

Kinetics of the Reduction of Hexacyanoferrate (III) with Metabisulfite as Function of pH

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Abstract: Kinetics of the reduction of potassium hexacyanoferrate(III) with sodium metabisulfite was investigated as a function of pH and at four temperatures, viz. 15°, 20°, 25° and 30°C. The ionic strength was maintained at 1.0 M KCl. The pH range used varied between 2.6 to 4.7 using McIlvaine phosphate/citric acid buffer system. The second order observed rate constant was found to follow an inverse H⁺ dependence of the form $k_{\text{obs}} = k_1 + k_2/[\text{H}^+]$. At 298.15 K, the second order rate constant $k_1 = (1.02 \pm 0.20) \times 10^{-2} \text{ s}^{-1} \text{ mol}^{-1} \text{ L}$ and the first order rate constant $k_2 = (6.33 \pm 0.12) \times 10^{-6} \text{ s}^{-1}$. The activation parameters for k_1 are: $\Delta H^\ddagger = 73.64 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -36.63 \text{ JK}^{-1} \text{ mol}^{-1}$ and $\Delta G^\ddagger = 84.56 \text{ kJ mol}^{-1}$ and for k_2 are 41.71 KJ mol⁻¹, -205.03 JK⁻¹ mol⁻¹ and 102.84 KJ mol⁻¹ respectively. The kinetic data were very well explained by invoking radical mechanism in which the HSO₃⁻ and SO₃²⁻ formed HSO₃^{*} and SO₃^{*} radicals, alternatively the redox process could take place by a mechanism in which a fast reversible equilibrium is established between the hydrogen ions and hexacyanoferrate(III), followed by a slow reaction of the protonated species with the sulfite ion leading to the formation of sulfite free radical.

Introduction

Electron transfer (ET) is a fundamental process in chemical and biological systems, occurring within and between various types of molecular species as well as protein molecules which serve as scaffolding for a variety of redox centers (metal ions, porphyrins, flavins, quinones, etc.)^[1-4]. The reduction of hexacyanoferrate was carried out by a number of reducing agents such as ascorbic acid^[5,6] and thiosulfate^[7].

The reaction between hexacyanoferrate(III) and sulfite has been of some interest for a number of years^[8,9] with a variety of mechanistic interpretations. Veprek-Siska *et al.*^[10] found that the reaction is slow, first order with respect to $\frac{1}{2}\text{Fe}(\text{CN})_6^{3-}$ and $\frac{1}{2}\text{SO}_3^{2-}$ and suggested an inner-sphere mechanism involving the formation of an intermediate $[\text{Fe}(\text{CN})_5\text{SO}_3]^{4-}$. Swinehart^[11] suggested an outer-sphere mechanism involving the formation of the sulfite radical anion $\text{SO}_3^{\cdot-}$. Maltz^[12] showed that for reaction in the presence of ^{14}C labeled cyanide ion, there is no radioactive tracer in the ferrocyanide product. He also found that sulfate was the only significant sulfur containing product. Murray^[13] in a series of papers suggested that the initial one electron transfer step was followed by a rapid reaction of the sulfite radical anion with ferricyanide to form an adduct, which underwent further reaction to form ferrocyanide and sulfate. Murray felt that a seven co-ordinate low spin cyanoferrate complex was unlikely and suggested that the sulfite radical anion added on to a cyanide ligand, $[\text{Fe}(\text{CN})_5(\text{CNSO}_3)]^{4-}$. Yet Dasgupta and Mahanti^[14] in their study of the alkaline oxidation of sulfite by $\text{Fe}(\text{CN})_6^{3-}$ suggested that the sulfite ion undergoes a one electron transfer *via* a $\text{SO}_3^{\cdot-}$ radical which dimerizes to give $\text{S}_2\text{O}_6^{2-}$. In the present study we report the reaction of potassium hexacyanoferrate(III) with sodium metabisulfite as a function of pH and temperatures, at ionic strength $I = 1.0\text{M}$, KCl. The pH range used varied between 2.6 to 4.7 using McIlvaine phosphate/citric acid buffer system.

