Interaction between Hexacyanoferrate(II) Ion and Mercury(II) and Silver(I) Ions

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The interaction between hexacyanoferrate(II) ion and mercury(II) or silver(I) ion was studied conductometrically in aqueous solution. The maximum decrease in conductivity occurred at a 1 : 2 mole ratio of $K_4[Fe(CN)_6]:HgCl_2$ or at a *ca.* 1 : 4 mole ratio of $K_4[Fe(CN)_6]:AgNO_3$. The decrease in conductivity is considered to be due to complex formation between hexacyanoferrate(II) ion and the metal ions. The salt effect on the Hg^{II}-catalysed dissociation of $[Fe(CN)_6]^{4-}$ to $[Fe(CN)_5H_2O]^{3-}$ is positive at low, but negative at high, ionic strength. The mechanism of this reaction is discussed.

THERMAL dissociation of $[Fe(CN)_6]^{4-}$ to $[Fe(CN)_5H_2O]^{3-}$ ions is a slow reversible process. The reaction is catalysed by metal ions such as Hg^{2+}, Hg_2^{2+}, Ag^+, Au^{3+}, Pt^{4+}, of which Hg_2^{2+} and Hg^{2+} ions are by far the most effective.[1] It has been previously suggested[2] that hexacyanoferrate(II) and mercury(II) ions form a 1 : 1 ion-pair preceding the Hg^{II}-catalysed dissociation of a CN^- ligand. In this work the interaction of the hexacyanoferrate(II) ion with mercury(II) and silver(I) ions has been studied conductometrically, together with the salt effect of the Hg^{II}-catalysed reaction, in order to elucidate the mechanism of catalysis.

RESULTS

Conductivities of Aqueous Solutions of $K_4[Fe(CN)_6]$ *and* $HgCl_2$ *and of* $K_4[Fe(CN)_6]$ *and* $AgNO_3$.—At mercury(II) concentrations equivalent to or greater than that of hexacyanoferrate(II), dissociation of aqueous solutions of the latter ions at room temperature was so fast that no reproducible conductivity measurements could be obtained. Even at 0·5 °C the conductivity measurements had to be performed very rapidly (in 3—5 s). It can be seen from Figure 1 that the maximum conductivity decrease was found at a 1 : 2 mole ratio of $K_4[Fe(CN)_6]$ to $HgCl_2$. The interaction of mercury(II) ions with hexacyanoferrate(II) ion is accompanied by a shift of equilibria between Hg^{2+}, $HgCl^+$, and $HgCl_2$, which diminishes the original conductivity effect but does not change the position of the maximum conductivity decrease.

Beck *et al.*[3] studied the interaction of $Hg(CN)_2$ with co-ordinatively saturated inert cyano-complexes and found that, with hexacyanoferrate(II) ion, the species $[Fe(CN)_6,Hg(CN)_2]^{4-}$ and $[Fe(CN)_6,2Hg(CN)_2]^{4-}$ were formed. These findings agree with our observation that hexacyanoferrate(II) ion forms complexes containing one[2] and two mercury ions per hexacyanoferrate(II) ion respectively.

The catalytic effect of silver(I) ions on the formation of aquopentacyanoferrate(II) from hexacyanoferrate(II) ions was smaller than that of mercury(II) so that the Ag^I interaction could be studied at 20 °C; the results are plotted in Figure 2. It can be seen that the maximum decrease in conductivity appeared at a *ca.* 1 : 4 mole ratio $K_4[Fe(CN)_6]$ to $AgNO_3$.

Salt Effect on the Rate of Formation of Aquopentacyanoferrate(II) *Ion in the Presence of Mercury*(II) *Ions.*—It has been previously reported[2] that the rate of the mercury(II)-catalysed decomposition of hexacyanoferrate(II) ion in the presence of nitrosobenzene, measured by the rate of formation of the violet $[Fe(CN)_5(PhNO)]^{3-}$ ion, showed a negative salt effect. On the other hand, Beck *et al.*[4] reported an increase in the rate of the catalysed decomposition in the presence of $NaClO_4$. We therefore re-examined the kinetic salt effect.

