Kinetics and Mechanism of the Oxidation of a Ferrous Complex with an α,α′-Diimine Chelate Ligand by Ceric Sulfate in Aqueous Acidic Medium by UV-Vis Absorption Spectroscopy

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Kinetics of the oxidation of tris(2,2′-bipyridine)iron(II) sulfate by ceric sulfate was spectrophotometrically studied in an aqueous sulfuric acid medium. Different methods, including isolation, integration and half-life, were employed to determine the reaction order. The redox reaction was found to be first-order with respect to the reductant, tris(2,2′-bipyridine)iron(II) sulfate, and the oxidant, ceric sulfate. Complex kinetics was observed with an increase in the initial concentration of the oxidant. The influence of the dielectric constant, $[H^+]$ and $[SO_4^{2-}]$ on the rate was also investigated. The increase in the dielectric constant and H^+ ion concentration of the medium retard the rate, while an increase in the SO_4^{2-} ion concentration first accelerates the rate, and then retards the reaction. The effect of each factor, *i.e.*, the dielectric constant, H^+ ions and SO_4^{2-} ions, suggests that $Ce(SO_4)_3^{2-}$ is the active species of cerium(IV). A rate law consistent with the observed kinetic data and the proposed mechanism is suggested to be:

$$-\frac{d\left[Fe(bipy)_3{}^{2+}\right]}{dt} = \frac{k\,K_1\,K_d\left[Fe(bipy)_3{}^{2+}\right]\left[Ce^{IV}\right]_t\left[SO_4{}^{2-}\right]_a}{K_d{}^2 + K_i\left[SO_4{}^{2-}\right]_a}$$

Keywords: Kinetics and mechanism, UV-Vis absorption spectroscopy, Redox reaction, Tris(2,2′-bipyridine)iron(II) sulfate, Ceric sulfate

INTRODUCTION

The tris(2,2′-bipyridine)iron(II) cation is of much importance and frequently used. It is employed for the spectrophotometric determination of iron by analytical chemists. The complex, due to its great stability, is also used to remove the interferences of iron while determining other metals. The intense red color of the tris bipyridine ferrous complex and very high molar extinction coefficient are responsible for the extensive use of the chelate ligand, 2,2′-

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bipyridine, as a colorimetric reagent and for the spectrophotometric determination of iron. It is also used as a redox indicator due to its high reduction potential (~1.02 V) [1]. The large cationic iron(II) complex is useful in the specific precipitation of anions in gravimetric procedures.

Redox reactions have drawn the attention of chemists and numerous kinetic investigators [2-4]. Studies involving electron transfer between ferrous/ferric ions and their complexes have been widely reported in recent years [5,6].

The oxidation of iron(II) complexes with α,α′-diimine chelate ligands, like 1,10-phenanthroline (ferroin), 2,2′-bipyridine or 2,2′-bipyridyl, as well as the oxidation of

substituted 1,10- phenanthroline and 2,2′-bipyridine, involves the loss of one electron from the complex cation, as follows.

$$[Fe(o-phen)_3]^{2+} \rightarrow [Fe(o-phen)_3]^{3+} + \overline{e}$$

$$[Fe(bipy)_3]^{2+} \rightarrow [Fe(bipy)_3]^{3+} + \overline{e}$$
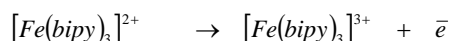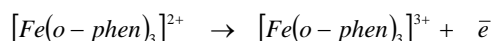
Such oxidations can readily be followed spectrophotometrically as the iron(II) complexes have large molar extinction coefficients at the wavelengths far removed from the less absorbing species of iron(III). Hence, the kinetics and mechanism for these types of reactions can easily be studied using spectrophotometry. Examples of such include the study by Ayodele, Olajire and Oladoye [7] of the kinetics and mechanism of the periodate oxidation of the 4,4′-dimethyl derivative of the ferrous bipyridine complex in acidic medium, and by Burgess and Prince [8] of the kinetics of the peroxydisulfate oxidation of iron(II) complexes with tris-2,2′-bipyridine, substituted tris-2,2′-bipyridine, tris-1,10-phenanthroline, substituted tris-1,10-phenanthroline and bis-2,2′:6′,2′′-terpyridine or bis-2,2′:6′,2′′-terpyridyl.

