

# Kinetics of the Partially Autocatalytic Hexacyanoferrate(II)–Iodate Reaction and the Effect of a Added Iodide

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**Abstract** The oxidation of  $[\text{Fe}(\text{CN})_6]^{4-}$  by  $\text{IO}_3^-$  in the pH 1.62–2.70 range is autocatalytic whether the reductant or oxidant is in excess. Typical first order plots of  $-\ln(A_\infty - A_t)$  versus time are curved showing an increase in rate with the progress of the reaction. It was possible, however, to obtain the pseudo first order rate constants ( $k_u$ ) for the uncatalyzed  $[\text{Fe}(\text{CN})_6]^{4-}$ – $\text{IO}_3^-$  reaction from the linear parts of these plots. The linearity of the plots decreases with increasing concentrations of  $[\text{Fe}(\text{CN})_6]^{4-}$ ,  $\text{IO}_3^-$  and  $\text{H}^+$ . The pseudo first order rate constant ( $k_{\text{obs}}$ ) for the whole reaction was obtained using  $\ln[(A_t/A_\infty)/(1 - A_t/A_\infty)]$  versus time and/or a nonlinear curve fitting for sigmoidal reactions. The rate constant,  $k_{\text{obs}}$  obtained by both methods varies with the initial concentration of  $[\text{Fe}(\text{CN})_6]^{4-}$  according to Eqn. (i), where  $k_u$  is the rate constant of the direct reaction between  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $\text{IO}_3^-$  and  $k_a$  is the rate constant of the autocatalytic reaction. The values of  $k_u$ , at different reactions conditions, obtained from plots of  $k_{\text{obs}}$  vs  $[\text{Fe}(\text{CN})_6]^{4-}$ , are in fairly good agreement with values obtained from linear sections of first order plots.

$$k_{\text{obs}} = k_u + k_a[\text{Fe}(\text{CN})_6]^{4-}_i \quad (\text{i})$$

Both  $k_u$  and  $k_a$  showed a first order dependence on  $[\text{IO}_3^-]$ . The dependence of  $k_u$  on  $[\text{H}^+]$  is complex as shown in Eqn. (ii). A polynomial fit of  $k_2(1 + K_1[\text{H}^+])$  vs  $[\text{H}^+]$  has a zero intercept in agreement with Eqn. (iii)

The catalytic rate constant varies with  $[\text{H}^+]$  according to Eqn. (iii)

$$k_2 = k_u/[\text{IO}_3^-] = \frac{\{(k_7K_1 + k_8K_3)[\text{H}^+] + (k_9K_1K_2 + K_1K_3)[\text{H}^+]^2\}}{(1 + K_1[\text{H}^+])} \quad (\text{ii})$$

$$k_2(1 + K_1[\text{H}^+]) = (k_7K_1 + k_8K_3)[\text{H}^+] + (k_9K_1K_2 + K_1K_3)[\text{H}^+]^2 \quad (\text{iii})$$

$$k_a = k_{11}[\text{H}^+][\text{IO}_3^-] \quad (\text{iv})$$

The overall dependence of  $k_{\text{obs}}$  on  $[\text{Fe}(\text{CN})_6]^{4-}$ ,  $[\text{IO}_3^-]$  and  $[\text{H}^+]$  is given by Eqn. (v).

$$k_{\text{obs}} = \frac{\{(k_7K_1 + k_8K_3)[\text{H}^+] + (k_9K_1K_2 + K_1K_3)[\text{H}^+]^2\}[\text{IO}_3^-]}{(1 + K_1[\text{H}^+])} + k_{11}[\text{Fe}(\text{CN})_6]^{4-}_i[\text{IO}_3^-][\text{H}^+] \quad (\text{v})$$

At pH 4.33 no reaction between  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $\text{IO}_3^-$  was observed. When iodide is added to the reaction mixture at this pH, the reaction proceeded at measureable rate.

