# THE KINETICS OF ABSTRACTION OF CN-FROM HEXACYANO FERRATE(II), BY MERCURIC CHLORIDE IN THE PRESENCE OF 2,2' BIPYRIDINE<sup>†</sup>

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Abstract—The kinetics of abstraction of  $CN^-$  from hexacyano ferrate (II) by HgCl<sub>2</sub> in the presence of excess 2.2' bipyridine is reported. The products formed are tetracyano bipyridine–Fe(II) and tris bipyridine–Fe(II) depending on whether Fe(CN)<sub>6</sub><sup>4-</sup> or HgCl<sub>2</sub> is present in at least three to four fold excess. The rate law is  $dp/dt = k_{Hg}[HgCl_2]$  and  $dp/dt = k_{Fe}[(Fe(CN)_6^{4-})]$  when Fe(CN)<sub>6</sub><sup>4-</sup> or HgCl<sub>2</sub> is present in excess respectively. Activation parameters are  $\Delta H^{\neq} = 25.6 \pm 0.4$  kCal mol<sup>-1</sup> and  $\Delta S^{\neq} - 17.6 \pm 1.0$  eu mol<sup>-1</sup> for the formation of the tetracyano complex and  $\Delta H^{\neq} = 18.7 \pm 0.5$  kcal mol<sup>-1</sup> and  $\Delta S^{\neq} - 9.6 \pm 1.5$  eu mol<sup>-1</sup> for the tris-bipyridine–Fe(II) complex. The nature of the products and kinetics suggest formation of 1:1 and 2:1 intermediates between Hg(II) and Fe(CN)<sub>6</sub><sup>4-</sup>, prior to abstraction of CN<sup>-</sup>.

#### **INTRODUCTION**

It has been reported earlier that hexacyano ferrate(II) and mercuric chloride form two different products in the presence of excess of 2,2'-bipyridine[1]. When  $[Fe(CN)_6^{4-}]/[HgCl_2]$  is > 4, only partial abstraction of  $CN^-$  takes place to give predominantly the orange yellow tetra cyano bipyridine-Fe(II) complex.

$$HgCl_{2} + Fe(CN)_{6}^{4-} \xrightarrow{Bipyridine} (CN)_{4}(Bipy)Fe(II) + Hg(CN)_{2} + 2Cl^{-}.$$

When  $(HgCl_2]/[Fe(CN)_6^{4-}]$  is > 3, the tris-bipyridine-Fe(II) complex is formed exclusively

$$3 \text{HgCl}_2 + \text{Fe}(\text{CN})_6^{4-} \xrightarrow{\text{Bipyridine}} (\text{Bipy})_3 \text{Fe}(\text{II}) + 3 \text{Hg}(\text{CN})_2 + 6 \text{Cl}^{-1}$$

The kinetics of these two reactions is reported.

# EXPERIMENTAL

All reagents were of AR grade. Double distilled water flushed with N<sub>2</sub> was used throughout. The concentrations of K<sub>4</sub>Fe(CN)<sub>6</sub> and HgCl<sub>2</sub> used ranged from 4 to  $16 \times 10^{-4}$  and 1 to  $3 \times 10^{-4}$  in excess K<sub>4</sub>Fe(CN)<sub>6</sub> sets and from 0.5 to  $2 \times 10^{-4}$  and 2 to  $6 \times 10^{-4}$ in excess HgCl<sub>2</sub> sets. In a typical kinetic run, aliquots from stock solutions of K<sub>4</sub>Fe(CN)<sub>6</sub>, 2,2'-bipyridine (at least a three fold excess over that required stoichometrically) and KNO3 were mixed quickly with an aliquot from a stock HgCl<sub>2</sub> solution such that the desired concentrations were obtained. The ionic strength was maintained at 0.1 M in most cases with potassium nitrate. The solutions were all thermostatted to the desired temperature, before mixing and transferred within 30-40 sec of mixing, to the cells of a Beckman DU or Carl-Zeiss Specord UV-Vis spectrophotometer. The cell compartments were thermostatted, to the desired temperature by circulation of water. The kinetics was followed by noting the absorbance at 520 nm at suitable time intervals. The rate constants were calculated according to first order kinetics from the slope of  $-\ln(A_{\alpha} - A_t)$  vs time where  $A_{\alpha}$ and  $A_t$  are the absorbance at the completion and at time t of the reaction.