Cerium in the tetravalent state (Ce^{4+}) is a strong oxidizing agent that apparently reacts only *via* a one-electron step to Ce^{3+}. Aqueous solutions containing cerium(IV) species are stable, despite the lower electrode potential for the O_2-H_2O couple (1.23 V), probably for kinetic reasons. Cerium(IV) oxidation is a valuable tool in organic chemistry and can be used for quantitative volumetric oxidation reactions, called cerate oxidimetry in analytical chemistry. It is widely used for the oxidation of many substrates in different aqueous acidic mediums [9-11].

The kinetics of the redox reaction between tris(2,2′-bipyridine)iron(II) sulfate and ceric sulfate in an aqueous sulfuric acid medium is investigated in the present report. The influence of different factors on the rate of the redox reaction was also studied and, according to these results, a rate law is derived that supports the proposed mechanism. Furthermore, the order of the reaction is determined using different methods, including isolation, integration and half-life. The stability of the complex [Fe(bipy)$_3$]SO$_4$ in different media has also been investigated.

EXPERIMENTAL

The diammoniumiron(II) sulfate-6-hydrate, sodium acetate-3-hydrate and sodium sulfate were of BDH AnalaR grade and cerium(IV) sulfate-4-hydrate, 2,2′-bipyridine, acetic acid, sulfuric acid and ethanol were of Merck AnalaR grade. Distilled and deionized water was employed for the preparation of solutions.

Instrumentation

All the spectra and the kinetic measurements were recorded on the spectrum and the photometric mode, respectively, of a Shimadzu UV-160 UV-Vis spectrophotometer using quartz cells, and pH measurements were carried out on a Mettler MP-220 pH meter.

Determination of Metal to Ligand Ratio and Empirical Formula of the Iron(II) Bipyridine Complex

The empirical formula of the complex, composed of iron(II) and 2,2′-bipyridine, was established by the Job's method of continuous variation. As the aqueous metal ion/ligand solutions at the required concentrations are colorless, several solutions were spectrophotometrically examined at the visible maximum absorption wavelength (λ_{max}) of 522 nm for the complex ion. For each solution, the value for the total concentration of metal plus ligand ($[M]_t + [L]_t$) were different but constant, including free and complexed forms. Measurements of the absorption intensity (optical density or absorbance) was plotted against composition (the ratio $[M]_t/([M]_t + [L]_t$ against $[M]_t$/constant). From the maximum absorbance on this plot, the ratio of $[M]_t$:$[L]_t$ of the complex was determined to be 1:3, and this optimal ratio was used in later experiments.

Solutions of the required concentrations were prepared by diluting the stock solution of diammmoniumiron(II) sulfate-6-hydrate in the distilled deionized water. The stock solution of the ligand was prepared by first dissolving the required amount of 2,2′-bipyridine in 1 ml ethanol. More dilute solutions were then made using distilled deionized water.

Synthesis of Tris(2,2′-bipyridine)iron(II) Sulfate

Tris(2,2′-bipyridine)iron(II) sulfate was synthesized by

mixing like volumes of diammoniumiron(II) sulfate-6-hydrate and 2,2′-bipyridine solutions, with the final concentrations of the reactants maintained at a 1:3 ratio, respectively. The complex was precipitated in the form of a sulfate salt crystal by adding sodium sulfate and ethanol to the reaction mixture. Intense red-colored crystals of the complex compound were recrystallized using ethanol. The crystals obtained were dried first with ether and then in a desiccator.

Stability of Tris(2,2′-bipyridine)iron(II) Sulfate in Different Media

The stability of the complex compound was studied at room temperature, 28 °C, in distilled water and 10 and 20% ethanol-water mixtures. The data were spectrophotometrically collected at 522 nm for a time interval of 1 min over a period of 3.5 h.

The stability of the complex compound was also determined at pH 3.71, 4.15 and 4.82, and maintained at these values using acetic acid-sodium acetate buffer. Standard solutions of the buffers were prepared as previously described [1]. The data were collected in the same manner as for the study of the stability in different media. Since the compound was found to be most stable at pH 4.82, this condition was employed in later experiments.

The kinetic study of the redox reaction between tris(2,2′-bipyridine)iron(II) sulfate and ceric sulfate was carried out in a sulfuric acid medium, under the pseudo-first order conditions with the ceric sulfate concentration always in excess of 3.33, 6.67, 10, 20 and 30-fold relative to the complex. This was monitored at 522 nm. The pseudo-first order rate constants were obtained from the slopes of the plots of $\ln[(A_o - A_\infty)/(A_t - A_\infty)]$ against time.

Results established that the complex compound is stable in all three media, water and 10 and 20% ethanol/water mixtures, at a pH of 4.82.

