Evidence for a Two-stage Process in Electron-transfer to a Transition-metal Complex

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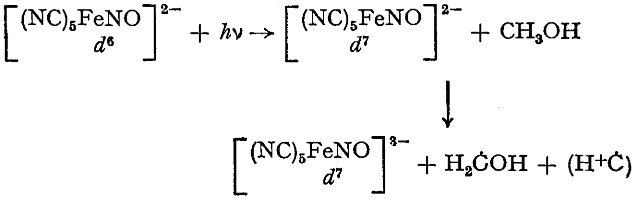
Summary The pentacyanonitrosylferrate(II) ion is shown, by e.s.r. spectroscopy, to gain an electron in two stages at 77 K.

THE work of Taube and his co-workers,[1] has shown that electron gain or loss by transition-metal complexes generally involves ligand participation, a 'conducting' ligand providing a low energy path for the electron. Conducting ligands are those having low-lying vacant orbitals, such as CN^- whilst ligands such as NH_3, having no low-lying vacant orbitals, are insulating. We report results for the pentacyanonitrosylferrate(II) ion, $(CN)_5FeNO^{2-}$, which underline Taube's concept in an interesting manner.

Treatment of $(CN)_5FeNO^{2-}$ with a range of reducing agents, or by electrolysis in fluid solution gives a paramagnetic ion (I) having a well defined e.s.r. spectrum which is, in our view,[2] characteristic of the anion $(CN)_5FeNO^{3-}$, having the unpaired electron strongly confined to the iron d_{z^2} orbital. Photolysis (254, 300, or 350 nm) of non-aqueous solutions also yields (I). Photolysis at 77 K in glassy methanol solution gave (I) together with $\dot{C}H_2OH$ (and $H\dot{C}O$) radicals from the solvent. [None of these radicals were formed in the absence of the pentacyanonitrosylferrate(II) ion.] This result is similar to that obtained with the hexacyanoferrate(III) ion, $Fe(CN)_6{}^{3-}$, which we have explained[3] in terms of a charge-transfer from ligand(s) to metal, followed by a redox process involving electron-transfer from methanol to the ligand(s) to give $(MeOH)^+$ which directly or indirectly gives $\dot{C}H_2OH$.



$$\begin{array}{l}\left[\underset{d^6}{(NC)_5FeNO}\right]^{2-} + h\nu \rightarrow \left[\underset{d^7}{(NC)_5FeNO}\right]^{2-} + CH_3OH \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\qquad \left[\underset{d^7}{(NC)_5FeNO}\right]^{3-} + H_2\dot{C}OH + (H^+\dot{C})\end{array}$$

In marked contrast, exposure of a similar rigid solution to ^{60}Co γ-rays gave a species (II) having e.s.r. parameters expected for a complex with the excess electron confined strongly to the NO ligand. [The results suggest that the g- and ^{14}N A-tensors for this species are far from being coaxial and hence that the NO group has become bent with respect to the $(CN)_5Fe$ unit. The species is similar in many respects to that detected[4] in γ-irradiated $Na_2Fe(CN)_5$-$NO{\cdot}2H_2O$ at 77 K, for which a similar structure was assigned.]

On annealing the γ-irradiated methanolic glass, species (II) was irreversibly, and almost quantitatively, converted into (I). We interpret these results to mean that acceptance of an electron from an external source occurs *via* the ligand(s), the NO group being favoured in this case, and that a minor, low energy, distortion then occurs to stabilise the new situation leaving the electron on the ligand. A more major distortion, involving movement of the cyanide ligands is then required to allow the electron to become transferred to the central metal atom. When, however, this transfer is internal, as in the photolyses, the electron is forced onto the metal atom in the absence of ligand relaxation, but, at least occasionally, such relaxation occurs prior to the return of the electron to the ligand(s) even at 77 K. All these results accord with Taube's original concepts.

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[3] M. C. R. Symons, D. X. West, and J. G. Wilkinson, unpublished results.

[4] M. B. D. Bloom, J. B. Raynor, and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1971, 3843.