

## KINETICS AND MECHANISM OF PRUSSIAN BLUE FORMATION

R.K. Adhikamsetty and S.B. Jonnalagadda\*

School of Chemistry, University of KwaZulu-Natal, Westville Campus, Chiltern Hills, Durban,  
South Africa

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**ABSTRACT.** The kinetics of reaction between ferrocyanide and ferric ions under acidic conditions was studied at fixed ionic strength (0.1 M) and  $(25 \pm 0.1)^\circ\text{C}$  by using the stopped flow technique, under limiting conditions of [ferrocyanide] and with other reactants in excess. The reaction had first-order dependence on ferrocyanide, Fe(III) and  $\text{H}^+$  ion concentrations and had negative salt effect. On the basis of the experimental findings, a plausible mechanism for the formation of soluble form of Prussian blue ( $\text{KFe}\{\text{Fe}(\text{CN})_6\}_x \text{H}_2\text{O}$ ) and rate law are proposed. The activation parameters for the title reaction are estimated. A relatively low energy of activation ( $23 \text{ kJ mol}^{-1}$ ) and high negative entropy of activation ( $-231 \text{ J K}^{-1} \text{ mol}^{-1}$ ) agree well with the proposed mechanism and configuration of complex ion leading to the formation of insoluble Prussian blue,  $\text{Fe}_4\{\text{Fe}(\text{CN})_6\}_3 \text{H}_2\text{O}$ .

**KEY WORDS:** Prussian blue, Kinetics, Ferrocyanide, Salt effect, Ferriferrocyanide

### INTRODUCTION

Prussian blue (PB) is the traditional inorganic dye and it is still the subject of considerable research interest. This intense blue colored pigment is used in the preparation of paints, printing inks, laundry dye, etc. [1]. The micro-porous character of PB and its analogues find applications as adsorbent, as sieves for molecular separation [2] and for catalytic processes [3]. It has wide industrial applications such as in removal of heavy metal ions in wine production [4], electrochemical application as battery building [5], electronic switching and electrochromic devices [6]. With the high insolubility and ion exchange properties, PB was also used to remove the  $^{137}\text{Cs}$  from radioactive waste solutions [7] and from humans and animals exposed to nuclear accidents [8]. PB and its analogues are playing a prime role in the field of molecular materials because of their magnetic properties at high temperature [9, 10].

Prussian blue is a well known member of hexacyanometallates, which can exist in water as 'soluble Prussian blue' ( $\text{KFe}\{\text{Fe}(\text{CN})_6\}_x \text{H}_2\text{O}$ ) and as 'insoluble Prussian blue' ( $\text{Fe}_4\{\text{Fe}(\text{CN})_6\}_3 \text{H}_2\text{O}$ ) [11]. The molar absorption coefficient of the soluble form is  $3.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  at 700 nm [12]. Its solubility is very low ( $K_s = 3.0 \times 10^{-41}$ ) [12]. The reduced form of PB is known as Everitt's salt,  $\text{K}_2\text{Fe}^{\text{II}}\{\text{Fe}(\text{CN})_6\}$  [13]. Conventionally, the reaction of ferric ion with ferrocyanide ion resulting in formation of PB is used as a qualitative test for ferric ion. Although Prussian blue is one of the most frequently used inorganic dyes, little is known about its formation processes and kinetics. In this paper, we report the kinetics of formation of PB under acidic conditions and propose a plausible mechanism.

### EXPERIMENTAL

#### *Materials and methods*

All the chemicals used were of analytical reagent grade. The stock solutions were made in A-grade glassware using double distilled and de-ionized water. The  $\text{Fe}^{3+}$  solutions were prepared