Effect of Dielectric Constant

The effect of the dielectric constant of the medium on the observed rate constant, k_{obs}, was studied by decreasing the dielectric constant of the medium gradually through the addition of ethanol to the medium. Distilled water and 10 and 20% ethanol-water mixtures were used for that purpose. The remaining conditions were kept unaltered.

Effect of $[H^+]$ and $[SO_4^{2-}]$

In order to study the effect of $[H^+]$ on the reaction rate, kinetic runs were carried out using acetic acid-sodium acetate buffer at pH 4.82 as the solvent for the $[Fe(bipy)_3]SO_4$ solution, instead of distilled water.

The influence of the $[SO_4^{2-}]$ on the reaction rate was investigated by varying $[SO_4^{2-}]_a$, using sodium sulfate (Na_2SO_4) as a source of sulfate ions, keeping $[H^+]$ almost constant and the other factors unaltered.

RESULTS AND DISCUSSION

Characterization of the Synthesized Complex Compound, $[Fe(bipy)_3]SO_4$ and Product Analysis

Measurements of the intensity of absorption plotted against composition reveal that the empirical formula of the intense red-colored complex cation is $[Fe(bipy)_3]^{2+}$, as displayed in Table 1 and Fig. 1. Tris(2,2′-bipyridine)iron(II) sulfate was characterized by its UV-Vis or absorption spectrum. The characteristic wavelengths at λ_{max} for the complex compound in the ultraviolet and visible regions were in excellent agreement with the values reported in the literature [12,13] and those established for the complex cation through Job's method of continuous variation. However, for further confirmation and characterization, the complex cation $[Fe(bipy)_3]^{2+}$ and the complex compound $[Fe(bipy)_3]SO_4$ were first oxidized to $[Fe(bipy)_3]^{3+}$ by ceric sulfate. The product was
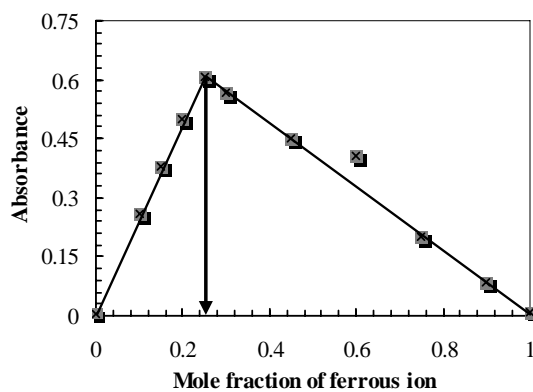
Fig. 1. The Job's plot obtained when the $[Fe(bipy)_3]^{2+}$ complex species is formed between ferrous ion and bipyridine.

Table 1. Determination of the Empirical Formula of the Iron(II) Bipyridine Complex Ion by Job's Method of Continuous Variation[a]

| S. No. | Composition of the reaction mixture | | Absorbance | Empirical formula for complex ion |
	$\dfrac{[Fe^{2+}]_t}{([Fe^{2+}]_t + [bipy]_t)}$	$\dfrac{[bipy]_t}{([Fe^{2+}]_t + [bipy]_t)}$		
1	0.00	1.00	0.003	
2	0.10	0.90	0.258	
3	0.15	0.85	0.378	
4	0.20	0.80	0.502	
5	0.25	0.75	0.609	
6	0.30	0.70	0.565	$[Fe(bipy)_3]^{2+}$
7	0.45	0.55	0.450	
8	0.60	0.40	0.408	
9	0.75	0.25	0.203	
10	0.90	0.10	0.086	
11	1.00	0.00	0.010	

[a]Diammoniumiron(II) sulfate-6-hydrate = 2.8×10^{-4} M, 2,2′-bipyridine = 2.8×10^{-4} M, medium = distilled and deionized water, λ_{max} = 522 nm, temperature = 28 ºC.

Table 2. Absorption Spectral Data of the Complex Cation and the Complex Compound in the Reduced and the Oxidized Forms

| Complex | Color | Observed values of wavelength maxima (nm) | | Literature values of wavelength maxima [12,13] (nm) | |
		UV	Vis.	UV	Vis.
$[Fe(bipy)_3]^{2+}$ (reduced form)	Intense red	284	522	297	522
$[Fe(bipy)_3]^{3+}$ (oxidized form)	Pale blue	-	610	-	610
$[Fe(bipy)_3]SO_4$ (reduced form)	Intense red	285	522	-	-
$[Fe(bipy)_3]^{3+}$ (oxidized form)	Pale blue	-	610	-	-

then examined for color and λ_{max} in the visible region. These results (Table 2) were in good agreement with previous reports [12,13].

$$[Fe(bipy)_3]^{2+} + Ce^{4+} \rightarrow [Fe(bipy)_3]^{3+} + Ce^{3+}$$
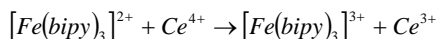
Ceric sulfate was used for the characterization of the complex compound because it oxidizes to (Ce^{4+}) and reduces to (Ce^{3+}),

both of which do not absorb in the visible region.