**Keywords** Hexacyanoferrate(II), Iodate, Iodide, Kinetics, Autocatalytic Oxidation

## 1. Introduction

The kinetics of oxidation of  $[\text{Fe}(\text{CN})_6]^{4-}$  by  $\text{IO}_3^-$  in the pH 1.77–2.65 range, under conditions where  $[\text{Fe}(\text{CN})_6]^{4-}$  is in vast excess has been reported previously[1]. It was observed that the reaction is autocatalytic whether  $\text{IO}_3^-$  or  $[\text{Fe}(\text{CN})_6]^{4-}$  is in vast excess. This is in agreement with an earlier report[2]. Nonetheless, rate constants were measured from the

linear parts of pseudo first order plots with the reductant in vast excess over that of the oxidant. The closely related reaction between  $\text{BrO}_3^-$  and  $[\text{Fe}(\text{CN})_6]^{4-}$  has also been reported and has shown a similar complexity[3,4]. The kinetics of this reaction in the relatively high  $[\text{H}^+]$  (0.05–0.5 M) was found to be partially autocatalytic. Autocatalysis is believed to be caused by  $\text{Br}_2$  formed from the relatively fast reaction between  $\text{Br}^-$  and  $\text{BrO}_3^-$  in the employed  $[\text{H}^+]$  range[3]. The  $\text{Br}_2$ – $[\text{Fe}(\text{CN})_6]^{4-}$  reaction is shown to be very fast[3]. The kinetics of the  $\text{BrO}_3^-$ – $[\text{Fe}(\text{CN})_6]^{4-}$  reaction in the pH 3.6–5.8 range is also complex. The complexity of this reaction in this  $[\text{H}^+]$  range, is claimed not to arise from the involvement of  $\text{Br}_2$ , which is not formed in the  $\text{BrO}_3^-$ – $\text{Br}^-$  system at this

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Published online at <http://journal.sapub.org/chemistry>

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pH range[4,5], but rather from the involvement of aquahexacyanoferrate(II) ( $[\text{Fe}(\text{CN})_5(\text{H}_2\text{O})]^{3-}$ ). Aquahexacyanoferrate(II) is formed very slowly in acidic solutions by replacing a  $\text{CN}^-$  by an  $\text{H}_2\text{O}$  and can be induced by light[6]. Deliberate addition of  $[\text{Fe}(\text{CN})_5(\text{H}_2\text{O})]^{3-}$  has shown a remarkable effect on the  $\text{BrO}_3^- - [\text{Fe}(\text{CN})_6]^{4-}$  reaction[4].

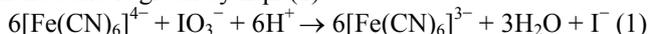
Autocatalysis in  $\text{IO}_3^- - [\text{Fe}(\text{CN})_6]^{4-}$  reaction most likely arises from reaction between the product iodide and iodate in acidic solutions. The lower redox potential of  $\text{I}^-$  facilitates its oxidation to  $\text{I}_2$  and/or  $\text{I}_3^-$  by  $\text{IO}_3^-$  [7,8] at the pH values employed. The effect of deliberately added  $\text{I}^-$  on the  $\text{IO}_3^- - [\text{Fe}(\text{CN})_6]^{4-}$  reaction has been reported[9]. It was found that added  $\text{I}^-$  accelerates this reaction considerably and the rate of reaction increases with increasing  $[\text{I}^-]$  even at pH values where the reaction does not take place in absence of iodide. It has known that  $\text{I}_2$  reacts very rapidly with  $[\text{Fe}(\text{CN})_6]^{4-}$  [10]. In recent years there has been a lot of interest and research activity in oscillating reactions. The system  $\text{IO}_3^- - \text{SO}_3^{2-} - [\text{Fe}(\text{CN})_6]^{4-}$  is oscillatory. In these types of reactions it is important to know the rate constant of the likely processes. These are used to build models for oscillating reactions[11]. In this study we report the kinetics of both the uncatalyzed and the autocatalytic processes in the  $\text{IO}_3^- - [\text{Fe}(\text{CN})_6]^{4-}$  reaction with iodate in large excess.

