

## Kinetic Studies on the Reaction of Sodium Hexacyanoferrate(II) Complex with Peroxydisulfate Anion

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The oxidation of  $\text{Na}_4\text{Fe}(\text{CN})_6$  complex by  $\text{S}_2\text{O}_8^{2-}$  anion was found to follow an outer-sphere electron transfer mechanism. We firstly carried out the reaction at  $\text{pH}=1$ . The specific rate constants of the reaction,  $k_{\text{ox}}$ , are  $(8.1 \pm 0.07) \times 10^{-2}$  and  $(4.3 \pm 0.1) \times 10^{-2} \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$  at  $\mu=1.0 \text{ mol} \cdot \text{L}^{-1}$   $\text{NaClO}_4$ ,  $T=298 \text{ K}$  for  $\text{pH}=1$  ( $0.1 \text{ mol} \cdot \text{L}^{-1}$   $\text{HClO}_4$ ) and 8, respectively. The activation parameters, obtained by measuring the rate constants of oxidation 283—303 K, were  $\Delta H^\ddagger=(69.0 \pm 5.6) \text{ kJ} \cdot \text{mol}^{-1}$ ,  $\Delta S^\ddagger=(-0.34 \pm 0.041) \times 10^2 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  at  $\text{pH}=1$  and  $\Delta H^\ddagger=(41.3 \pm 5.5) \text{ kJ} \cdot \text{mol}^{-1}$ ,  $\Delta S^\ddagger=(-1.27 \pm 0.33) \times 10^2 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  at  $\text{pH}=8$ , respectively. The cyclic voltammetry of  $\text{Fe}(\text{CN})_6^{3-/4-}$  shows that the oxidation is a one-electron reversible redox process with  $E_{1/2}$  values of 0.55 and 0.46 V vs. normal hydrogen electrode at  $\mu=1.0 \text{ mol} \cdot \text{L}^{-1}$   $\text{LiClO}_4$ , for  $\text{pH}=1$  and  $\text{pH}=8$  (Tris), respectively. The kinetic results were discussed on the basis of Marcus theory.

**Keywords** sodium hexacyanoferrate(II) complex, outer-sphere electron transfer mechanism, cyclic voltammetry, specific rate constants, Marcus theory

### Introduction

In the previous studies on the oxidation reaction, peroxydisulfate was widely used as an oxidizing agent.<sup>1-5</sup> One of the advantages of this oxidant lies in its stability in a wide range of pH values. The reaction between  $\text{Fe}(\text{CN})_5\text{L}^{3-}$  ( $\text{L}=\text{N}$ -aromatic heterocyclic ligands) and  $\text{S}_2\text{O}_8^{2-}$  has been proved to proceed through an outer-sphere electron transfer mechanism.<sup>5</sup> For a reaction [(Eq. (1)) to be under an outer-sphere mechanism, the steps involved are the formation of a reactant ion pair or outer-sphere precursor complex [(Eq. (2)), electron transfer [(Eq. (3)), and dissociation of the product of ion pair or outer-sphere successor complex [(Eq. (4)).



The first and the third steps are diffusion-controlled reactions, and Eq. (3) is often the rate determining step. If one of the reactants is in excess (usually oxidant) and the reaction proceeds to completion, this mechanism leads to the rate law given by

$$k_{\text{obs}} = \frac{2k_{\text{et}}Q_{\text{IP}}[\text{ox}_1]}{1+Q_{\text{IP}}[\text{ox}_1]} \quad (5)$$

Due to the instability of  $\text{N}$ -aromatic heterocyclic complexes in acidic solutions,<sup>1</sup> previous studies on the oxidation of  $\text{Fe}(\text{CN})_5\text{L}^{3-}$  complexes were never carried out in a solution at  $\text{pH} \leq 4$ . For this reason we would like to extend our study to the oxidation of  $\text{Fe}(\text{CN})_6^{4-}$  complex in an acidic medium because the complex is rather stable in the acid solution. In this paper we report the results of our kinetic study on the oxidation of  $\text{Fe}(\text{CN})_6^{4-}$  complex in  $0.1 \text{ mol} \cdot \text{L}^{-1}$   $\text{HClO}_4$  solution. For the purpose of comparison, the oxidation of  $\text{Fe}(\text{CN})_6^{4-}$  at  $\text{pH}=8$  was also carried out.