\*Corresponding author. E-mail: jonnalagaddas@ukzn.ac.za

using ferric ammonium sulfate. The acid solutions were prepared by diluting the sulfuric acid (AnalaR, Merck) and standardizing the stock solutions. The ionic strength of the reaction mixture was maintained constant by adding potassium sulfate (AnalaR, BDH, Bristol, UK) solution. Normally, the hexacyanoferrate(II) solution is prepared in alkaline conditions, to have it in stable form [14-16]. In our studies, 0.10 g of potassium hexacyanoferrate(III) was added to 2.10 g of potassium ferrocyanide dissolved in aqueous solution to avoid hydrolysis of Fe(III) [17]. The formation kinetics of PB was studied at  $(25 \pm 0.1)^\circ\text{C}$  and ionic strength (0.1 M), using a Hi-Tech SF-61 double mixing stopped-flow apparatus (Salisbury, UK) equipped with photomultiplier/diode array spectrometer. Requisite volumes of Fe(III), acid and salt and ferrocyanide and salt solutions were separately thermostated and transferred to the two syringes of the stopped flow equipment. Change in the absorbance due to formation of PB was monitored at 680 nm. Factor analysis and global fitting were performed to obtain rate constants, using the computer program, SPECFIT from spectrum software associates (TgK Scientific Limited, Brasford on Avon, UK). Best fits were obtained with equation for simple first-order reaction, with single exponential function ( $y = -A \exp(-k \cdot x) + C$ ), which gave the computed *pseudo* first-order rate coefficients. Cary 1E double beam spectrophotometer (Varian, Australia) was used for recording spectra. All the rate constants reported are average of values from at least five replicate runs. The standard error in determination of kinetic data was less than 5 %.

## RESULTS AND DISCUSSION

The Prussian blue formation reaction between ferric ion and ferrocyanide complex ions was studied under excess concentrations of ferric iron and acid and with low and limiting concentration of ferrocyanide ion. Figure 1 illustrates the spectra of the repetitive scans showing the formation of PB at 680 nm at 1 min intervals for 10 cycles. Figure 2 shows the typical absorbance *versus* time curve with excess concentrations of acid ( $1.5 \times 10^{-3}$  M) and ferric ion ( $3.0 \times 10^{-2}$  M) and at limiting concentration of ferrocyanide ( $4.0 \times 10^{-4}$  M). The profiles of the absorption-time plots were not sharp curves due to the sparse solubility of the PB formed and the processes leading to its precipitation. The kinetic curves analysed using the SPECFIT software programme gave good fits to first-order rate expressions indicating the kinetics follow *pseudo* first-order reaction with respect to ferrocyanide ion. Figure 2 shows the analyzed run fit of the kinetic curve together with residuals indicating a good fit. Kinetic experiments were conducted by varying the initial concentrations of either ferric ion or acid, while other initial concentrations and ionic strength were held constant. The *pseudo* first-order rate constants obtained from data analysis of those curves are summarized in Table 1. The plot of  $\log k'$  *versus*  $\log [\text{Fe(III)}]$  and  $\log k'$  *versus*  $\log [\text{H}^+]$  gave good straight lines (Figure 3 **a** and **b**) with gradients 0.92 and 0.85, respectively, both with  $R^2 = 0.99$  suggesting that order with respect to both the reactants is about one each. Further, the variation of the ionic strength,  $I$  in the range 0.080 to 0.126 showed that the reaction experiences negative kinetic salt. The plot of  $\log k'$  *versus*  $I^{1/2}$  gave a gradient of -0.835 and  $R^2 = 0.986$  (Figure 4).

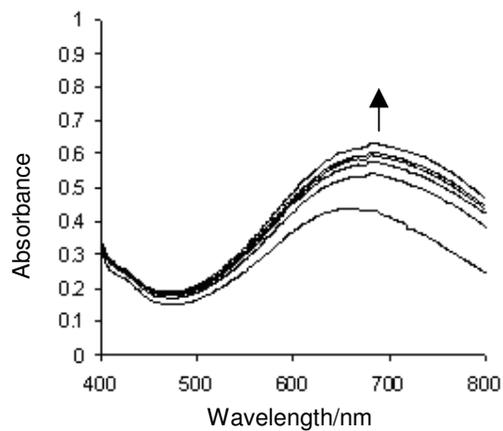


Figure 1. Absorption spectra of formation of soluble Prussian blue: Repetitive scans (10 cycles) at 1 min interval.