#### RESULTS

Two distinct kinetic patterns are observed with excess  $K_4Fe(CN)_6$  or  $HgCl_2$ . When  $[Fe(CN)_6^{4-}]/[HgCl_2]$  is >4, the rate of the reaction is independent of the concentration of  $Fe(CN)_6^{4-}$  and varies linearly with the concentration of  $HgCl_2$  (Figs. 1 and 2). The experimental data at various temperatures corresponds to rate equation (1).

$$\frac{\mathrm{d}[P_1]}{\mathrm{d}t} = k_{\mathrm{Hg}}[\mathrm{HgCl}_2] \tag{1}$$

where  $P_1$  represents the product  $K_2(CN)_4$  Bipy-Fe(II) formed as a result of partial abstraction of  $CN^-$ .

When HgCl<sub>2</sub> is used in excess so that  $[HgCl_2]/(Fe(CN)_6^{4-}]$  is > 3, the rate is independent of HgCl<sub>2</sub> concentration and varies linearly with the concentration of  $Fe(CN)_6^{4-}$  (Figs. 3 and 4). The experimental data is consistent with rate equation (2)

$$\frac{\mathrm{d}[P_2]}{\mathrm{d}t} = k_{\mathrm{Fe}}(\mathrm{Fe}(\mathrm{CN})_6^{4-}]$$
(2)

where  $P_2$  is the tris-bipyridine-Fe(II) formed by complete abstraction of  $CN^-$ .



Fig. 1. Non dependence of rate on concentration of  $K_4$ Fe(CN)<sub>6</sub> when present in excess (15°C). [HgCl<sub>2</sub>] =  $2 \times 10^{-4}$  M and [K<sub>4</sub>Fe(CN)<sub>6</sub>] = 6, 8, 12 and  $16 \times 10^{-4}$  M in a, b, c and d.

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Fig. 2. Linear dependence of rate on HgCl<sub>2</sub> concentration when  $K_4Fe(CN)_6$  is in excess (15°C). [HgCl<sub>2</sub>] = 1, 2, 3 and  $5 \times 10^{-4}$  M and [ $K_4Fe(CN)_6$ ] = 0.5, 1.0, 1.5 and  $2 \times 10^{-3}$  M in a, b, c and d.



Fig. 3. Nondependence of rate on concentration of HgCl<sub>2</sub> when present in excess (26°C).  $[K_4Fe(CN)_6] = 1 \times 10^{-4} \text{ M}$  and  $[HgCl_2] = 3, 4, 5 \times 10^{-4}$  in a, b, and c.

The rates in both cases were independent of the concentration of bipyridine, provided a slight excess over the stoichiometrically required amounts for complexation was maintained.

First order rate constants  $k_{Hg}$  and  $k_{Fe}$  were calculated from the slope of  $-\ln (A_{\alpha} - A_t)$  vs t, by using the data till at least 60% completion of the reaction. Beyond this, there was deviation especially with excess K<sub>4</sub>Fe(CN)<sub>6</sub>, due to the slow formation of some tris-bipyridine-Fe(II) complex also. The rate constants at different temperatures are given in Tables 1 and 2.

# Activation parameters

The enthalpy and entropy of activation for both reactions were calculated from the rate constants at various temperatures from the absolute reaction rate theory. The values are given in Table 3.

# Effect of ionic strength

The effect of varying the ionic strength on the rate of the reaction when excess  $Fe(CN)_6^{4-}$  was used, was not significant. The rates fell in the range  $2.6 \pm 0.2 \times$ 



Fig. 4. Linear dependence of rate on  $K_4Fe(CN)_6$  concentration when  $HgCl_2$  is in excess (22°C).  $[K_4Fe(CN)_6] = 0.5$ , 0.75, 1.0 and  $1.5 \times 10^{-4}$  M and  $[HgCl_2] = 4 \times 10^{-4}$  in a, b, c and  $6 \times 10^{-4}$  M in d. (Time axis in all figures represents only initial increments and not absolute time elapsed.)

 $10^{-3} \text{ sec}^{-1}$  (at 19°) when the concentration of KNO<sub>3</sub> added varied between 0.1 and 0.4 M. At  $\mu < 0.05$  M the rates were slightly higher and in the range  $3.0 \pm 0.3 \times 10^{-3} \text{ sec}^{-1}$ , being greatest when no KNO<sub>3</sub> was added. There was again a small but discernible decrease in the rate with increase in ionic strength when excess HgCl<sub>2</sub> was present. The results are given in Table 4.