### Experimental

#### Materials

$\text{Na}_4\text{Fe}(\text{CN})_6$  was purchased from Beijing Red Star Chem Co.  $\text{Na}_2\text{S}_2\text{O}_8$ ,  $\text{NaOH}$  were purchased from Beijing Chemical Reagent Co.  $\text{NaClO}_4$  and  $\text{LiClO}_4$  were purchased from Beijing Nanshangle Chem. Co. Tris(hydroxymethyl)aminomethane (tris) was purchased from Beijing Sino-American Chem. Co. Water used in this experiment was obtained by distilling deionized water twice.

#### Analytical instruments

UV-visible spectra were measured on a HP 8453

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UV-visible spectrophotometer. Electrochemical measurements were performed on a PAR model 273A potentiostat/galvanostat system which was interfaced with a SNC 486-33 computer. The standard three-electrode electrochemical cell was used for measurements with the carbon paste as the working electrode and a platinum wire as the counter electrode. A standard calomel electrode was used as the reference standard. The pH measurements were carried out with a Beckman  $\Phi 50$  pH meter. Temperature of the reactions was controlled by a Huber polystat cc1 temperature bath.

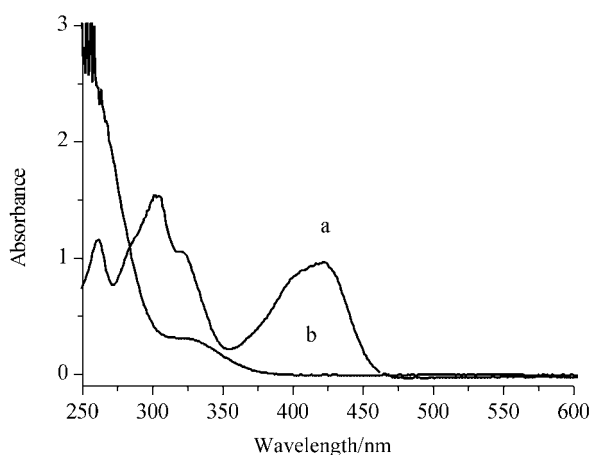
### Kinetic measurements

All the kinetic measurements were carried out on the HP 8453 UV-visible spectrometer. The cell holder of the spectrophotometer was modified appropriately so that the temperature of the reaction can be controlled properly. The solutions of the reactants were deaerated by bubbling with argon before mixing. The reactions were monitored by following the formation of  $\text{Fe}(\text{CN})_6^{3-}$  complex at  $\lambda = 420$  nm. Pseudo-first-order rate constants ( $k_{\text{obs}}$ ) were obtained from the slopes of linear least square fits of  $\ln(A_\infty - A_t)$  vs. time plots.

## Results

### Absorption spectra

The UV-visible absorption spectra are shown in Figure 1.



**Figure 1** UV-visible spectra of complexes in aqueous solutions. a:  $\text{Fe}(\text{CN})_6^{3-}$ ,  $c = 1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ ; b:  $\text{Fe}(\text{CN})_6^{4-}$ ,  $c = 1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ .

$\text{Fe}(\text{CN})_6^{4-}$  shows only a weak absorption at 323 nm ( $\epsilon = 232 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$ ), which is expected to be the d-d band. For  $\text{Fe}(\text{CN})_6^{3-}$  complex three absorptions were observed. The strong absorption at  $\lambda = 261$  nm ( $\epsilon = 1.16 \times 10^3 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$ ), 303 nm ( $\epsilon = 1.53 \times 10^3 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$ ) with shoulder peak  $\lambda = 322$  nm ( $\epsilon = 1.12 \times 10^3 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$ ), and  $\lambda = 421$  nm ( $\epsilon = 9.68 \times 10^2 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$ ) may be assigned as ligand to metal charge transfer (LMCT) band,<sup>6</sup> while the weak d-d transition may be covered by these stronger absorption

bands.