Experimental

Reagent grade chemicals were used in all preparations. The water used was doubly distilled. Potassium hexacyanoferrate(II) $\text{K}_4\text{Fe}(\text{CN})_6$ and potassium hexacyanoferrate(III) $\text{K}_3\text{Fe}(\text{CN})_6$ were obtained from Fluka or BDH and used without further purification. McIlvaine phosphate-citrate buffers^[15] were used for reactions done at a pH 3.0 – 5.0. The pH of the solution in all buffered experiments was measured using Mettler Toledo Seven Easy pH meter at controlled temperature and calibrated using standard buffers at three pH values (4.01, 7.00 and 9.21). For the kinetic experiments all pH values were determined at the beginning and end of the reaction.

The reaction rates were followed by photometric method using UV-Vis spectrophotometer Shimadzu model UV-260A equipped with thermo-stated ($\pm 0.1^\circ\text{C}$) cell compartment. The temperature inside the cell was kept at the desired temperature by circulating water through the thermo-stated cell holder with Haake temperature bath model GD1 constant temperature circulator. All reactions were done under pseudo-first order conditions in which the concentration of the reducing reagent sodium metabisulphite was at least 10 times as large as that of the iron(III) complex. The concentration of the iron(III)

complex was 2.00×10^{-4} M whereas that of the metabisulphite was 2.00×10^{-3} M. All reactions were done at four temperatures *viz.* 15, 20, 25 and 30°C.

The kinetic experiment was initiated by the addition of sodium metabisulphite to the iron(III) complex dissolved in the phosphate–citrate McIlvaine buffer of the desired pH and adjusted to ionic strength $I = 1.0$ M, KCl and thermo-stated at the desired temperature. The mixed reaction mixture is transferred to the spectrophotometer quartz cell, placed in the cell holder and the experiment started. Initially as well as in a number of experiments, full spectral scans between $\lambda = 460$ nm and $\lambda = 315$ nm were done. In the remainder of the experiments reactions were monitored at a fixed wavelength $\lambda = 420$ nm representing the maximum wavelength for the disappearance of iron(III).

All kinetic experiments were done under pseudo-first order conditions. Under these conditions, the rate of the reaction was found to be well-fitted by the assumption of first order kinetics. The data were thus treated by the application of equation (1)

$$\ln(A_t - A_\infty) = \ln(A_0 - A_\infty) - kt \quad (1)$$

where A_0, A_t and A_∞ are the absorbances of the solution at times zero, t and ∞ respectively. A plot of $\ln(A_t - A_\infty)$ Vs. t should give a straight line with a slope of “-k” if equation [1] is applicable. Final values of the rate constants are obtained from linear least squares fit of the data using “EXCEL” program package.

The activation parameters ΔG^\ddagger , ΔH^\ddagger and ΔS^\ddagger for the reactions studied were calculated using the relationship of the rate constant and the temperature as given by the transition state theory^[16,17,18]

$$k = \frac{RT}{Nh} \exp\left[\frac{\Delta S^\ddagger}{R}\right] \exp\left[-\frac{\Delta H^\ddagger}{RT}\right] \quad (2)$$

where k is the rate constant at a given temperature T , R the ideal gas law constant, N , Avogadro’s number; h , Planck’s constant, ΔS^\ddagger the entropy of activation and ΔH^\ddagger the enthalpy of activation.

Equation [2] in logarithmic form takes the form:

$$\ln\left(\frac{k}{T}\right) = \ln\left(\frac{R}{Nh}\right) + \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} \quad (3)$$

A plot of $\ln(k/T)$ vs. $(1/T)$ gives a straight line of slope $(-\Delta H^\ddagger/R)$ and intercept of $\ln(R/Nh) + \Delta S^\ddagger/R$.