# DISCUSSION

It is well known that Hg(II) being a class b metal ion possesses high affinity for ligands like halides,  $(I^-Br^-Cl^-)$ , suplhide,  $CN^-$  and  $CNS^-$  etc. and is thus capable of abstracting these when coordinated to Fe(II), Co(III), Pd(II), Cr(III), Rh(III), etc. The kinetics and mechanism of such abstraction from several cationic species have been reported [2-9]. Only two instances of abstraction from anionic complexes viz. pentacyano Co(III) and hexacyanoferrate(II) are available [10-14]. Asperger et al. studies the kinetics of abstraction of CNfrom  $Fe(CN)_6^{4-}$  in the presence of  $C_6H_5NO$ , when a violet complex Fe(CN)<sub>5</sub>·C<sub>6</sub>H<sub>5</sub>NO is formed[11-13]. Their studies were complicated by further abstraction of CN<sup>-</sup> from this complex and hence the kinetic data were limited only to 5% reaction. The present investigation is comparatively free from such complications and gives consistent values for the rate constants, till more than 60% of the reaction.

Two distinct products, the tetracyano(bipyridine)-Fe(II) and tris-bipyridine-Fe(II) complexes are formed

Table 1. Rate constants in the presence of excess  $K_4$ Fe(CN)<sub>6</sub> (u = 0.1 M)

Temp ( <sup>O</sup> K)	<u>Hg x <math>10^3</math> (sec<sup>-1</sup>)</u>
288	1.3 ± 0.2
292	2.5 <u>+</u> 0.2
297	5.2 <u>+</u> 0.2
302	10.9 <u>+</u> 0.3

0 2 (
Fe x 10 <sup>4</sup> (sec <sup>-1</sup> )
5.0 <u>+</u> 0.2
8.7 <u>+</u> 0.15
15.1 <u>+</u> 0.25

Table 2. Rate constants in the presence of excess  $HgCl_2$  (U = 0.1 M)

(Rate constants reported in tables 1 and 2 are the

averages of six or more replicates).

Table 3. Activation parameters

<b>.</b>	H <sup>+</sup> (k cal/mole)	S (e.u)
Excess K <sub>4</sub> Fe(CN) <sub>6</sub>	25.6 <u>+</u> 0.4	17.6 <u>+</u> 1.0
Axcess HgCl <sub>2</sub>	18.7 <u>+</u> 0.5	- 9.6 <u>+</u> 1.5

Table 4. Effect of ionic strength on rate constants

Excess K4Fe(CN)6	Runs. (Temp = $292^{\circ}$ K)
<u>u(M</u> )	$k_{\rm Hg} \ge 10^{3} ({\rm sec}^{-1})$
0.0	3.2 <u>+</u> 0.2
0.02	2.9 <u>+</u> 0.15
0.05	2.86 <u>+</u> 0.2
0.10	2.56 <u>+</u> 0.2
0.20	2.6 <u>+</u> 0.1
0.40	2.5 <u>+</u> 0.15

Excess HgCl<sub>2</sub> Runs (Temp. 297°K)

u(M)	$k_{\rm Fe} \ge 10^4 (\rm sec^{-1})$
0.0	12.0 <u>+</u> 0.2
0.05	9.2 <u>+</u> 0.2
0.10	8.7 <u>+</u> 0.2
0.30	7.8 ± 0.2

when excess  $Fe(CN)_6^4$  or  $HgCl_2$  respectively is present. Further, the rate law is similar in both cases, being first order in the minor reactant. The rates are independent of the concentration of the major reactant. Both observations point strongly to the formation of two different intermediates, depending on the ratio of the concentration of the reactants. The nature of products formed, further suggests that 1:1 and 2:1 adducts between Hg(II) and Fe(CN)\_6<sup>4-</sup> are likely intermediates when excess  $Fe(CN)_6^{4-}$  or HgCl<sub>2</sub> is present. Such adducts have been reported earlier [13, 15–17]. Hence, the probable paths of the reactions, compatible with the observed kinetics are 3a and 3b.