Matching molar extinction coefficients of the synthesized complex compound and its oxidized form with the values given in the literature [12,13] was also used to confirm the synthesized complex as $[Fe(bipy)_3]SO_4$.

Kinetic Measurements

The pseudo-first order rate constants were obtained from the slopes of the plots of $\ln[(A_o - A_\infty)/(A_t - A_\infty)]$ against time,

Table 3. Dependence of the Redox Reaction Rate on the Reductant and the Oxidant[a]

No.	10^4 [Ce(IV)]$_t$ (M)	Distilled water		Effect of H$^+$ ions on k_{obs}	
		Integration method $10^1 k_{obs}$ (s^{-1})	Half-life method $10^1 k_{obs}$ (s^{-1})	Integration method $10^1 k_{obs}$ (s^{-1})	Half-life method $10^1 k_{obs}$ (s^{-1})
1	0.25	0.725	0.719	0.540	0.529
2	0.50	1.450	1.446	1.100	1.121
3	0.75	1.891	1.898	1.469	1.260
4	1.50	2.493	2.475	1.778	1.848
5	2.25	1.969	1.540	1.548	1.429

[a][Fe(bipy)$_3$SO$_4$] = 0.75 × 10^{-5} M, [H$_2$SO$_4$] = 9.0 × 10^{-2} M, temperature = 28 ℃.

which were always linear.

The course of the reaction was followed under isolation conditions, as if;

Rate = k [reductant] [oxidant]$_t$

where [reductant] $<<<$ [oxidant]$_t$.

The effect of the [reductant] on the rate of the redox reaction could be studied independently of the [oxidant]$_t$ because, under the conditions employed, the [oxidant]$_t$ will be effectively constant. Similarly, the effect of the [reductant] on the rate of the redox reaction could be studied independently of the [oxidant]$_t$. Hence,

Rate = k_{obs} [reductant]

$k_{obs} = k$ [oxidant]$_t$

k_{obs} = pseudo-first order rate constant with the unit s^{-1}. The above mentioned equations will thus help to evaluate the value of the rate constant and to investigate the order of the reaction with respect to the [reductant] and the [oxidant]$_t$, respectively.

Dependence of the Rate of Redox Reaction on the Reductant

The order of the redox reaction and value of the pseudo-first order rate constant (k_{obs}), with respect to the reductant [Fe(bipy)$_3$]SO$_4$, was determined by employing the integration and half-life methods. Both methods showed first-order dependence of the redox reaction rate on tris(2,2′-bipyridine)

iron(II) sulfate. Similar results were obtained while different initial concentrations of the oxidizing agent were employed, keeping all other factors constant. Results are recorded in Table 3. Matching values of k_{obs} substantiates our claim that the first-order kinetics is being followed.

Dependence of the Reaction Rate on the Oxidant

The reaction order with respect to ceric sulfate, [oxidant]$_t$, was established through $k_{obs} = k$ [oxidant]$_t$. The kinetic runs were carried out by varying the initial concentration of the oxidant, keeping the remaining conditions unaltered. The values of the pseudo-first order rate constant (Table 3) were found to be dependent upon the ratio between the two reactants, tris(2,2′-bipyridine)iron(II) sulfate and ceric sulfate. A plot of k_{obs} vs. [Ce(IV)]$_t$ (Fig. 2) was found to be a curve
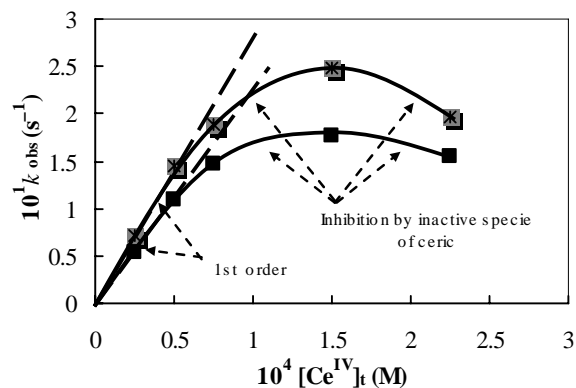
Fig. 2. k_{obs} vs. [Ce(IV)]$_t$ in distilled water and in acidic medium: (⊠) pure water, (■) effect of hydrogen ions.