## 2. Experimental

All the chemicals were reagent grade and were used as received. Stock solutions, buffer ( $\text{HSO}_4^-/\text{SO}_4^{2-}$ ) and solutions of  $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$  were freshly prepared and used immediately as described earlier[1]. The absorption of the product  $[\text{Fe}(\text{CN})_6]^{3-}$  was monitored at  $\lambda_{\text{max}}$  420 nm using a Perkin Elmer Model Lambda 25 or a Shimadzu 1800 UV/VIS absorption spectrophotometer both equipped with a thermostatted cell-holder. The absorbance-time traces were recorded on XY recorder. The pH of the reaction solutions was measured using an ELICO LI 120 pH meter. The kinetics of the reaction was investigated under constant reaction conditions with  $[\text{IO}_3^-]$  in vast excess over that of  $[\text{Fe}(\text{CN})_6]^{4-}$ . Both reactants concentrations as well as the pH were varied.

## 3. Results and Discussions

The stoichiometry of the  $\text{IO}_3^- - [\text{Fe}(\text{CN})_6]^{4-}$  is well established and is given by Eqn.(1).



It was previously reported that the  $\text{IO}_3^- - [\text{Fe}(\text{CN})_6]^{4-}$  reaction is autocatalytic[1,2]. The absorbance-time trace for the  $\text{IO}_3^- - [\text{Fe}(\text{CN})_6]^{4-}$  reaction does not display the exponential growth of  $[\text{Fe}(\text{CN})_6]^{3-}$  expected for a first order reaction. A similar behavior was observed in the  $[\text{Fe}(\text{CN})_6]^{4-} - \text{BrO}_3^-$  reaction at relatively high  $[\text{H}^+]$ [3]. Plots of  $\ln(A_\infty - A_t)$  versus time, where  $A_\infty$  and  $A_t$  are absorbance values at infinity and time  $t$  respectively, show marked deviation from

linearity as shown in Fig. 1. The deviation from linearity of the plots depends on the initial concentrations of  $\text{IO}_3^-$ ,  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{H}^+]$ . The higher the concentration of the reactants, the shorter is the linearity of the plots. The first order rate constants for the uncatalyzed path,  $k_u$ , were obtained from the linear parts of these plots. It was found that  $k_u$  is fairly constant and does not depend on the initial concentration of  $[\text{Fe}(\text{CN})_6]^{4-}$  at fixed reaction conditions as shown in Table 1. The data of Fig. 1 is analyzed using a treatment for an autocatalytic reaction[12-14]. Plots of  $\ln\{(A_t/A_\infty)/(1 - A_t/A_\infty)\}$  versus time are linear as shown in Fig. 2. This treatment was applied only in the range where autocatalysis becomes dominant. In the low pH range autocatalysis starts early and a nearly S-shaped form of absorbance-time curve is observed. The values of the slopes ( $k_{\text{obs}}$ ,  $\text{s}^{-1}$ ) obtained from Fig. 2 and similar plots are dependent on the initial concentration of  $[\text{Fe}(\text{CN})_6]^{4-}$ . The absorbance-time data were also treated using a nonlinear curve fitting using an Origin 7.0 sigmoidal growth curve fitting program. A typical nonlinear fit for the data in Fig. 1 is shown in Figure 3. Values of  $k_{\text{obs}}$  obtained using both methods are within 0- 8% variation. Most of  $k_{\text{obs}}$  values were obtained using the non-linear curve fitting program.

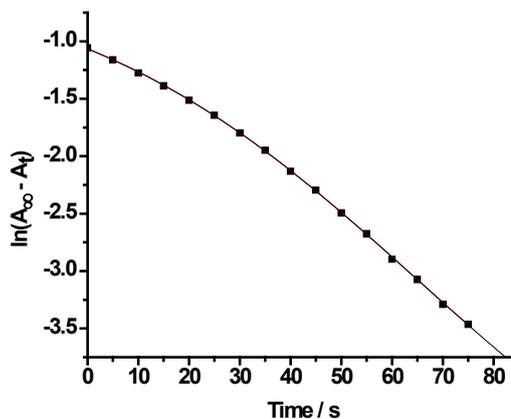


Figure 1. First order plot of the  $\text{IO}_3^- - [\text{Fe}(\text{CN})_6]^{4-}$  reaction,  $[\text{IO}_3^-] = 5.0 \times 10^{-3} \text{ M}$ ,  $[\text{Fe}(\text{CN})_6]^{4-} = 5.4 \times 10^{-4} \text{ M}$ ,  $\text{pH} = 1.53$ ,  $\text{I} = 1.0 \text{ M}$  and  $T = 25.0 \text{ }^\circ\text{C}$

