec.$^{-1}$ for authentic $Co(CN)_5^{3-}$ in the presence of 0·01M V^{2+} and 0·257 sec.$^{-1}$ in the absence of V^{2+}.

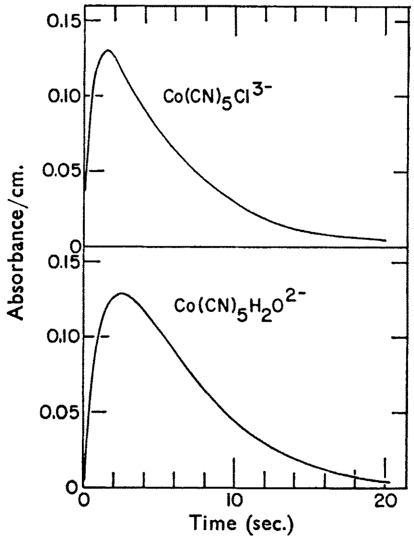

FIGURE. *Observed absorbance–time traces at λ 280 nm. for the reaction of* $Co(CN)_5X^{3-}$ *with* V^{2+} *at* 25·0° *and* μ = 1·00M. *Upper curve* 5 × 10^{-5}M $Co(CN)_5Cl^{3-}$, 0·0105M V^{2+}; *lower curve* 7 × 10^{-5}M $Co(CN)_5OH_2^{2-}$, 0·0053M V^{2+}.

The product of the scavenging experiments, $Co(CN)_5SCN^{3-}$, was separated by ion exchange, and identified by its known absorption spectrum.[7] In these experiments the vanadium(II) concentration was less than the total Co^{III} concentration, and the conversion into $Co(CN)_5SCN^{3-}$ was only partial owing to the reaction of this ion with V^{2+}. Under the conditions chosen, the direct reaction of V^{2+} and $Co(NH_3)_5NCS^{2+}$ was unimportant.[8]

(*Received, November* 21*st*, 1968; *Com.* 1596.)

---

† Work performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

[1] R. C. Patel and J. F. Endicott, *J. Amer. Chem. Soc.*, 1968, **90**, 6364.
[2] J. H. Espenson and J. R. Pipal, *Inorg. Chem.*, 1968, **7**, 1463.
[3] N. K. King and M. E. Winfield, *J. Amer. Chem. Soc.*, 1961, **83**, 3366.
[4] K. M. Davies and J. H. Espenson, to be published.
[5] J. P. Candlin, J. Halpern, and S. Nakamura, *J. Amer. Chem. Soc.*, 1963, **85**, 2517.
[6] I. Stotz, W. K. Wilmarth, and A. Haim, *Inorg. Chem.*, 1968, **7**, 1250.
[7] J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Amer. Chem. Soc.*, 1964, **86**, 1019.