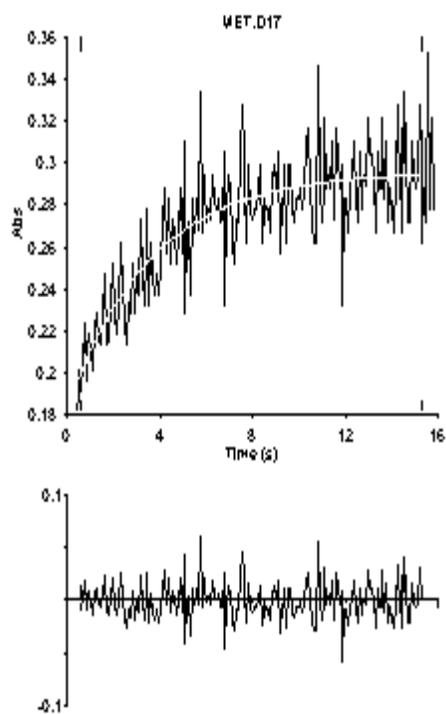


Figure 2. Analysed run fit of kinetic curve (stopped-flow) with residuals.

Table 1. Rate constants for the formation of Prussian blue. ([Ferrocyanide] =  $4.0 \times 10^{-4}$  M and temperature 25 °C).

[Fe(III)]/ $10^{-2}$ M	[H <sup>+</sup> ]/ $10^{-3}$ M	I/M	k'/s <sup>-1</sup>	k/ $10^3$ M <sup>2</sup> s <sup>-1</sup>
1.8	1.5	0.10	0.27	9.85
2.2	1.5	0.10	0.32	9.70
2.6	1.5	0.10	0.37	9.49
3.0	1.5	0.10	0.41	9.11
3.4	1.5	0.10	0.47	9.22
3.8	1.5	0.10	0.55	9.65
3.0	1.1	0.10	0.30	9.09
3.0	1.3	0.10	0.35	8.97
3.0	1.5	0.10	0.40	8.89
3.0	1.7	0.10	0.44	8.63
3.0	1.9	0.10	0.48	8.42
3.0	2.1	0.10	0.52	8.25
3.0	1.5	0.080	0.431	9.56
3.0	1.5	0.090	0.413	9.18
3.0	1.5	0.100	0.404	8.96
3.0	1.5	0.108	0.396	8.80
3.0	1.5	0.117	0.380	8.44
3.0	1.5	0.126	0.375	8.33

The data are mean of five replicate experiments. Mean  $k = (9.1 \pm 0.5) \times 10^3 \text{ M}^2 \text{ s}^{-1}$  at  $I = 0.10 \text{ M}$ .

The reaction orders obtained represent the species involved in the rate limiting step of the formation of the soluble form of the Prussian blue,  $(\text{KFe}\{\text{Fe}(\text{CN})_6\}x\text{H}_2\text{O})$ , which consequently crystallizes to its insoluble form. The first-order dependence of the reaction on the initial concentrations of  $\text{Fe}^{3+}$ , acid and ferrocyanide ions and the observed strong negative salt effect, suggests the rate limiting step of the formation of soluble PB involves one molecule each of the three reactant species and the rate-limit reaction is between oppositely charged species. The slightly lower order ( $< 1$ ) with respect to  $\text{H}^+$  and salt effect ( $< 1$ ) also indicate the possible existence of other alternate paths to the formation of soluble form of PB,  $(\text{HFe}\{\text{Fe}(\text{CN})_6\})$ . Broadly, there are various possibilities for the rate limiting step of the reaction. The slow step of the reaction could be one of the following or the combination of reactions, i.e. (i) between  $\text{Fe}^{3+}$  and  $\{\text{Fe}(\text{CN})_6\}^4$ , (ii)  $\text{H}^+$  and  $\{\text{Fe}(\text{CN})_6\}^4$ , (iii)  $\text{Fe}^{3+}$  and  $\text{H}\{\text{Fe}(\text{CN})_6\}^{3-}$  and (iv)  $\text{H}^+$  and  $\text{Fe}\{\text{Fe}(\text{CN})_6\}^-$  ions. For the reactions (i) or (ii) reactions to be slow steps, the plots of  $\log k'$  versus  $I^{1/2}$  plot should have slopes of -12 or -4, respectively, which is not the case. Similar plots for reactions (iii) and (iv) reactions would give gradients of -9 and -1, respectively. Further for (i), for the formation of ferriferrocyanide, the reaction is between high spin ferric and low spin ferrocyanide ions which is relatively fast [18]. The protonation of ferrocyanide ion too is fast and  $\text{H}\{\text{Fe}(\text{CN})_6\}^{3-}$  ion is known to react with other species [19], but with its first protonation constant  $\text{pK} = 4.19$ , i.e.  $K = 6.45 \times 10^{-5}$  [20], maximum possible concentration of  $\text{H}\{\text{Fe}(\text{CN})_6\}^{3-}$  under current reaction conditions will be as low as  $3.87 \times 10^{-12} \text{ M}$  to  $5.42 \times 10^{-12} \text{ M}$ . An increase in acid concentration could lead to higher concentration of  $\text{H}\{\text{Fe}(\text{CN})_6\}^{3-}$  ion. Hence, the reaction between  $\text{H}\{\text{Fe}(\text{CN})_6\}^{3-}$  and  $\text{Fe}^{3+}$  ions although is possible, could only be a minor path. Thus, the reaction between  $\text{H}^+$  and  $\text{Fe}\{\text{Fe}(\text{CN})_6\}^-$  ions could be the probable major path way and rate-limiting step for the formation of soluble Prussian blue,  $\text{HFe}\{\text{Fe}(\text{CN})_6\}$ . Thus, of the various possibilities, concurring with the reaction orders with respect to ferrocyanide and ferric ion slightly lower order with respect to  $[\text{H}^+]$  (0.85) and observed salt effect (-0.845), the following mechanism is proposed for the formation of soluble and insoluble forms of Prussian blue.