Table 4. Dependence of k_{obs} on the Dielectric Constant of the System[a]

Medium	Dielectric constant[b]	$10^4/D$	$10^1\,k_{obs}$ (s^{-1})	$10^4\,\log k_{obs}$
Distilled water	78.54	127.32	1.969	-7057.5
10% Ethanol-water mixture	65.80	151.97	2.824	-5491.3
20% Ethanol-water mixture	54.90	182.15	5.723	-2423.7

[a][Fe(bipy)$_3$SO$_4$] = 0.75 × 10^{-5} M, [Ce(IV)]$_t$ = 2.25 × 10^{-4} M, [H$_2$SO$_4$] = 9.0 × 10^{-2} M, temperature = 28 ºC.
[b]Values of the dielectric constant are not recalculated for presence of sulfuric acid in the medium, but are used as they were reported in the literature [22].

indicating complex kinetics with respect to the oxidant.

Effect of the Dielectric Constant of the Medium

The results in Table 4 reveal that the value of the pseudo-first order rate constant (k_{obs}) increases with a decrease in the dielectric constant of the medium; however the plot of $\log k_{obs}$ *vs.* 1/D was found to be a straight line with a positive slope (85.144) and a y-intercept (-1.8087) through which the rate determining step clearly involves the reacting species with unlike charges.

Although cerium(IV) is well known to oxidize alcohols in different aqueous acidic media under certain conditions [9,14-16], but under the experimental conditions employed in this study, the rate of ethanol oxidation by ceric sulfate in the aqueous sulfuric acid medium is known to be very slow [14,15] and negligible when compared to the oxidation reaction under observation. Thus, considering the stability of the complex in 10 and 20% ethanol-water mixtures, ethanol was used to investigate the effect of the dielectric constant of this medium on the rate of the redox reaction.

Effect of [H$^+$]

Wiberg and Ford [17] have shown the existence of the equilibrium in 85% aqueous acetic acid solution.

$$CeOH^{3+} + HOAc \leftrightarrow CeOAc^{3+} + H_2O$$
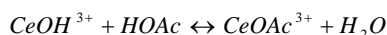
However, there is no evidence for the formation of CeOH^{3+} and CeOAc^{3+} in a mixture of acetic acid-sodium acetate buffer and aqueous sulfuric acid. A literature survey [10,17,18] reveals that, in this mixture, cerium(IV) exists in the form of sulfato complexes; however, acetate buffer tends to increase

the concentration of hydrogen ions in the mixture. For this reason, for the study regarding the effect of [H$^+$] on the reaction rate, we used acetic acid-sodium acetate buffer as the solvent for the [Fe(bipy)$_3$]SO$_4$ solution instead of distilled water. All the remaining conditions were kept constant. Table 3 and Fig. 2 show the effect of the [H$^+$] on the pseudo-first order rate constant. Values of the rate constant (k_{obs}) were found to decrease with an increase in the concentration of hydrogen ions of the system.

Effect of [SO$_4^{2-}$]

Results (Table 5, Fig. 3) show that an increase in [SO$_4^{2-}$]$_a$ in the medium accelerates the k'_{obs} first and then tends toward retardation, where k'_{obs} is the second-order rate constant with the unit of mol^{-1} dm^3 s^{-1} or M^{-1} s^{-1}. [ ]$_a$ indicates the actual concentration of the species for which the dissociation
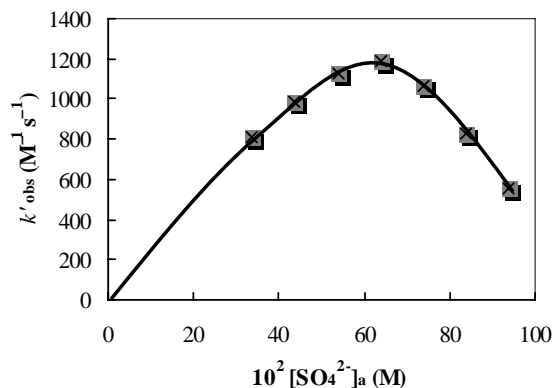
Fig. 3. Plot of k'_{obs} *vs.* [SO$_4^{2-}$]$_a$, showing the influence of sulfate ions in the electron transfer reaction between tris(2,2′-bipyridine)iron(II) sulfate and ceric sulfate.