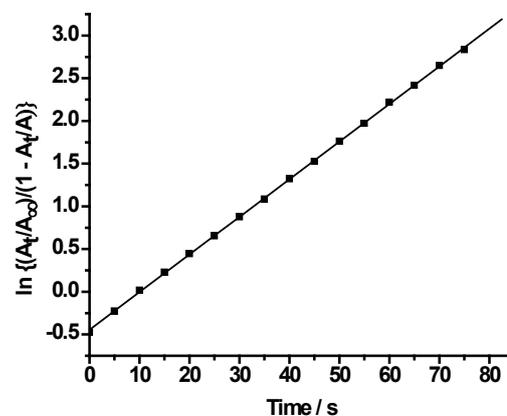
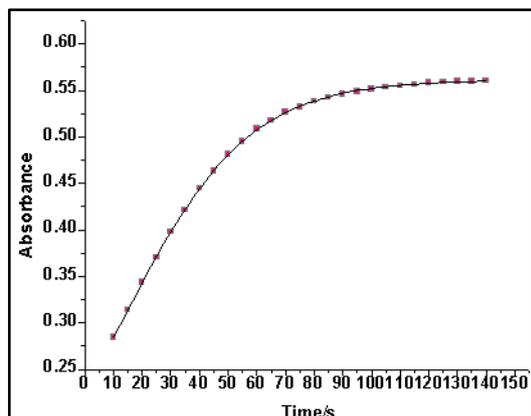


Figure 2. Data in Fig. 1 plotted using  $\ln\{(A_t/A_\infty)/(1 - A_t/A_\infty)\}$  versus time



**Figure 3.** Data in Fig. 1 plotted using Boltzmann sigmoidal growth for a non-linear curve fitting program

**Table 1.** Kinetic data for the for the uncatalyzed  $[\text{Fe}(\text{CN})_6]^{4-} - \text{IO}_3^-$  reaction at 25.0 °C,  $I = 1.0 \text{ M}$

pH	$10^2 [\text{IO}_3^-] / \text{M}$	$10^3 [\text{Fe}(\text{CN})_6^{4-}] / \text{M}$	$10^3 k_u / \text{s}^{-1}$
2.70	20.0	5.4	$1.51 \pm 0.01$
2.57		5.3	$2.62 \pm 0.02$
2.51		5.2	$3.30 \pm 0.02$
2.41	5.00	7.0	$1.24 \pm 0.01$
2.30		5.7	$1.93 \pm 0.04$
2.13		5.3	$3.22 \pm 0.03$
1.96	2.50	5.0	$2.10 \pm 0.01$
		5.00	$4.86 \pm 0.06$
		7.50	$7.72 \pm 0.15$
	10.0	5.0	$9.87 \pm 0.14$
1.92		1.9	$5.21 \pm 0.05$
		7.9	$5.02 \pm 0.03$
	5.8	$5.09 \pm 0.04$	
1.84	5.00	2.6	$5.32 \pm 0.11$
		10.2	$6.35 \pm 0.12$
		7.3	$6.33 \pm 0.09$
1.82		3.8	$6.55 \pm 0.06$
		10.1	$7.34 \pm 0.11$
		7.5	$6.90 \pm 0.08$
1.70		5.2	$7.00 \pm 0.08$
		3.9	$6.89 \pm 0.05$
		7.8	$9.96 \pm 0.32$
1.64		5.3	$10.96 \pm 0.16$
1.62		5.3	$11.00 \pm 0.23$

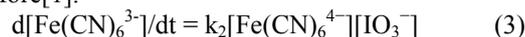
**Table 2.** Kinetic data for the catalyzed  $[\text{Fe}(\text{CN})_5]^{4-} - \text{IO}_3^-$  reaction at 25.0 °C,  $I = 1.0 \text{ M}$