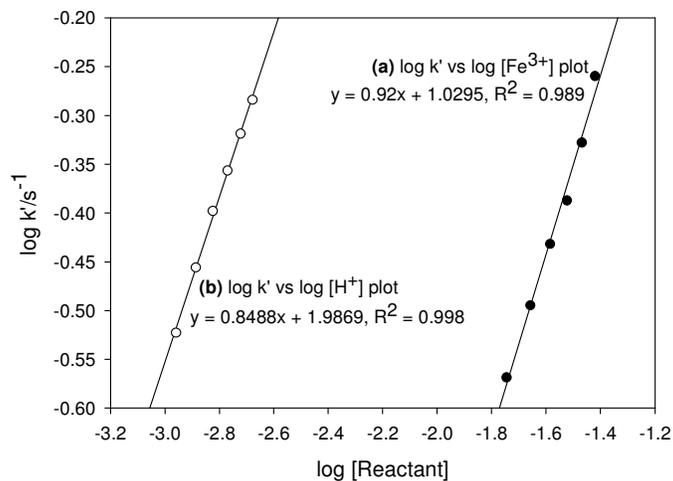


Figure 3. Plot of  $\log k'$  versus  $\log [\text{Reactant}]$  plots at constant ionic strength. (a) Variation of  $[\text{Fe}^{3+}]$  concentration:  $[\text{Fe}(\text{CN})_6]^{4-} = 4.0 \times 10^{-4} \text{ M}$ ,  $[\text{H}^+] = 1.5 \times 10^{-3} \text{ M}$  and  $I = 0.1 \text{ M}$ . (b) Variation of  $[\text{H}^+]$ :  $[\text{Fe}(\text{CN})_6]^{4-} = 4.0 \times 10^{-4} \text{ M}$ ,  $[\text{Fe}^{3+}] = 3.0 \times 10^{-2} \text{ M}$  and  $I = 0.1 \text{ M}$ .