Table 5. Dependence of k'_{obs} on $[SO_4^{2-}]^a$

No.	$10^2 [Na_2SO_4]$ (M)	$10^2 [SO_4^{2-}]_a$ (M)	$10^2 [SO_4^{2-}]_a^{-1}$ (M^{-1})	$10^1 k_{obs}$ (s^{-1})	k'_{obs} $(M^{-1}s^{-1})$	$10^5 1/k'_{obs}$ (M s)
1	30	33.767	296.147	1.830	813.3	122.955
2	40	43.767	228.482	2.213	983.5	101.677
3	50	53.767	185.987	2.534	1126.2	88.794
4	60	63.767	-	2.680	1191.1	83.956
5	70	73.767	-	2.390	1062.2	94.144
6	80	83.767	-	1.860	826.6	120.977
7	90	93.767	-	1.257	558.6	179.019

[a]Medium = distilled water, $[Fe(bipy)_3SO_4] = 0.75 \times 10^{-5}$ M, $[Ce(IV)]_t = 2.25 \times 10^{-4}$ M, $[H_2SO_4] = 15.9 \times 10^{-2}$ M, temperature = 28 °C.

constant of bisulfate ions is considered.

From earlier reports [18,19], it appears that, in aqueous sulfuric acid medium, cerium(IV) can exist in several forms, such as Ce^{4+}, $Ce(SO_4)^{2+}$, $Ce(SO_4)_2$, $Ce(SO_4)_3^{2-}$, $HCe(SO_4)_3^-$ and $H_2Ce(SO_4)_4^{2-}$, depending upon the concentration of cerium(IV) and sulfuric acid.

Some of the equilibria leading to the formation of sulfato complexes of cerium(IV) include [18,19]:

$$Ce^{4+} + HSO_4^- \leftrightarrow CeSO_4^{2+} + H^+$$

$$CeSO_4^{2+} + HSO_4^- \leftrightarrow Ce(SO_4)_2 + H^+$$

$$Ce(SO_4)_2 + HSO_4^- \leftrightarrow Ce(SO_4)_3^{2-} + H^+$$

$$Ce(SO_4)_2 + HSO_4^- \leftrightarrow HCe(SO_4)_3^-$$

$$Ce(SO_4)_3^{2-} + H^+ \leftrightarrow HCe(SO_4)_3^-$$

$$HCe(SO_4)_3^- + HSO_4^- \leftrightarrow H_2Ce(SO_4)_4^{2-}$$
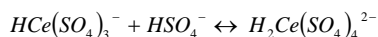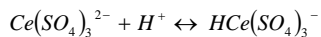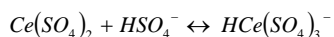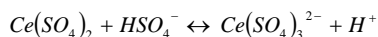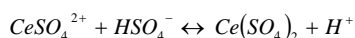
In the oxidation of different substrates by cerium(IV) in aqueous sulfuric acid medium, one or more of the equilibria can be involved in the kinetics of the reaction and one or more of the species can be considered to be the reactive species of cerium(IV).

Through the effects of the dielectric constant and the $[H^+]$ and $[SO_4^{2-}]$ of the medium on the reaction rate, the difficulty in choosing the active and inactive species among the abovementioned options can easily be overcome for this particular kinetic study of this cerium(IV) reaction under the experimental conditions employed. Under the experimental conditions of the present work, the most relevant equilibria appear to be the four latest above given equations.
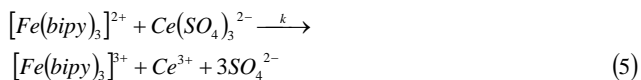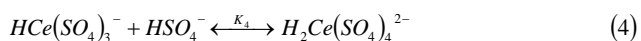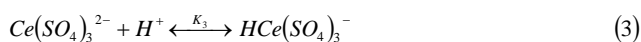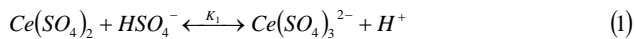
The effects of the different factors suggest which of these forms are the active and inactive species involved in these reaction kinetics. The influence of the dielectric constant on k_{obs} shows that the reacting species have unlike charges, whereas a literature survey [7,8,20] indicates that, under these experimental conditions, the reductant exists in the form of the complex cation $[Fe(bipy)_3]^{2+}$ and reacts as such. It is expected that the reactive species of cerium(IV) is $Ce(SO_4)_3^{2-}$, $HCe(SO_4)_3^-$ or $H_2Ce(SO_4)_4^{2-}$, and the inactive species is $Ce(SO_4)_2$. However, the effect of the $[H^+]$ on the reaction rate clearly supports the fact that participation of $Ce(SO_4)_3^{2-}$ is that of an active species and $Ce(SO_4)_2$, $HCe(SO_4)_3^-$ and $H_2Ce(SO_4)_4^{2-}$ act as inactive species in the redox reaction between tris(2,2'-bipyridine)iron(II) sulfate and ceric sulfate. Furthermore, this conclusion is also favored by the influence of $[SO_4^{2-}]_a$ on k'_{obs}, because initially, at the lower sulfate ion concentration, the value of the second-order rate constant increases due to the formation of the active species through the third equation. However, at higher concentrations, it decreases due to the conversion of the reactive species $Ce(SO_4)_3^{2-}$ into the inactive species $H_2Ce(SO_4)_4^{2-}$ through the last three equations.