### Oxidation kinetics

The pseudo-first-order rate constants of oxidation of  $\text{Fe}(\text{CN})_6^{4-}$  complex at pH=1 ( $0.1 \text{ mol} \cdot \text{L}^{-1} \text{ HClO}_4$ ) and 8 ( $0.02 \text{ mol} \cdot \text{L}^{-1}$  tris) according to Eq. (6) are listed in Table 1 and Table 2, respectively.



**Table 1** Pseudo-first-order rate constants for the oxidation of  $\text{Fe}(\text{CN})_6^{4-}$  by  $\text{S}_2\text{O}_8^{2-}$ <sup>a</sup>

$[\text{S}_2\text{O}_8^{2-}]/(\text{mol} \cdot \text{L}^{-1})$	$k_{\text{obs}}/\text{s}^{-1}$
$4.09 \times 10^{-2}$	$6.51 \times 10^{-3}$
$6.09 \times 10^{-2}$	$9.80 \times 10^{-3}$
$8.10 \times 10^{-2}$	$1.28 \times 10^{-2}$
$1.00 \times 10^{-1}$	$1.66 \times 10^{-2}$

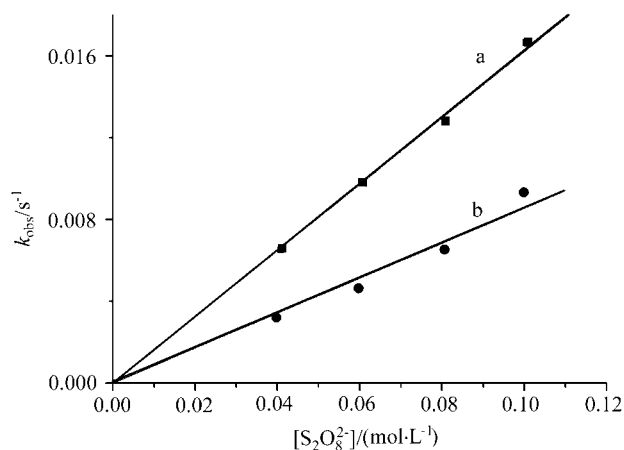
<sup>a</sup> pH=1 ( $0.1 \text{ mol} \cdot \text{L}^{-1} \text{ HClO}_4$ ),  $\mu = 1.0 \text{ mol} \cdot \text{L}^{-1} \text{ NaClO}_4$ ,  $T = 298$  K.

**Table 2** Pseudo-first-order rate constants for the oxidation of  $\text{Fe}(\text{CN})_6^{4-}$  by  $\text{S}_2\text{O}_8^{2-}$ <sup>a</sup>

$[\text{S}_2\text{O}_8^{2-}]/(\text{mol} \cdot \text{L}^{-1})$	$k_{\text{obs}}/\text{s}^{-1}$
$3.98 \times 10^{-2}$	$3.16 \times 10^{-3}$
$5.98 \times 10^{-2}$	$4.57 \times 10^{-3}$
$8.06 \times 10^{-2}$	$6.52 \times 10^{-3}$
$1.00 \times 10^{-1}$	$9.29 \times 10^{-3}$

<sup>a</sup> pH=8 ( $0.02 \text{ mol} \cdot \text{L}^{-1}$  tris-HCl),  $\mu = 1.0 \text{ mol} \cdot \text{L}^{-1} \text{ NaClO}_4$ ,  $T = 298$  K.

Linear relationships were observed in the  $k_{\text{obs}}$  vs.  $[\text{S}_2\text{O}_8^{2-}]$  plots as shown in Figure 2. The specific rate constants of oxidation,  $k_{\text{ox}}$ , were obtained from the slopes of the one-parameter linear least square fits of the plots. The values are  $(8.1 \pm 0.07) \times 10^{-2} \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$ ,



**Figure 2** Plots of  $k_{\text{obs}}$  vs.  $[\text{S}_2\text{O}_8^{2-}]$  at 298 K. (a) pH=1 ( $0.1 \text{ mol} \cdot \text{L}^{-1} \text{ HClO}_4$ ),  $\mu = 1.0 \text{ mol} \cdot \text{L}^{-1} \text{ NaClO}_4$ ; (b) pH=8 ( $0.02 \text{ mol} \cdot \text{L}^{-1}$  tris-HCl),  $\mu = 1.0 \text{ mol} \cdot \text{L}^{-1} \text{ NaClO}_4$ .