The specific rate was determined from $k = (2{\cdot}303/t)\log_{10}[A/(A - A_t)]$, where A is the optical density of 0·0005M-$[Fe(CN)_5(PhNO)]^{3-}$ and A_t that at the reaction time t. Unfortunately the violet nitrosobenzene complex is not stable and also undergoes catalytic decomposition to

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[1] S. Ašperger and D. Pavlović, *J. Chem. Soc.*, 1955, 1449.

[2] S. Ašperger, I. Murati, and D. Pavlović, *J. Chem. Soc.* (*A*), 1969, 2044.

[3] M. T. Beck and E. Cs. Porzsolt, *J. Co-ordination Chem.*, 1971, **1**, 57.

[4] M. T. Beck, L. Dózsa, D. A. Durham, J. Farkas, and T. Szahey, Mechanism of Inorganic Reactions Conference, Bedford College, London, 1969.

iron(II) and cyanide ions; this caused the decrease in the specific rate of reaction in a given run. Therefore, only initial specific rates of reaction (up to 5% completion of reaction), where decomposition of the nitrosobenzene complex was negligible, were considered. Specific rates of reaction determined in this way could be reproduced within 10%.

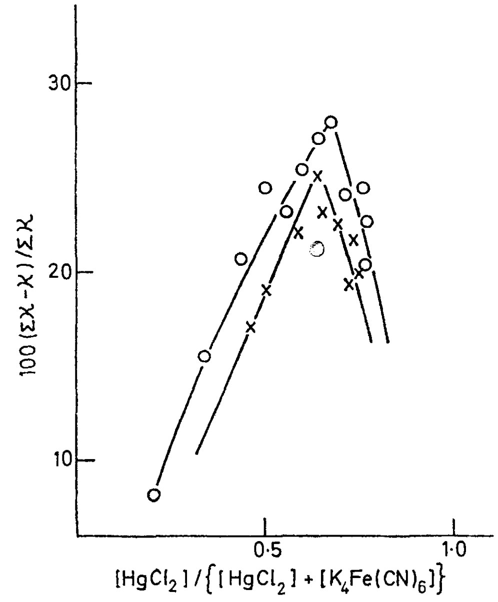


FIGURE 1 Dependence of the decrease of the conductivities of the $K_4[Fe(CN)]_6$–$HgCl_2$ system ($\Sigma\kappa - \kappa$) divided by the sum of the individual conductivities ($\Sigma\kappa$) as a function of the amount of $HgCl_2$ at 0·5 °C: $[K_4Fe(CN)_6]$ = 0·0004 (○); 0·0006M (×). $[HgCl_2]$ was varied between 10^{-4} and $1·5 \times 10^{-3}$M

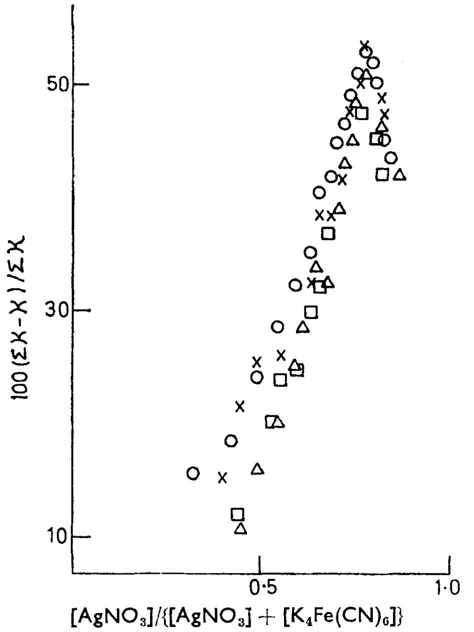


FIGURE 2 Dependence of the decrease of the specific conductivities of the $K_4[Fe(CN)_6]$–$AgNO_3$ system ($\Sigma\kappa - \kappa$) divided by the sum of the individual conductivities ($\Sigma\kappa$) as a function of the amount of $AgNO_3$ at 20 °C: $[K_4Fe(CN)_6]$ = 0·00004 (○); 0·00006 (×); 0·00008 (△); and 0·0001M (□). The concentration of $AgNO_3$ was varied between 0·00002 and 0·00008M