Final values of ΔS^\ddagger and ΔH^\ddagger are obtained from linear least squares fit of the temperature dependent values of $\ln(k/T)$ vs. $(1/T)$. The ΔG^\ddagger_{298} value is calculated from the relationship (4) with $T=298.15$.

$$\Delta G^\ddagger_{298} = \Delta H^\ddagger - T\Delta S^\ddagger \quad (4)$$

The Cyclic Voltammetric Experiment was done using Metrohm 746 VA Trace analyzer. The concentration of the iron(III) complexes solutions was 1.00×10^{-3} M, meanwhile that for the supporting electrolyte used (NaNO_3) was 0.1M. The three-electrode measurements were carried out at 298 K under nitrogen atmosphere with a platinum working electrode, a platinum wire auxiliary electrode and Ag/AgCl reference electrode. The scan rates used were 20 and 40 mVs^{-1} . The potentials reported in this work are uncorrected for junction contributions.

Results and Discussions

Cyclic Voltammetry

Figures 1 and 2 give the respective voltammograms using scan rates of 20 mVs^{-1} and 40 mVs^{-1} . and show that the derived parameters are significantly altered by the use of different potential scan rates. Such a behavior can be attributed to: 1. High potential drop between the electrodes termed iR drop (potential = current (i) \times solution resistance (R)), 2. Slow electron transfer kinetics and 3. Irreversible redox reaction^[19].

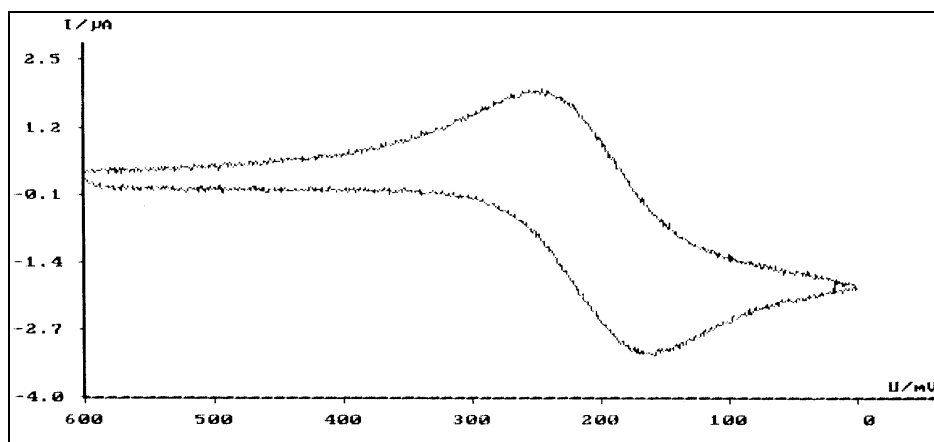


Fig. 1: CV for $[\text{Fe}(\text{CN})_6]^{3-}$ at scan rate 20 mVs^{-1} .

Although the addition of fully dissociated salts improves the conductivity of the electrolyte solution, many electrolyte solutions (particularly those based on

non-aqueous solvents) have significant resistance (hundreds of ohms). This leads to a potential drop between the electrodes termed iR drop. Some of this iR drop can be compensated by the three electrode system. However, some resistance (between the working and reference electrodes) remains uncompensated. If the uncompensated resistance is significant (hundreds of ohms), then the peak potential separation increases and the peak current decreases. These effects become more pronounced with increasing scan rate. Such are the observations in our redox system where lower scan rates give much better results and conform with available data for the ferricyanide system. For a redox reaction to be reversible, the concentrations of the oxidized and reduced species at the electrode surface must be maintained at the values required by the Nernst equation. In practical terms, a redox reaction is reversible if the rate of electron transfer is fast relative to the scan rate (the rate of change of potential) and if the oxidized and reduced species are stable on the experimental time scale (*i.e.*, they do not undergo any significant chemical reactions). The peak potential difference for a reversible system is about 60-70 mV (the theoretical value is about 58–59 mV, depending on the temperature and the switching potential), and the peak currents are equal. It should be emphasized here that peak potential separation and peak currents can be affected by slow electron transfer kinetics as well as uncompensated solution resistance. Our data at a scan rate of 20 mVs^{-1} indicate that the ferri/ferrocyanide system is a reversible one electron transfer process. It should be noted that all the potential data are given relative to the Ag/AgCl electrode.