pH	$10^2 [\text{IO}_3^-] / \text{M}$	$10^4 [\text{Fe}(\text{CN})_5^{4-}] / \text{M}$	$10^3 k_{\text{obs}} / \text{s}^{-1}$	$k_u / \text{M}^{-1} \text{s}^{-1}$
2.70	20.0	5.4	$5.87 \pm 0.54$	$8.07 \pm 0.72$
2.57		5.3	$8.36 \pm 0.16$	$10.85 \pm 0.22$
2.51		5.2	$11.30 \pm 0.23$	$15.41 \pm 0.31$
2.41	5.0	10.0	$10.34 \pm 0.32$	$8.33 \pm 0.26$
2.30		7.2	$11.11 \pm 0.80$	$9.68 \pm 0.90$
2.13		10.3	$21.32 \pm 0.52$	$17.50 \pm 0.43$
	10.0	6.9	$15.50 \pm 0.31$	$17.89 \pm 0.36$
1.96		5.0	$25.71 \pm 0.70$	$36.04 \pm 0.90$
		7.5	$22.72 \pm 0.30$	$26.30 \pm 0.41$
	5.0	5.1	$14.18 \pm 0.24$	$14.30 \pm 0.70$
	2.5	5.0	$6.02 \pm 0.12$	$9.58 \pm 0.19$
1.92		10.9	$27.30 \pm 0.39$	$20.17 \pm 0.40$
		7.7	$22.11 \pm 0.55$	$21.82 \pm 0.37$
	5.7	$17.40 \pm 0.21$	$21.39 \pm 0.35$	
1.84		2.6	$10.80 \pm 0.22$	$21.70 \pm 0.29$
		10.2	$30.72 \pm 0.60$	$24.14 \pm 0.47$
		7.3	$24.11 \pm 0.48$	$24.25 \pm 0.48$
1.82	5.00	3.8	$16.40 \pm 0.31$	$24.19 \pm 0.46$
		10.1	$34.90 \pm 0.50$	$27.10 \pm 0.11$
		7.5	$28.12 \pm 0.10$	$28.18 \pm 0.14$
		5.2	$20.90 \pm 0.27$	$27.13 \pm 0.36$
1.70		3.9	$17.82 \pm 0.20$	$27.96 \pm 0.31$
		7.8	$35.45 \pm 0.37$	$33.67 \pm 0.34$
	5.4	$28.08 \pm 0.30$	$34.14 \pm 0.32$	
1.64		5.3	$31.52 \pm 0.45$	$39.01 \pm 0.80$
1.62		5.2	$31.61 \pm 0.34$	$40.47 \pm 0.44$
1.53		5.4	$46.22 \pm 0.77$	$49.67 \pm 0.82$

The value of  $k_{\text{obs}}$  varies with the  $[\text{Fe}(\text{CN})_6^{4-}]_i$ , at fixed reaction conditions, according to Eqn. (2). The values of  $k_u$  obtained from plots of Eq. (2) are in fairly good agreement with values obtained directly from linear portions of the first order plots. The rate constants  $k_u$  and  $k_a$  are rate constants for the uncatalyzed and the autocatalytic reactions pathways respectively. Values of  $k_a$  were also calculated from Eqn. (2) using known values of  $k_{\text{obs}}$ ,  $k_u$  and  $[\text{Fe}(\text{CN})_6^{4-}]_i$ .

$$k_{\text{obs}} = k_u + k_a [\text{Fe}(\text{CN})_6^{4-}]_i \quad (2)$$

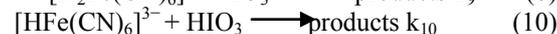
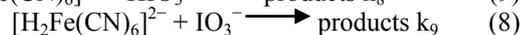
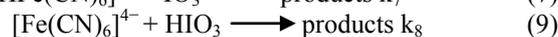
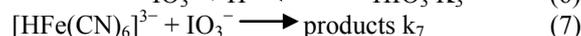
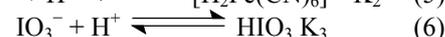
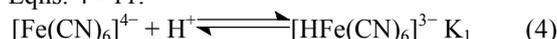
Table 1 shows that  $k_u$  varies linearly with  $[\text{IO}_3^-]$  at fixed reaction conditions. The results in Table 1 also show that  $k_u$  is pH-dependent. The dependence of  $k_{\text{uc}}$  on  $[\text{H}^+]$  seems to be complex as a plot of  $\log k_u$  versus  $\log [\text{H}^+]$  has a slope  $\approx 1.3$ . The rate law for the uncatalyzed oxidation of  $[\text{Fe}(\text{CN})_6^{4-}]$  by  $\text{IO}_3^-$  is given by Eqn. (3) at fixed pH, ionic strength and temperature. The form of this rate law is the same as that reported before[1].



