

Formation of the Pentacyanocobalt(I) Ion in Highly Alkaline Solutions

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STUDY of the reduction mechanism of $\text{Co}(\text{CN})_5^{3-}$ at the dropping-mercury electrode has shown that the pentacyanocobalt(I) ion, $\text{Co}(\text{CN})_5^{4-}$, is formed as the primary product¹ The reaction between *p*-benzoquinone and $\text{Co}(\text{CN})_5\text{H}^{3-}$ (ref. 2) also gives evidence for the existence of $\text{Co}(\text{CN})_5^{4-}$ ions in alkaline solutions of $\text{Co}(\text{CN})_5\text{H}^{3-}$. From these results it was concluded that the $\text{Co}(\text{CN})_5^{4-}$ ion is a very strong base which extracts hydrogen ions from both proton donors and water molecules; for this reason it could exist only in solutions of very low proton activity.

We present direct electrochemical evidence for the existence and formation of the pentacyanocobalt(I) complex in highly alkaline solutions of $\text{Co}(\text{CN})_5\text{H}^{3-}$.

Aqueous solutions of $\text{Co}(\text{CN})_5\text{H}^{3-}$, prepared by electrochemical reduction of $\text{Co}(\text{CN})_5^{3-}$, are electrochemically inactive up to $[\text{OH}^-] = 4\text{M}$. At $[\text{OH}^-] > 4\text{M}$ an oxidation process begins at the dropping-mercury electrode at a potential of -1.2 v (S.C.E.), *i.e.* at the same potential at which the reduction of $\text{Co}(\text{CN})_5^{3-}$ takes place.

The current corresponding to this oxidation process (i_a) increases with hydroxide-ion concentration up to ca. 95% of the theoretical diffusion-limited value (i_h) for a one-electron process involving the total cobalt in solution (Figure). For $i_a/i_h < 0.5$ the limiting current is reaction-rate controlled showing that, under these conditions, the anodically active species is formed in a reaction preceding

the redox reaction of electrochemically inactive species, $\text{Co}(\text{CN})_5\text{H}^{3-}$, which predominates in the bulk of the solution. The product of this oxidation process was shown, on the basis of its electrochemical and spectrophotometrical properties, to be $\text{Co}(\text{CN})_5^{3-}$.

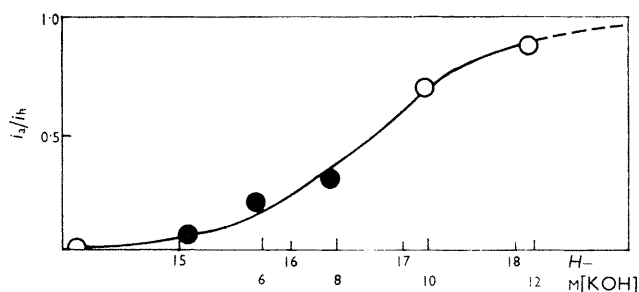
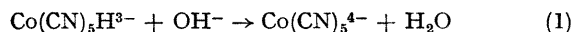


FIGURE. Dependence of the oxidation current of $\text{Co}(\text{CN})_5^{4-}$ upon the concentration of hydroxide: i_a = anodic current observed, i_h = hypothetical current of a one-electron oxidation of total cobalt present: ● reaction-rate controlled current; ○ diffusion controlled current.

The redox process for $\text{Co}(\text{CN})_5^{3-}$ is completely reversible, electrochemically as well as chemically and proceeds without the formation of cyanide ions.

The formation of an electrochemically active species, which is reversibly oxidised at the Co(CN)_5^{3-} reduction potential is clearly hydroxide-ion concentration-dependent. The same oxidation wave, and therefore same species, is observed during commutator³ studies of the Co(CN)_5^{3-} reduction in strongly alkaline media.

All these results, combined with the general rules governing the relations between the structure and redox behaviour of co-ordination compounds,⁴ provide direct evidence that the species which is oxidized reversibly to Co(CN)_5^{3-} is a univalent cobalt complex, of composition Co(CN)_5^{4-} , formed from the hydride complex $\text{Co(CN)}_5\text{H}^{3-}$ by deprotonation. It is suggested that the pseudo acid-base equilibrium shown in equation (1) is involved. Since the



observed current due to the oxidation of Co(CN)_5^{4-} in solutions of $[\text{OH}^-] < 10\text{M}$, is reaction-rate controlled, substantial equilibrium concentrations of this species would only be expected at the higher hydroxide-ion concentrations. The pK value of the equilibrium (1) cannot be deduced unambiguously from these experiments only. However,

together with previous results,² these findings suggest a pK value for (1) *ca.* 18—19.

The ion Co(CN)_5^{4-} is a very strong reducing agent [E° for the couple Co(CN)_5^{4-} – Co(CN)_5^{3-} is -1.2 v (S.C.E.) in 12M-KOH] and reacts very rapidly in two-electron reductions, in contrast to $\text{Co(CN)}_5\text{H}^{3-}$. This is obviously connected with the fact that the electron pair in Co(CN)_5^{4-} is very easily accessible whereas in the hydride species it is shielded by hydrogen. The evidence available up to now shows that compounds undergoing reduction by way of an electron-transfer or redox addition mechanism react predominantly with the Co(CN)_5^{4-} ion, which is present in kinetically significant concentration even at $\text{pH } 10$. The hydride species seems to react, on the other hand, *via* a hydrogen-transfer mechanism.

This behaviour of the pair $\text{Co(CN)}_5\text{H}^{3-}$, Co(CN)_5^{4-} fits completely into the general scheme of other hydride-anion systems which also show much greater reductive activity under strongly deprotonating conditions.⁵ The hydride species seem to be potential reductants in which the electron pair becomes active only after the removal of hydrogen.

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