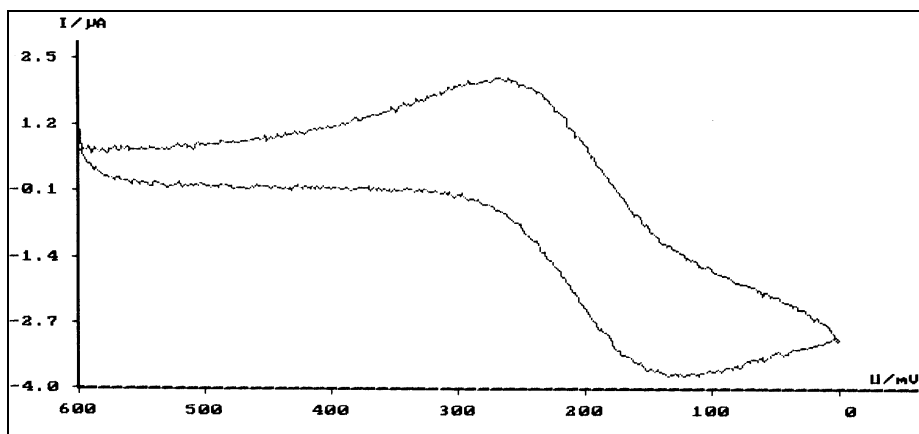


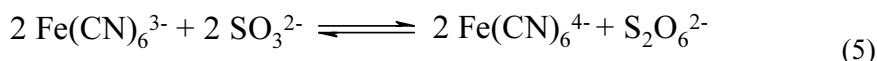
Fig. 2: CV for $[\text{Fe}(\text{CN})_6]^{3-}$ at scan rate 40 mVs^{-1} .

Table 1: Cyclic Voltammetric Data For $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ at scan rates 20 and 40 mVs^{-1} .

Scan rate mVs^{-1}	E_{pc} mV	E_{pa} mV	ΔE_p mV	$E_{1/2}$ mV	I_{pc} μA	I_{pa} μA	I_{pa}/I_{pc}
20	170	238	68	204	3.03	2.60	0.86
40	136	236	100	130	3.73	1.95	0.52

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The overall reaction can be represented by equation (5):



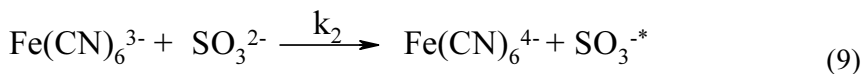
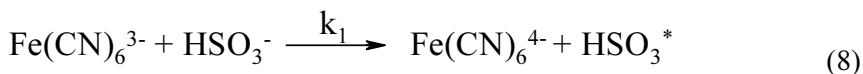
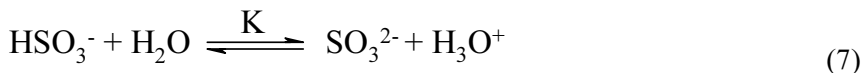
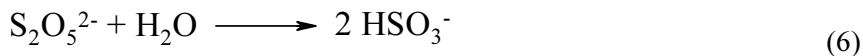
The oxidation of sulphite to the dithionate was established by the precipitation of a white solid of BaS_2O_6 soluble in dilute hydrochloric acid. No evidence for the formation of sulfate was observed, however. The kinetic data were analyzed at 420 nm. In all cases good straight lines were obtained in the plots of $\ln(A-A_\infty)$ vs t . The final values for the observed rate constants k_{obs} were obtained from linear least squares treatment of the data. The values of k_{obs} at the pH's studied are tabulated in Table 2 at the various temperatures used.