Hexacyanoferrate(II) is known to be extensively protonated in aqueous acidic solutions[15].

The thermodynamic dissociation constants for the mono- and diprotonated species ( $[\text{HFe}(\text{CN})_6]^{3-}$  and  $[\text{H}_2\text{Fe}(\text{CN})_6]^{2-}$  respectively) have been determined as  $5.25 \times 10^{-5}$  and  $4.3 \times 10^{-3}$  at 25 °C respectively. At 1.0 M ionic strength and 25 °C the values of the dissociation constants are  $4.68 \times 10^{-3}$  and 0.32 for the mono and diprotonated species respectively[16]. The iodate ion is appreciably protonated in aqueous acidic solutions and has a thermodynamic dissociation constant of 0.16 at 25 °C[17]. The value of the dissociation constant at  $I = 1.0 \text{ M}$ , and  $T = 25 \text{ °C}$  is reported as 0.514 M[18].

The major reaction steps for the uncatalyzed path are given by Eqns. 4 - 11.



From the above equilibria and reactions the rate law in Eq. (10) is derived.

Rate =

$$\frac{\{(k_7 K_1 + k_8 K_3) [\text{H}^+] + (k_9 K_1 K_2 + k_{10} K_1 K_3) [\text{H}^+]^2\} [\text{IO}_3^-] [\text{Fe}(\text{CN})_6^{4-}]_i}{(1 + K_1 [\text{H}^+]) (1 + K_1 K_2 [\text{H}^+]^2) (1 + K_3 [\text{H}^+])} \quad (11)$$

Since the reaction is first order in both  $[\text{Fe}(\text{CN})_6^{4-}]_i$  and  $[\text{IO}_3^-]$ , the second order rate constant  $k_2$  ( $k_2 = k_u / [\text{IO}_3^-]$ ) varies with  $[\text{H}^+]$  according to Eqn. (11).

$$k_2 = \frac{\{(k_7 K_1 + k_8 K_3) [\text{H}^+] + (k_9 K_1 K_2 + k_{10} K_1 K_3) [\text{H}^+]^2\}}{(1 + K_1 [\text{H}^+]) (1 + K_1 K_2 [\text{H}^+]^2) (1 + K_3 [\text{H}^+])} \quad (12)$$

Under conditions where  $(1 + K_1 [\text{H}^+]) \gg (1 + K_1 K_2 [\text{H}^+]^2)$  ( $1 + K_3 [\text{H}^+]$ ), Eqn. (12) takes the form of Eqn. (13).

$$k_2 = \frac{\{(k_7 K_1 + k_8 K_3) [\text{H}^+] + (k_9 K_1 K_2 + k_{10} K_1 K_3) [\text{H}^+]^2\}}{(1 + K_1 [\text{H}^+])} \quad (13)$$

$$k_2(1 + K_1[H^+]) = (k_7K_1 + k_8K_3)[H^+] + (k_9K_1K_2 + k_{10}K_1K_3)[H^+]^2 \quad (14)$$

Eqn. (13) may be rearranged to the form of Eqn. (14). A polynomial of the second degree fit of a plot of  $k_2(1 + K_1[H^+])$  vs  $[H^+]$  is shown in Fig. 4. From the polynomial fit (Fig.4) the value  $(k_7K_1 + k_8K_3) = (81.4 \pm 17.2)$  and  $(k_9K_1K_2 + k_{10}K_1K_3) = (2.01 \pm 0.07) \times 10^4$ . These values are approximately twice as much as the previously determined values[1]. It was previously reported that the rate constant, contrary to expectation, decreases with increasing ionic strength. This may be rationalized by recalling that the protonation constants  $K_1$  and  $K_2$  of  $[\text{Fe}(\text{CN})_6]^{4-}$  (for the formation of  $[\text{HFe}(\text{CN})_6]^{3-}$ ,  $[\text{H}_2\text{Fe}(\text{CN})_6]^{2-}$  respectively) are lower at higher ionic strength values. Thus values of  $1.49 \times 10^4 \text{ M}^{-1}$  and  $2.14 \times 10^2 \text{ M}^{-1}$  are reported for  $K_1$  at infinite dilution and  $I = 1.0 \text{ M}$  respectively[15,16].