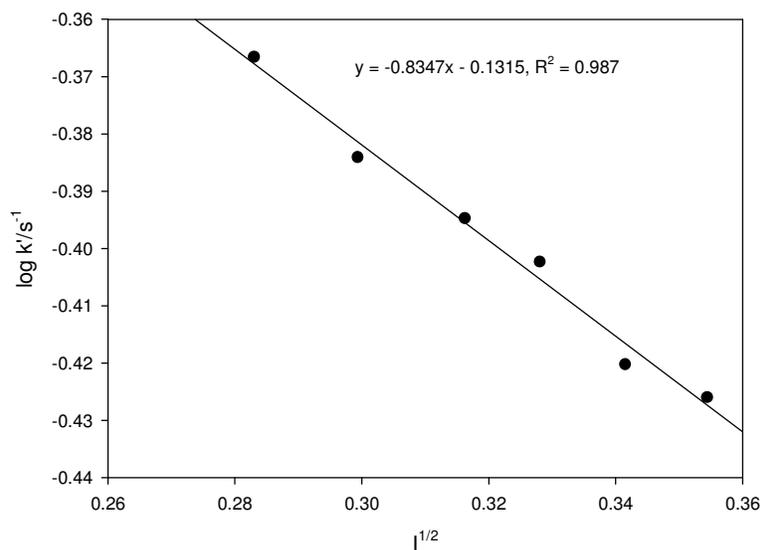
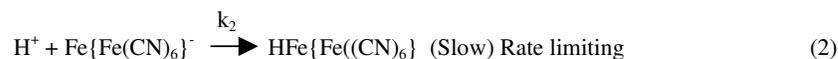
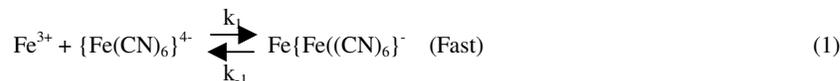
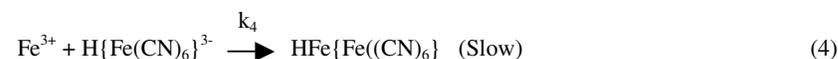
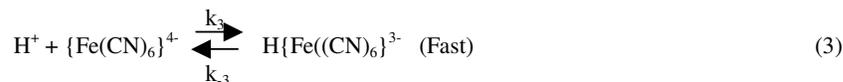


Figure 4. Plot of  $\log k'$  versus  $I^{1/2}$ .  $[\text{Fe}(\text{CN})_6]^{4-} = 4.0 \times 10^{-4} \text{ M}$ ,  $[\text{Fe}^{3+}] = 3.0 \times 10^{-2} \text{ M}$  and  $[\text{H}^+] = 1.5 \times 10^{-3} \text{ M}$ .

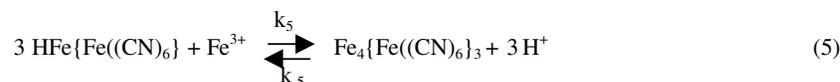
Major path:



Minor path:



Then three molecules of soluble PB and ferric ion assemble slowly in to the face centered cubic structure, leading finally to the formation of insoluble Prussian blue.



Rate law:

Based on the proposed mechanism, neglecting the contribution of the minor path, a simplified rate equation for the formation of soluble form of PB can be expressed as follows:

$$\frac{d[\text{HFe}\{\text{Fe}(\text{CN})_6\}]}{dt} = k_2[\text{H}^+][\text{Fe}\{\text{Fe}(\text{CN})_6\}^-] \quad (6)$$

Assuming fast equilibrium with equations 1 and 3, eqn. 6 may be written as

$$r = \frac{k_1 k_2}{k_{-1}} [\text{H}^+][\text{Fe}^{3+}][\text{Fe}(\text{CN})_6^{4-}] \quad (7)$$

When the concentrations of  $\text{H}^+$  and  $\text{Fe}^{3+}$  ions are in excess, as in the present case, above equation reduces to

$$r = k' [\{\text{Fe}(\text{CN})_6\}^{4-}] \quad (8)$$

$$\text{where } k' = \frac{k_1 k_2}{k_{-1}} [\text{H}^+][\text{Fe}^{3+}] = k[\text{H}^+][\text{Fe}^{3+}] \quad (9)$$

$$\text{The overall third-order rate constant, } k = \frac{k'}{[\text{H}^+][\text{Fe}^{3+}]} \quad (10)$$

where the pseudo first-order rate constant  $k'$  equals to  $(k_1 k_2 / k_{-1})$  in a simplified rate law.