$(4.3 \pm 0.1) \times 10^{-2} \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$ , for pH=1 and 8, respectively, at  $\mu=1.0 \text{ mol} \cdot \text{L}^{-1} \text{ NaClO}_4$  and  $T=298 \text{ K}$ .

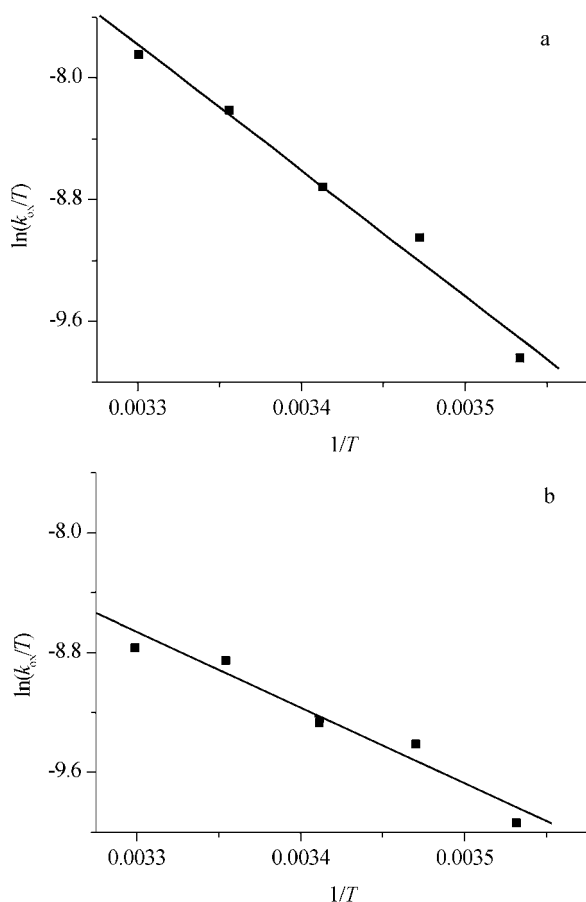
The temperature dependence of the oxidation reaction has been studied and the results are shown in Table 3.

**Table 3** Temperature dependence for the oxidation of  $\text{Na}_4\text{Fe}(\text{CN})_6^a$

T/K	$k_{\text{ox}}/(\text{mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1})$	
	pH=1	pH=8
283	0.0151	0.0137
288	0.0341	0.0236
293	0.0481	0.0276
298	0.0811	0.0428
303	0.1190	0.0471

<sup>a</sup>pH=1 (0.1  $\text{mol} \cdot \text{L}^{-1} \text{ HClO}_4$ ) and pH=8 (0.02  $\text{mol} \cdot \text{L}^{-1} \text{ tris-HCl}$ ),  $\mu=1 \text{ mol} \cdot \text{L}^{-1} \text{ NaClO}_4$ .

The plots of  $\ln(k_{\text{ox}}/T)$  vs.  $1/T$  are linear as shown in Figure 3, yielding  $\Delta H^\ddagger = 69.0 \pm 5.6$  and  $41.3 \pm 5.5 \text{ kJ} \cdot \text{mol}^{-1}$ , and  $\Delta S^\ddagger = (-0.34 \pm 0.04) \times 10^2$  and  $(-1.3 \pm 0.3) \times 10^2 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  for pH=1 and 8, respectively.

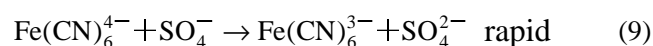
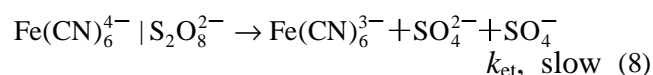
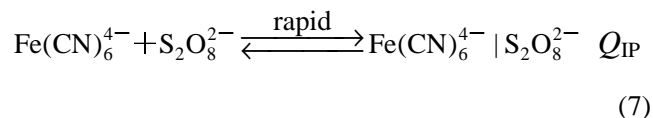


**Figure 3** Plot of  $\ln(k_{\text{ox}}/T)$  vs.  $1/T$  of the oxidation of  $\text{Na}_4\text{Fe}(\text{CN})_6$  by  $\text{Na}_2\text{S}_2\text{O}_8$ . (a) pH=1; (b) pH=8.