Proposed Mechanism

The stoichiometry of the reaction is given as:

$$[Fe(bipy)_3]^{2+} + Ce^{4+} \rightarrow [Fe(bipy)_3]^{3+} + Ce^{3+}$$
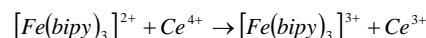
Keeping in mind the various aspects as well as the kinetic evidence obtained for the existence of different forms of cerium(IV) in the present investigation, we propose a mechanism that involves the following reactions:

$$Ce(SO_4)_2 + HSO_4^- \xleftrightarrow{K_1} Ce(SO_4)_3^{2-} + H^+ \tag{1}$$

$$Ce(SO_4)_2 + HSO_4^- \xleftrightarrow{K_2} HCe(SO_4)_3^- \tag{2}$$

$$Ce(SO_4)_3^{2-} + H^+ \xleftrightarrow{K_3} HCe(SO_4)_3^- \tag{3}$$

$$HCe(SO_4)_3^- + HSO_4^- \xleftrightarrow{K_4} H_2Ce(SO_4)_4^{2-} \tag{4}$$

$$[Fe(bipy)_3]^{2+} + Ce(SO_4)_3^{2-} \xrightarrow{k}$$
$$[Fe(bipy)_3]^{3+} + Ce^{3+} + 3SO_4^{2-} \tag{5}$$

Equations (1-4) are involved in the mechanism and lead to the formation of different species:

$$[Ce(SO_4)_2]_a = \frac{[Ce(SO_4)_3^{2-}]_a[H^+]_a}{K_1[HSO_4^-]_a} \tag{6}$$

$$[HCe(SO_4)_3^-]_a = \frac{K_2[Ce(SO_4)_3^{2-}]_a[H^+]_a}{K_1} \tag{7}$$

$$[HCe(SO_4)_3^-]_a = K_3[Ce(SO_4)_3^{2-}]_a[H^+]_a \tag{8}$$

$$[H_2Ce(SO_4)_4^{2-}]_a = K_4[HCe(SO_4)_3^-]_a[HSO_4^-]_a \tag{9}$$

$$[H_2Ce(SO_4)_4^{2-}]_a =$$
$$K_4[Ce(SO_4)_3^{2-}]_a[HSO_4^-]_a[H^+]_a\left\{\frac{K_2 + K_1K_3}{K_1}\right\} \tag{10}$$

The total cerium(IV) concentration is given by:

$$[Ce^{IV}]_t = [Ce(SO_4)_2]_a + [Ce(SO_4)_3^{2-}]_a + [HCe(SO_4)_3^-]_a +$$
$$[H_2Ce(SO_4)_4^{2-}]_a \tag{11}$$

where $[\ ]_t$ is the total concentration of the species and $[\ ]_a$ is the actual concentration of the species.

The dissociation constant of the bisulfate ion is also considered [21] when ion concentrations in the aqueous sulfuric acid are being calculated under the experimental conditions employed.

$$[HSO_4^-]_a = \frac{[H^+]_a[SO_4^{2-}]_a}{K_d} \tag{12}$$

where K_d is the dissociation constant of the bisulfate ion. Thus, the use of the Eqs. (6-8) and (10-12) lead to

$$[Ce(SO_4)_3^{2-}]_a =$$
$$\frac{K_1K_d[Ce^{IV}]_t[SO_4^{2-}]_a}{K_d^2 + [SO_4^{2-}]_a[K_d(K_1 + [H^+]_a\{K_2 + K_1K_3\}) + (K_4[H^+]_a[SO_4^{2-}]_a)(K_2 + K_1K_3)]} \tag{13}$$