$$\frac{\text{Excess Fe(CN)}_{6}^{4-}}{\text{Fe(CN}_{6}^{4-} + \text{Hg(II)}} \stackrel{\kappa_{1}}{\longrightarrow} \text{Fe(CN)}_{6}^{4-} - \text{Hg(II)}$$

$$\xrightarrow{^{k}\text{Hg}}_{\text{Bisynthing}} (\text{CN})_{4} (\text{Bipy}) \text{Fe(II)} + \text{Hg(CN)}_{2} \qquad (3a)$$

$$\frac{\text{Excess HgCl}_2}{\text{Fe}(\text{CN})_6^{4-} + 2\text{Hg}(\text{II})} \stackrel{\kappa_2}{\longrightarrow} \text{Fe}(\text{CN})_6^{4-} - 2\text{Hg}(\text{II})$$

$$\stackrel{k\text{Fe}}{\underset{\text{Bipyridine}}{\longrightarrow}} (\text{Bipy})_3\text{Fe}(\text{II}) + 2\text{Hg}(\text{CN})_2 + 2\text{CN}. \quad (3b)$$

The fact that the rates are independent of the concentrations of the excess reactants, suggests that  $K_1$  and  $K_2$ are quite large so that the intermediates are formed almost completely at the ratios of reactants used in these experiments. The formation of stable adducts, prior to abstraction of soft ligands by Hg(II) has been shown to occur in almost all cases of abstraction even when both Hg(II) and the complexes decomposed are cationic [2-14]. Hence mechanisms (3a) and (3b) seem quite reasonable. Whether one or two cyanides are coordinated to each Hg(II) at a time is not clear. The nature of the bonding of CN<sup>-</sup> and the tetrahedral geometry of Hg<sup>2+</sup> would favour bridging through one CN<sup>-</sup> at a time, rather than the simultaneous coordination to two CN<sup>-</sup>. The former would lead to penta cyano Fe(II) first, which reacts fast with bipyridine, which spans two coordination sites on the Fe(II). The decomposition step for (3a) would then be as eqn (4a).

$$Fe(CN)_{6} \cdot Hg(II) \xrightarrow{kHg} Fe(CN)_{5}^{3-} + HgCN(II)$$

$$+ \downarrow_{Bipyridine} \downarrow_{Fast}$$

$$(CN)_{4}(Bipy)Fe(II) + Hg(CN)_{2} \qquad (4a)$$

similarly decomposition of (3b) will be as in eqn (4b); the tetra cyano ferrate (II) being formed first, to be converted by a fast step to  $(Bipy)_3Fe(II)$ .

$$Hg-Fe(CN)_{6}Hg(II) \stackrel{k^{Fe}}{\rightarrow} Fe(CN)_{4}^{2-} + 2Hg(CN)^{-}$$

$$Fast \qquad \qquad Fast \qquad \qquad Fast \qquad F$$

Asperger *et al.*, suggested a mechanism similar to (3a) for the formation of violet penta cyano nitroso benzene Fe(II), by the abstraction of  $CN^{-}$  from Fe(CN)<sub>6</sub><sup>4-</sup> from Fe(CN)<sub>6</sub><sup>4-</sup> by HgCl<sub>2</sub>[12, 13]. They, however, postulated a

weak ion pair equilibrium for the association step, and hence first order kinetics with respect to both  $[HgCl_2]$ and  $[Fe(CN)_6^{4-}]$ . It is however, important to note that the rate constants reported by them vary with the ratio of concentrations of  $HgCl_2$  and  $Fe(CN)_6^{4-}$ . Formation of a red complex with excess  $HgCl_2$  was also observed. The rates decreased with excess  $HgCl_2$ . It is thus possible that two different reactions also take place, depending on the ratio of concentrations of  $Fe(CN)_6^{4-}$  and  $HgCl_2$ , in this case.

Very large differences in the activation parameters for the two reactions show very clearly that the activated complexes in the two cases are widely different. The fairly high positive entropy of activation in the tetracyano Fe(II) formation points to a less polar activated complex, whereas the negative entropy of activation for the tris-bipyridine Fe(II) formation is indicative of a polar activated complex.

The effect of ionic strength is what is expected of a first order decomposition of the intermediates which are fairly large. It is not meaningful to interpret the small changes in rates in any quantitative manner, as the experimental errors within a set of runs themselves are practically of the same magnitude as the differences observed. The effect of  $\mu$  can best be attributed to activity considerations [12].

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