## Discussion

Since  $\text{Fe}(\text{CN})_6^{4-}$  is substitution inert and no additional site available for the coordination of  $\text{S}_2\text{O}_8^{2-}$ , the oxidation of  $\text{Fe}(\text{CN})_6^{4-}$ , just like all other  $\text{Fe}(\text{CN})_5\text{L}^{3-}$  and  $\text{Ru}(\text{NH}_3)_5\text{L}^{2+}$  systems previously studied,<sup>5,7,8</sup> is expected to proceed through an outer-sphere mechanism, as shown in Eqs. (7)–(9). In Eq. (7), the cleavage of the peroxide bond in  $\text{S}_2\text{O}_8^{2-}$  is involved.<sup>8,10</sup>

One of the reactants is in excess ( $[\text{S}_2\text{O}_8^{2-}] \gg [\text{Fe}(\text{II})]$ ) and the reaction proceeds to completion, this mechanism leads to the rate law given by (10) and (11), when  $1 \gg Q_{\text{IP}}[\text{S}_2\text{O}_8^{2-}]$ , which usually is the case for reactants of like charges, Eq. (11) can be simplified as Eq. (12)



$$\text{Rate} = -\frac{d[\text{Fe}(\text{CN})_6^{4-}]}{dt} = \frac{2k_{\text{et}}Q_{\text{IP}}[\text{S}_2\text{O}_8^{2-}][\text{Fe}(\text{CN})_6^{4-}]}{1+Q_{\text{IP}}[\text{S}_2\text{O}_8^{2-}]} = k_{\text{obs}}[\text{Fe}(\text{CN})_6^{4-}] \quad (10)$$

$$k_{\text{obs}} = \frac{2k_{\text{et}}Q_{\text{IP}}[\text{S}_2\text{O}_8^{2-}]}{1+Q_{\text{IP}}[\text{S}_2\text{O}_8^{2-}]} \quad (11)$$

$$k_{\text{ox}} = k_{\text{et}}Q_{\text{IP}} \quad (12)$$

The factor of 2 is necessary in order to account for the two electron oxidation of  $\text{S}_2\text{O}_8^{2-}$ . According to Marcus theory<sup>5,8-12</sup> the rate constant for an outer-sphere reaction can be expressed as

$$k_{12} = \sqrt{k_{11}k_{22}K_{12}f_{12}W_{12}} \quad (k_{12} = k_{\text{ox}}) \quad (13)$$

$$\ln f = \frac{[\ln K_{12} + (w_{12} - w_{21})/RT]^2}{4[\ln(k_{11}k_{22}/10^{22}) + (w_{11} + w_{22})/2RT]} \quad (14)$$

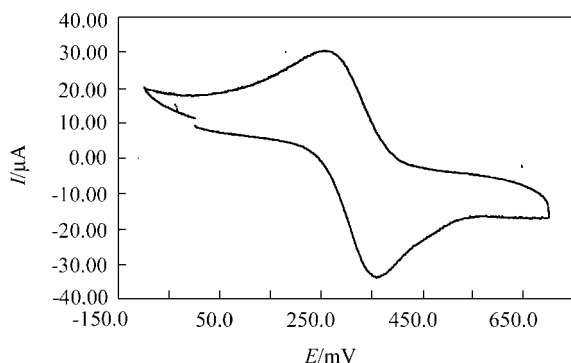
$$W_{12} = \exp[-(w_{12} + w_{21} - w_{11} - w_{22})/2RT] \quad (15)$$

$$w_{ij} = \frac{z_i z_j e^2}{D_s a_{ij} (1 + \beta a_{ij} \mu^{1/2})} \quad (16)$$