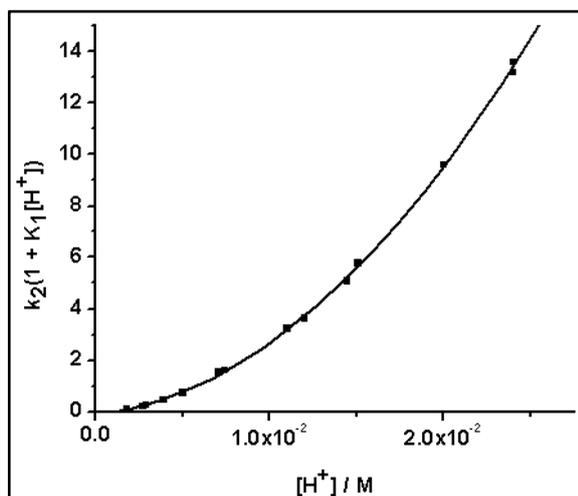


Figure 4. A second degree polynomial plot of  $k_2(1 + K_1[H^+])$  vs  $[H^+]$ ,  $[\text{IO}_3^-] = 5.0 \times 10^{-3}$ ,  $I = 1.0 \text{ M}$ ,  $T = 25.0 \text{ }^\circ\text{C}$

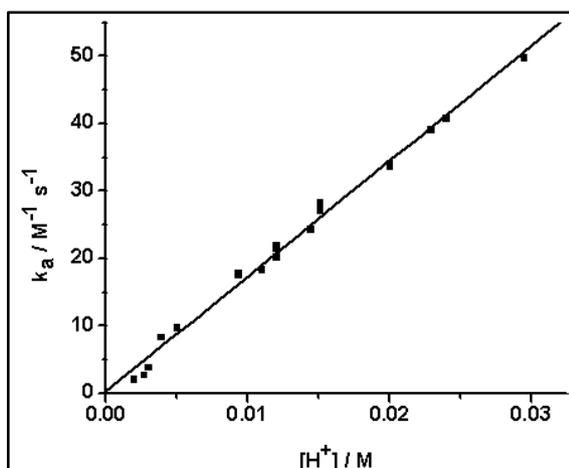
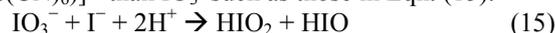


Figure 5. Dependence of  $k_a$  on  $[H^+]$ ,  $[\text{IO}_3^-] = 5.0 \times 10^{-3} \text{ M}$ ,  $I = 1.0 \text{ M}$ ,  $T = 25.0 \text{ }^\circ\text{C}$

The dependence of  $k_{\text{obs}}$  on  $[(\text{Fe}(\text{CN})_6)^{4-}]_i$  is indicative of the relationship between the concentration of the iodide product and the  $[(\text{Fe}(\text{CN})_6)^{4-}]_i$ ; the higher the concentration of the latter, the higher would be the rate of formation of iodide. The iodide produced would react with  $\text{IO}_3^-$  according

to Eqn.4 to generate iodine that would react rapidly with  $[(\text{Fe}(\text{CN})_6)^{4-}]$  (Eqn. 5). Values of  $k_a$  at several pH values are shown in Table 2 at constant  $[\text{IO}_3^-]$ , ionic strength and temperature. The dependence of  $k_a$  on  $[H^+]$  (Fig. 5) shows a linear plot of  $k_a$  versus  $[H^+]$  with an almost zero intercept.

The autocatalytic pathway is caused by a product generated by the uncatalyzed reaction. The  $\Gamma$  produced in the direct reaction between  $[(\text{Fe}(\text{CN})_6)^{4-}]$  and  $\text{IO}_3^-$  in acidic solutions (Eqn.1) reacts with  $\text{IO}_3^-$  to produce a more reactive species with  $[(\text{Fe}(\text{CN})_6)^{4-}]$  than  $\text{IO}_3^-$  such as those in Eqn. (15).