Kinetic salt effect in the formation of the $[Fe(CN)_5(PhNO)]^{3-}$ ion in the presence of Hg^{II} at 25 °C

(*a*) 0·0005M-$K_4[Fe(CN)_6]$, 0·003M-PhNO, $1·0 \times 10^{-6}$M-$Hg(ClO_4)_2$, and $HClO_4$ to initial pH 4·1 [a]

$[LiClO_4]$/M	0	0·0005	0·001	0·005	0·01	0·05	0·3	1
$10^6k/s^{-1}$	6·0	8·0	8·6	8·4	7·8	5·7	3·2	1·7

(*b*) 0·001M-$K_4[Fe(CN)_6]$, 0·002M-PhNO, $2·0 \times 10^{-6}$M-$HgSO_4$, and H_2SO_4 to initial pH 4·1 [a]

$[Na_2SO_4]$/M	0	0·0007	0·001	0·005	0·01	0·05	0·1
$10^6k/s^{-1}$	6·1	6·3	8·2	6·7	6·6	5·8	5·3

[a] See ref. 1.

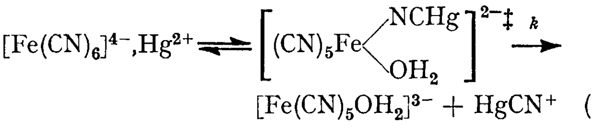
The Table shows that the salt effect is positive only at low salt concentrations, while at higher concentrations it becomes negative. The salt effect of KCl was also slightly positive when the concentration of KCl was less than 0·025M, and negative at higher concentrations. The small positive kinetic salt effect at low ionic strength was also found in the absence of the mercury(II) ion catalyst, but only in acidic solution (pH *ca.* 4) where the hydrogen ion probably acts as a catalyst in a manner similar to that of mercury(II). When the inert salt concentration was greater than 0·1M the salt effect was always negative, as in the presence of the mercury(II) ion catalyst.

DISCUSSION

The conductivity measurements suggest that, at a mole ratio of 2 : 1 for mercury(II) to hexacyanoferrate(II) ions, a complex (or ion association) containing two mercury(II) ions per hexacyanoferrate(II) ion is formed. [Analogously, at a mole ratio of 4 : 1 of silver(I) to hexacyanoferrate(II) ions, the complex contains four silver(I) ions per hexacyanoferrate(II) ion.] When the concentration of mercury(II) is less than that of the hexacyanoferrate(II) ion, a binuclear complex is formed[2] in the rapid equilibrium (1). The binuclear complex

$$[Fe(CN)_6]^{4-} + Hg^{2+} \rightleftharpoons [Fe(CN)_6]^{4-},Hg^{2+} \quad (1)$$

reacts relatively slowly, according to reaction (2), to yield aquopentacyanoferrate(II) ion. In the presence of nitrosobenzene, the water molecule of the aquopentacyanoferrate(II) ion is quickly replaced, as in reaction (3), and the violet nitrosobenzene complex is the product.



$$[Fe(CN)_6]^{4-},Hg^{2+} \rightleftharpoons \left[(CN)_5Fe\begin{matrix}\diagup NCHg \\ \diagdown OH_2\end{matrix}\right]^{2-\ddagger} \xrightarrow{k} [Fe(CN)_5OH_2]^{3-} + HgCN^+ \quad (2)$$

$$[Fe(CN)_5OH_2]^{3-} + PhNO \longrightarrow [Fe(CN)_5(PhNO)]^{3-} + H_2O \quad (3)$$

It is known[5,6] that Hg^{2+} and $MeHg^+$ ions form binuclear complexes with cyano-complexes of cobalt(III)

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[5] H. Siebert, *Z. anorg. Chem.*, 1964, **327**, 63.