Table 2: k_{obs} as a function of pH and temperature.

pH $10^5 k_{\text{obs}}, \text{s}^{-1}$ 15°C		pH $10^4 k_{\text{obs}}, \text{s}^{-1}$ 20°C		pH $10^4 k_{\text{obs}}, \text{s}^{-1}$ 25°C		pH $10^4 k_{\text{obs}}, \text{s}^{-1}$ 30°C	
2.79	00.66 ± 0.01	2.78	0.12 ± 0.01	2.72	0.17 ± 0.01	2.79	0.23 ± 0.01
2.95	00.81 ± 0.01	2.95	0.18 ± 0.01	2.89	0.25 ± 0.01	2.95	0.26 ± 0.01
3.11	01.35 ± 0.01	3.08	0.23 ± 0.01	3.04	0.26 ± 0.01	3.14	0.35 ± 0.01
3.29	01.91 ± 0.03	3.26	0.29 ± 0.01	3.18	0.32 ± 0.01	3.30	0.65 ± 0.01
3.45	02.73 ± 0.02	3.43	0.42 ± 0.01	3.42	0.52 ± 0.01	3.51	0.74 ± 0.01
3.68	03.76 ± 0.02	3.63	0.56 ± 0.01	3.59	0.74 ± 0.01	3.71	1.10 ± 0.01
3.86	05.15 ± 0.03	3.85	0.82 ± 0.01	3.84	1.16 ± 0.01	3.88	1.55 ± 0.01
4.04	07.95 ± 0.04	4.04	1.14 ± 0.01	4.02	1.66 ± 0.01	4.06	2.20 ± 0.03
4.25	11.81 ± 0.40	4.23	1.61 ± 0.02	4.21	2.39 ± 0.03	4.27	3.32 ± 0.03
4.45	18.38 ± 0.30	4.43	2.48 ± 0.02	4.41	3.44 ± 0.02	4.47	4.93 ± 0.04
4.59	26.41 ± 0.40	4.62	3.49 ± 0.05	4.61	5.19 ± 0.04	4.65	7.13 ± 0.05

The kinetic data can be explained by invoking a radical mechanism in which the products of the aquated metabisulfite namely hydrogen sulfite HSO_3^- and sulfite SO_3^{2-} interact with the hexacyanoferrate(III) *via* slow one electron transfer steps to give the hexacyanoferrate(II) and HSO_3^* and/or SO_3^{*-} radicals (11,20).

One could thus envisage the overall reduction process to take place by the following sequence of steps:



The above mechanism gives a rate law of the form:

$$\frac{-\partial \ln[\text{Fe}(\text{CN})_6^{3-}]}{\partial t} = k_{obs} \quad (11)$$

$$k_{obs} = k_1[\text{HSO}_3^-] + k_2[\text{SO}_3^{2-}] \quad (12)$$

The total SO_3^{2-} is given by:

$$\sum[\text{SO}_3^{2-}] = [\text{HSO}_3^-] + [\text{SO}_3^{2-}] \quad (13)$$

Substituting 13 into 12 gives:

$$k_{obs} = \frac{\{k_1[\text{H}^+] + k_2K\}}{\{[\text{H}^+] + K\}} \sum[\text{SO}_3^{2-}] \quad (14)$$

$$k_{obs}' = \frac{k_{obs}}{\sum[\text{SO}_3^{2-}]} = \frac{\{k_1[\text{H}^+] + k_2K\}}{\{[\text{H}^+] + K\}} \quad (15)$$