$$\beta = \left( \frac{8N\pi e^2}{1000D_s k_B T} \right)^{1/2} \quad (17)$$

where  $k_{11}$  and  $k_{22}$  are self exchange rate constants,  $K_{12}$  and  $k_{12}$  are the equilibrium and rate constants of Eq. (6).  $w_{ij}$  are the corresponding work terms.  $a_{ij}$  is the internuclear distance between reactants.  $D_s$  is the static dielectric constant,  $R$  and  $k_B$  are gas and Boltzmann's constants, and  $\mu$  is the ionic strength of the reaction. The value of  $K_{12}$  can be obtained from the electrochemical results of the reactants. The reduction potentials of  $\text{Fe}(\text{CN})_6^{3-/4-}$  complex, measured in the present work, are 0.55, 0.46 V at pH=1 and 8, respectively.

The cyclic voltammogram at pH=1 was shown in Figure 4. The higher value of the complex in acidic medium may arise from the protonation of the cyanide ligand.



**Figure 4** Cyclic voltammogram for the  $\text{Fe}(\text{CN})_6^{3-/4-}$  couple ( $\text{Fe}(\text{CN})_6^{3-} = 1.70 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ , pH=1,  $\mu = 1.0 \text{ mol} \cdot \text{L}^{-1}$   $\text{LiClO}_4$ ,  $T = 298 \text{ K}$ ).

Taking  $E_{1/2} = 1.45 \text{ V}$  for  $\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{2-}\text{SO}_4^-$  couple,<sup>13</sup> the values of  $K_{12}$  were calculated as  $1.7 \times 10^{15}$ ,  $5.6 \times 10^{16}$ , for pH=1 and 8, respectively. The self-exchange rate constant of  $\text{Fe}(\text{CN})_6^{3-/4-}$  is  $5 \times 10^3 \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$ ,<sup>14,15</sup> and that of  $\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{2-}\text{SO}_4^-$  is estimated<sup>8</sup> as  $10^{-18} \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$ . Taking the values of  $a = 4.5 \times 10^{-8} \text{ cm}^{16}$  and  $3.4 \times 10^{-8} \text{ cm}^8$  for  $\text{Fe}(\text{CN})_6^{4-}$  and  $\text{S}_2\text{O}_8^{2-}$ , respectively. Substituting above information into Eqs. (14)–(17), we calculated  $W_{12} = 1.07$  and  $1.03$ ;  $f_{12} = 2.52 \times 10^{-2}$  and  $1.17 \times 10^{-2}$  for pH=1 and 8, respectively. Thus the rate constants can be obtained from Eq. (13), and the values are  $0.49$  and  $1.87 \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$ , for pH=1 and 8, respectively. The theoretical calculated values were greater than our measured rate constants of oxidation by nearly two order of magnitude, similar to those observed for the oxidation of the pentacyanoferrate(II) complexes. Apparently, the oxidation of  $\text{Fe}(\text{CN})_6^{4-}$  complex, like the others, occurs in the non-adiabatic regime.<sup>11</sup>

It is noteworthy that the rate constant of oxidation is expected to be smaller for the reaction carried out in the acidic medium than that in the neutral or basic solution on the basis of both electrostatic ( $W_{12}$ ) and thermodynamic ( $K_{12}$ ) concern as predicted from Marcus theory. However, our measured value at pH=1 is larger than

that value measured at pH=8 by nearly a factor of 2. As have been mentioned previously,<sup>3,10</sup> the non-adiabatic character of the system arises predominantly from the diminished coupling of the orbitals as a result of electrostatic repulsion between like charged species. Due to the protonation of the cyanide ligand, the charge distribution of the reactants at pH=1 is 3<sup>-</sup>, 2<sup>-</sup>, while that for the reaction at pH=8 is 4<sup>-</sup>, 2<sup>-</sup>. Although the work term contribution difference is not significant as evidenced from the values of  $W_{12}$  which is 1.07 at pH=1 as compared to 1.03 at pH=8, the larger repulsion of the reactants in the neutral or basic solution will make the close approach of the reactants more difficult than that in the acidic medium. As a consequence, the extent of the coupling of orbitals will be much more diminished and the non-adiabaticity of the reaction will be increased. Thus, a slower rate of the reaction is expected.

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