Further the kinetics of the reaction was studied as function of temperature at fixed ionic strength. Table 2 summarises the temperatures at which the reaction studies, the corresponding *pseudo* first-order rate constants and the calculated overall third-order rate coefficients. The plot of  $\log k$  against  $1/T$  gave a straight line ( $R^2 = 0.99$ ) with a slope of  $-1216$ , indicating the energy of activation for the reaction is  $(23.3 \pm 1.3) \text{ kJ mol}^{-1}$ . The enthalpy of activation for the third-order reaction is found to be  $(15.9 \pm 0.8) \text{ kJ mol}^{-1}$ . While the pre-exponential factor was about

$1.0 \times 10^8 \text{ M}^{-2} \text{ s}^{-1}$ , the entropy of activation values was  $-231 \text{ J K}^{-1} \text{ mol}^{-1}$ . While low energy of activation agrees with relatively fast reaction of formation of soluble Prussian blue, high and negative entropy of activation is obviously expected for the compact structure of the final products, soluble and insoluble forms of Prussian blue.

Table 2. Rate constants for the formation of Prussian blue under varied temperatures.  $[\text{Fe}^{3+}] = 3.0 \times 10^{-2} \text{ M}$ ,  $[\text{H}^+] = 1.5 \times 10^{-3} \text{ M}$  and  $[\text{Ferrocyanide}] = 4.0 \times 10^{-4} \text{ M}$ .

Temp (K)	$k'$ ( $\text{s}^{-1}$ )	$K$ ( $10^3 \text{ M}^{-2} \text{ s}^{-1}$ )
288	0.28	6.22
293	0.32	7.11
298	0.40	8.89
303	0.47	10.44
308	0.52	11.56
313	0.60	13.33

Estimated activation parameters: Energy of activation,  $E_a = (23.3 \pm 1.3) \text{ kJ mol}^{-1}$ . Enthalpy of activation,  $\Delta H^\ddagger = (15.9 \pm 0.8) \text{ kJ mol}^{-1}$ . Arrhenius factor,  $A = (1.04 \pm 0.06) \times 10^8 \text{ M}^{-2} \text{ s}^{-1}$ . Entropy of activation,  $\Delta S^\ddagger = (-231 \pm 13) \text{ J K}^{-1} \text{ mol}^{-1}$ .

Prussian blue is reported to consist of a network of high-spin iron(III) ions bound to the nitrogen of cyanide ions and the low-spin iron(II) ions bridge the high-spin iron(III) and low-spin iron(II) ions so effectively resulting in an intense charge transfer arising to the blue color in PB. In its crystal structure, channels run through the solid and connect holes similar to those in zeolites [21]. PB is unstable at higher pH values, which transforms to  $\text{Fe}(\text{OH})_3$ .

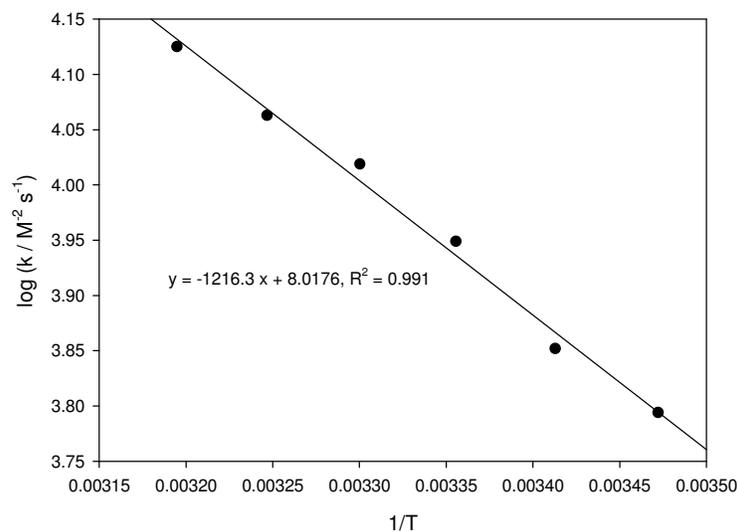


Figure 5. Energy parameters: Plot of  $\log k$  versus  $1/T$ .  $[\text{Fe}(\text{CN})_6]^{4-} = 4.0 \times 10^{-4} \text{ M}$ ,  $[\text{Fe}^{3+}] = 3.0 \times 10^{-2} \text{ M}$ ,  $[\text{H}^+] = 1.5 \times 10^{-3} \text{ M}$  and  $I = 0.1 \text{ M}$ .

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