Since K , the acid ionization constant of $\text{HSO}_3^- = 6.2 \times 10^{-8} \ll [\text{H}^+]$, equation (14) reduces to:

$$k_{obs}' = k_1 + \frac{k_2'}{[\text{H}^+]} \quad (16)$$

where $k_2' = k_2K$

It is important to realize that while k_{obs} is a first order rate constant of units s^{-1} , k_{obs}' is a second order rate constant of units $\text{s}^{-1}\text{mol}^{-1}\text{L}$. In addition k_1 is a second order rate constant of units $\text{s}^{-1}\text{mol}^{-1}\text{L}$, where as k_2' is a first order rate constant of units s^{-1} . Table 3. gives the values of k_{obs}' as functions of pH at the four temperatures studied. The corresponding k_1 and k_2' values from least squares treatment of the data are given in Table 4 together with the corresponding activation parameters.

Table 3: Final values of k_1 and k_2' as functions of temperature and the corresponding activation parameters.

T, K	$10^2 k_1, \text{s}^{-1}\text{mol}^{-1}\text{L}$	$10^6 k_2', \text{s}^{-1}$
288.15	0.25 ± 0.07	3.28 ± 0.04
293.15	0.84 ± 0.14	4.15 ± 0.09
298.15	1.02 ± 0.20	6.33 ± 0.12
303.15	1.30 ± 0.23	7.84 ± 0.13
$\Delta H^\ddagger, \text{kJ mol}^{-1}$	73.64	41.71
$\Delta S^\ddagger, \text{JK}^{-1} \text{mol}^{-1}$	- 36.63	- 205.03
$\Delta G^\ddagger_{(298.15 \text{ K})}, \text{kJ mol}^{-1}$	84.56	102.84

Table 4: Final values of k as functions of temperature and the corresponding activation parameters.

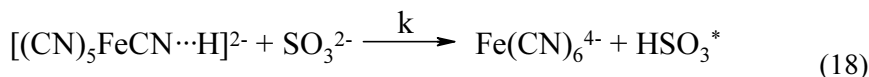
T, K	$10^4 k \text{ s}^{-1}\text{mol}^{-1}\text{L}$
288.15	0.90
293.15	1.87
298.15	2.54
303.15	3.20
$\Delta H^\ddagger, \text{kJ mol}^{-1}$	57.68
$\Delta S^\ddagger, \text{JK}^{-1} \text{mol}^{-1}$	- 120.83
$\Delta G^\ddagger_{(298.15 \text{ K})}, \text{kJ mol}^{-1}$	93.70

The suggested mechanism given in the sequence of reactions (11 to 15) implies that the rate determining step involves the interaction of two anionic species. This unfavorable situation manifests itself in the large activation barrier and the large negative values of ΔS^\ddagger . In addition the single negative charge on the hydrogen sulfite ion compared to the doubly charged sulfite ion implies a lower negative value for ΔS^\ddagger ($-36.6 \text{ JK}^{-1} \text{mol}^{-1}$ for k_1 compared to $-205 \text{ JK}^{-1} \text{mol}^{-1}$ for k_2'). All these species are, however, highly solvated and the anions are surrounded in the outer coordination spheres by the dipolar water molecules reducing the electrostatic repulsion and causing the reaction to proceed via an outer sphere mechanism.

The reaction with the hydrogen sulfite ion, however could proceed by a bridged mechanism where the proton attaches itself to the lone pair on the cyanide ligand leading to bridge formation and the electron is transferred from S^{IV} to Fe^{III} across the bridge via the S-O d -p and the N-C p -p system.

In this case a fast reversible equilibrium is established between the hydrogen ions and hexacyanoferrate(III). This is followed by a slow reaction of the protonated species with the sulfite ion leading to the formation of hydrogen sulfite free radicals which combine to form dithionate in a fast reaction.

The entire series of reactions are as follows:



Reaction 18 suggests a bridged mechanism during the electron transfer *via* an activated complex of the form $[(\text{CN})_5\text{FeCN}\cdots\text{H}\cdots\text{SO}_3^{2-}]$.