[6] G. Schwarzenbach and M. Scheellenberg, *Inorg. Chim. Acta*, 1965, **48**, 28.

and chromium(III). Recent kinetic studies[7] on the formation of a binuclear complex of $[CrCN]^{2+}$ with Hg^{2+} suggest that mercury is bonded to carbon $Cr{-}NC{-}Hg^{4+}$, as a consequence of a fast linkage isomerisation process, which is preceded by a stable association.[8] In Co^{III} cyano-complexes the rate of isomerisation has a half-life of 1·6 s at 25 °C.[9]

The above mechanism postulated for the catalytic action of mercury(II) ions can explain the positive salt effect at low ionic strength; at high ionic strength the negative effect is probably explained by cations such as Li^+ or Na^+ displacing mercury(II) from the binuclear complex.

The rate of the formation of the violet nitrosobenzene complex at low ionic strength is given by equation (4),

$$d[Fe(CN)_5(PhNO)^{3-}]/dt = k_{obs}[Fe(CN)_6{}^{4-}] \quad (4)$$

where $k_{obs} = kK_{Hg}[Hg^{2+}]$ and K_{Hg} is the equilibrium constant of reaction (1). At a given ionic strength, k_{obs} is constant since the concentration of the mercury(II) ion catalyst is constant. It can be shown that, in the presence of an inert salt such as $LiClO_4$, the observed rate constant is given by equation (5), K_{ip} being the

$$k_{obs}' = kK_{Hg}[Hg^{2+}]/(1 + K_{ip}[Li^+]) \quad (5)$$

ion-pair formation constant of Li^+ and $[Fe(CN)_6]^{4-}$ ions. At low ionic strengths $k_{obs}' = k_{obs}$. An increase in ionic strength decreases the concentration of the ion-pair $[Fe(CN)_6]^{4-},Hg^{2+}$, *i.e.* $K_{Hg}[Hg^{2+}]$ decreases. On the other hand, the specific rate of reaction k increases with increasing ionic strength because reaction (2) involves charge separation. The dependence of $[Fe(CN)_6{}^{4-},Hg^{2+}]$ on ionic strength is given by equation (6) (see Appendix), where K_{Hg^0} is the thermodynamic

$$-\frac{d}{dI}\ln[Fe(CN)_6{}^{4-},Hg^{2+}] = \frac{2{\cdot}30\,z^2A}{2(\sqrt{I} + 2I + I^{\frac{3}{2}})\{1 + [Fe(CN)_6{}^{4-}]\,K_{Hg^0}\gamma_{4-}\}} \quad (6)$$

equilibrium constant for (1), γ_{4-} the activity coefficient of $[Fe(CN)_6]^{4-}$ ion, and $A = 0{\cdot}51$ for water. If K_{Hg^0} is sufficiently large that 90% of the Hg^{2+} added is complexed, the decrease in $[Fe(CN)_6{}^{4-},Hg^{2+}]$ is about 3%, as calculated from (6) at the ionic strengths employed. In fact the maximum conductivity decrease at the mole ratio $[Fe(CN)_6{}^{4-}] : [Hg^{2+}] = 1 : 2$ strongly suggests that Hg^{2+} is complexed to a greater extent than is anticipated by this calculation. Hence, the decrease in $K_{Hg}[Hg^{2+}]$ should be even less than 3%. Under such conditions, the increase in k could more than offset the decrease in $K_{Hg}[Hg^{2+}]$, so that k_{obs} could, at low ionic strength, increase with increasing ionic strength.