The reaction may also proceed to produce  $\text{I}_2$  which also reacts very rapidly with  $[(\text{Fe}(\text{CN})_6)^{4-}]$  and this may cause autocatalysis in the  $[(\text{Fe}(\text{CN})_6)^{4-}] - \text{IO}_3^-$  reaction[10]. The  $\text{IO}_3^- - \Gamma$  reaction is thus the rate determining step and the catalyzed reaction is simply an indirect method for the measurement of the kinetics of this reaction under condition of low  $[\Gamma]$ . The kinetics of the  $\text{IO}_3^- - \Gamma$  reaction has been studied extensively and different forms of the rate law has been reported[19]. The most accepted rate law is the one showing first order dependence on  $[\text{IO}_3^-]$  and second order in both  $[\Gamma]$  and  $[H^+]$ . Results in Table 2 and Fig.5 show that  $k_a$  varies linearly with  $[H^+]$  and is described by Eqn. (16).

$$k_a = k_{11}[H^+][\text{IO}_3^-] \quad (16)$$

In conclusion the iodate – hexacyanoferrate(II) reaction is partially autocatalytic whether the reductant or the oxidant is in excess. Autocatalysis becomes important at high reactant concentrations and low pH. Autocatalysis may be caused by  $\text{I}(\text{III})$ ,  $\text{I}(\text{I})$  and/or  $\text{I}_2$  that are produced during  $\text{IO}_3^- - \Gamma$  reaction. At low reactants concentration and high pH autocatalysis only appears at late stages of the reaction. Qualitative experiments showed that the deliberate addition of  $\Gamma$  speeds up the reaction and it proceeds at a measurable rate at pH values it would not usually take place.

## ACKNOWLEDGEMENTS

Y. S would like to thank Professor Ahmed A. Abdel-Khalek of the Department of Chemistry, Cairo University, Beni-Suef Branch, Egypt, for his help with some kinetic runs and Professor J. F. Perez-Benito of the Department of Chemistry, University of Barcelona, Portugal for useful information.

## REFERENCES

- [1] Sulfab, Y.; Elfaki, H. *Can. J. Chem.* 52, 2001 (1974)
- [2] Eggert, J.; Scharnow, B. *Z. Elektrochem.* 27, 455 (1921)
- [3] J. Birk, J; Kozub, S. G. *Inorg. Chem.* 12 (1973) 2460
- [4] Rabai, Gy.; Epstein, I. R. *Inorg. Chem.* 28, 732 (1989)
- [5] Rabai, Gy.; Bazsa, Gy.; Beck, M. T. *Int. J. Chem. Kinet.* 13, 1277 (1981)

- [6] Gaspar, V.; Beck, M. T. *Polyhedron* 2, 38 (1983)
- [7] Dushman, S. J. *Phys. Chem.* 8, 453 (1904).
- [8] Schildcrout S. M.; Fortunato, F. A. *J. Phys. Chem.* 79, 31 (1975)
- [9] Rabai, G.; Kaminaga, A.; Hanazaki, I. *J. Phys. Chem.* 99, 9795 (1995)
- [10] Reynolds, W. L. *J. Am. Chem. Soc.*, 80, 1830 (1958)
- [11] Gaspar, V.; Showalter, K. *J. Phys. Chem.* 94, 4973 (1990)
- [12] Angus-Dunne, S. J.; Irwin, J. A.; Burns, R. C.; Lawrance, G. A.; Craig, D. C. *J. Chem. Soc. Dalton Trans.* 2717 (1993)
- [13] Nolan, A. L.; Burns, R. C.; Lawrance, G. A. *J. Chem. Soc. Dalton Trans.* 3065 (2002)
- [14] Dahal, M.; Lawrance, G. A. *Inorganic Reaction Mechanism* 5, 117 (2004)
- [15] Jordan, J.; Ewing, G. J. *Inorg. Chem.* 1, 587 (1962)
- [16] Lavison, S. A.; Marcus, R. A. *J. Phys. Chem.* 72, 358 (1968)
- [17] Pethybridge, A. D.; Prue, J. E. *Trans. Faraday Soc.* 63, 2019 (1967)
- [18] Ramette, R. W. *J. Chem. Educ.* 36, 191(1959)
- [19] Wilson, I. R. in “*Comprehensive Chemical Kinetics*”, C. H. Bamford and C. F. H. Tipper, Ed. Amsterdam, Vol. 6. (1972)