The above mechanism gives a rate law of the form:

$$\left[\frac{1}{\sum [\text{SO}_3^{2-}]} \right] \left[\frac{\delta \ln [\text{Fe}(\text{CN})_6^{3-}]}{\delta t} \right] = k_{obs}' \quad (20)$$

$$k_{obs}' = kK + \frac{k}{K[\text{H}^+]} = k_1 + \frac{k_2}{[\text{H}^+]} \quad (21)$$

In this case the second order rate constant "k" of reaction 18 is obtained from the relationship:

$$k = (k_1 \times k_2)^{\frac{1}{2}} \quad (22)$$

The values of the second order rate constant k are given in Table 5 together with the corresponding activation parameters.

Again the smaller negative value of ΔS^\ddagger ($-121 \text{ JK}^{-1} \text{ mol}^{-1}$) is further evidence of bridge formation. The later value of ΔS^\ddagger is actually the mean of the two values for the first mechanism. This is expected since reaction 8 and 9 are related to reaction 18 by the second ionization of sulfurous acid.

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دراسة حركية لاختزال سداسي سيانو فيريت مع ميثا الكبريتات الثنائية

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المستخلص. التأثير الحركي تُحرى بدراسة تفاعل $K_3[Fe(CN)_6]$ مع $Na_2S_2O_5$ كدالة في pH عند أربع درجات حرارة هي: 15, 20, 25, 30°C وقوة أيونية ثابتة مقدارها 1 M, KCl. قيم الأس الهيدروجيني (pH) تراوحت بين ٢,٦ - ٤,٧ باستخدام محلول McIlvaine المنظم المكوّن من نظام phosphate/citric acid. دُرس تأثير درجة الحرارة للحصول على معايير التنشيط ΔH^\ddagger ، ΔS^\ddagger و ΔG^\ddagger . وقد وُجد أن ثابت معدل التفاعل ذو الرتبة الثانية، الملاحظ k_{obs} يتناسب تناسباً عكسياً مع تركيز H^+ حسب العلاقة: $k_{obs} = k_1 + k_2/[H^+]$. وعند درجة حرارة 298.15K وُجد أن قيمة ثابت المعدل ذو الرتبة الثانية $k_1 = 1.02 \pm$ $=k_2 = 0.20 \times 10^{-2} s^{-1} mol^{-1} L$ بينما قيمة ثابت المعدل ذو الرتبة الأولى $\Delta H^\ddagger = 73.64 kJ mol^{-1}$ ، ومعايير تنشيط k_1 هي: $(6.33 \pm 0.12) \times 10^{-6} s^{-1}$

$\Delta S^\ddagger = -36.63 \text{ JK}^{-1} \text{ mol}^{-1}$ و $\Delta G^\ddagger = 84.56 \text{ kJ mol}^{-1}$ و k_2 هي: $41.71 \text{ kJ mol}^{-1}$ ، $-205.03 \text{ JK}^{-1} \text{ mol}^{-1}$ و $102.84 \text{ kJ mol}^{-1}$ على التوالي. وتم تفسير البيانات الحركية بالاستناد إلى ميكانيكية الشقوق، حيث ينتج من تفاعل HSO_3^- و SO_3^{2-} مع معقد الحديد الثلاثي تكوين شقوق حرة هي HSO_3^* و SO_3^{*-} وذلك بانتقال إلكترون منهما إلى الحديد الثلاثي، ويُمكنُ أَنْ تُحَدَّثَ عملية الأكسدة والاختزال مِنْ قِبَل ميكانيكية يحصل فيها اتزان عكسي سريع بين أيونات الهيدروجين و hexacyanoferrate(III) متبوعاً بتفاعل بطيء للمعقد الناتج مع أيون السلفايت لتكوين شق السلفايت الحر.