EXPERIMENTAL

All chemicals were of Merck analytical grade purity. Redistilled water had a conductivity of $0{\cdot}9 \times 10^{-6}$—$1{\cdot}1 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$. The complex $Na_3[Fe(CN)_5(PhNO)],4{\cdot}5H_2O$ was used from a batch which had been prepared and analysed previously.[10]

Aqueous solutions of nitrosobenzene and $Hg(ClO_4)_2$, at a definite ionic strength, were thermostatted to ±0·05 °C, mixed with the thermostatted solution of $K_4[Fe(CN)_6]$, and the rate of the reaction determined at 528 nm, where the violet nitrosobenzene complex has a molar absorption coefficient of 5300 l mol^{-1} cm^{-1} and $[Fe(CN)_6]^{4-}$ does not absorb.

Light absorption measurements were made with a Unicam SP 500 spectrophotometer (10 mm cell). Conductometric measurements were made with Mullard E. 7566 and Cambridge 4392 conductivity bridges at 0·50 ± 0·05 °C for the hexacyanoferrate(II)–mercury(II) system and at 20 ± 0·05 °C for the hexacyanoferrate(II)–silver(I) system.

APPENDIX

The thermodynamic equilibrium constant for binuclear complex formation is $K_{Hg^0} = (\gamma_{2-}/\gamma_{4-}\gamma_{2+})K_{Hg}$, where $K_{Hg} = [Fe(CN)_6{}^{4-},Hg^{2+}]/[Fe(CN)_6{}^{4-}][Hg^{2+}]$. The product $K_{Hg}[Hg^{2+}]$ is equal to $[Fe(CN)_6{}^{4-},Hg^{2+}]/[Fe(CN)_6{}^{4-}]$. At low ionic strength, the concentration of $[Fe(CN)_6]^{4-}$ remains constant, for practical purposes, when I is increased, because $[Fe(CN)_6{}^{4-}]$ is so large compared to the increase of this concentration when the ion-pair partly dissociates. If the change of concentration of $Fe(CN)_6{}^{4-}$ with I is taken into account, the term $[Hg^{2+}]K_{Hg^0}\gamma_{4-}$ is added to the sum within the braces in the denominator of equation (6); since $[Hg^{2+}] \ll [Fe(CN)_6{}^{4-}]$ the more exact equation reduces to equation (6). On the other hand, the increase in ionic strength does cause the concentration of $[Fe(CN)_6{}^{4-}],Hg^{2+}$, and the quantity $K_{Hg}[Hg^{2+}]$ to decrease. Since $K_{Hg}[Hg^{2+}] = K_{Hg^0}\gamma_{4-}[Hg^{2+}]$ we find that equation (7) is

$$\frac{d}{dI}(K_{Hg}[Hg^{2+}]) = \frac{1}{[Fe(CN)_6{}^{4-}]}\frac{d}{dI}[Fe(CN)_6{}^{4-},Hg^{2+}] = \frac{d}{dI}\left\{K_{Hg^0}[Hg^{2+}]\exp\left[-2{\cdot}30 \times 0{\cdot}51z^2\left(\frac{\sqrt{I}}{1+\sqrt{I}}\right)\right]\right\} \quad (7)$$

applicable. Since $d[Hg^{2+}]/dI = -d/dI[Fe(CN)_6{}^{4-},Hg^{2+}]$ (when increasing I causes some $Fe(CN)_6{}^{4-},Hg^{2+}$ to dissociate, an equal amount of Hg^{2+} is formed), the solution of (7) leads to equation (6).

[2/2670 *Received, 27th November*, 1972]

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[9] J. Halpern and S. Nakamura, *J. Amer. Chem. Soc.*, 1965, **87**, 3002.

[10] D. Pavlović, I. Murati, and S. Ašperger, *J.C.S. Dalton*, 1973, 602.