The rate of the redox reaction, equal to k [Fe(bipy)$_3^{2+}$] [Ce(SO$_4$)$_3^{2-}$]$_a$, is

$$-\frac{d[Fe(bipy)_3^{2+}]}{dt} =$$
$$\frac{k K_1K_d[Fe(bipy)_3^{2+}][Ce^{IV}]_t[SO_4^{2-}]_a}{K_d^2 + [SO_4^{2-}]_a[K_d(K_1 + [H^+]_a\{K_2 + K_1K_3\}) + (K_4[H^+]_a[SO_4^{2-}]_a)(K_2 + K_1K_3)]} \tag{14}$$

Equation (14) explains unit order for [Fe(bipy)$_3^{2+}$] and [Ce(IV)]$_t$, acceleration as well as inhibition by [SO$_4^{2-}$]$_a$ and inhibition by [H$^+$]$_a$. Upon combining Rate = k_{obs} [reductant] and Eq. (14), we obtain:

$$k_{obs} =$$
$$\frac{k K_1K_d[Ce^{IV}]_t[SO_4^{2-}]_a}{K_d^2 + [SO_4^{2-}]_a[K_d(K_1 + [H^+]_a\{K_2 + K_1K_3\}) + (K_4[H^+]_a[SO_4^{2-}]_a)(K_2 + K_1K_3)]} \tag{15}$$

Under the experimental conditions of [SO$_4^{2-}$]$_a$ >>>> [Ce(IV)]$_t$ >>> [Fe(bipy)$_3^{2+}$]

$$k_{obs} = k'_{obs}[Ce^{IV}]_t \tag{16}$$

$$k'_{obs} = \frac{k K_1K_d[SO_4^{2-}]_a}{K_d^2 + K_i[SO_4^{2-}]_a} \tag{17}$$

where the second order rate constant, k'_{obs}, has the unit M^{-1} s^{-1} (*i.e.*, conc.$^{-1}$ time^{-1}) and K_i is the inhibition constant. K_i is represented by the following:

$$K_i = [K_d(K_1 + [H^+]_a\{K_2 + K_1K_3\}) + (K_4[H^+]_a[SO_4^{2-}]_a)(K_2 + K_1K_3)]$$

There are two limiting cases for k_{obs} and k'_{obs}. As depicted in Fig. 2, k_{obs} depends on $[Ce(IV)]_t$ in a complex manner. For k_{obs}, the excess of cerium(IV) is small when $Ce(SO_4)_3^{2-}$ is the only species of cerium(IV) present at significant concentrations under the experimental conditions employed, i.e. at low concentrations of SO_4^{2-} [18]. Thus,
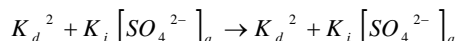
$$K_d^{\,2} + K_i \left[SO_4^{\,2-} \right]_a \rightarrow K_d^{\,2}$$
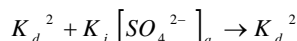
and

$$k_{obs} = \frac{k\,K_1\left[Ce^{IV}\right]_t\left[SO_4^{\,2-}\right]_a}{K_d} \qquad (18)$$

and the reaction rate is proportional to $[Ce(IV)]_t$, which is first order with respect to ceric sulfate.

The excess of cerium(IV) is large, when all the specie, including active and inactive cerium(IV) specie, are present at significant concentrations [18,19] under the stated experimental conditions of high SO_4^{2-} concentration:
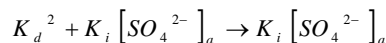
$$K_d^{\,2} + K_i \left[SO_4^{\,2-} \right]_a \rightarrow K_d^{\,2} + K_i \left[SO_4^{\,2-} \right]_a$$

and

$$k_{obs} = \frac{k\,K_1 K_d\left[Ce^{IV}\right]_t\left[SO_4^{\,2-}\right]_a}{K_d^{\,2} + K_i \left[SO_4^{\,2-}\right]_a} \qquad (19)$$

By taking the reciprocal of both the sides of Eq. (19), we obtain:

$$\frac{1}{k_{obs}} = \frac{K_d}{k\,K_1\left[Ce^{IV}\right]_t\left[SO_4^{\,2-}\right]_a} + \frac{K_i}{k\,K_1 K_d\left[Ce^{IV}\right]_t} \qquad (20)$$

and the reaction rate is inhibited by ceric sulfate at higher concentrations.

For k'_{obs}, the excess of sulfate ions is very large, and

$$K_d^{\,2} + K_i \left[SO_4^{\,2-} \right]_a \rightarrow K_i \left[SO_4^{\,2-} \right]_a$$

and

$$k'_{obs} = \frac{k\,K_1 K_d}{K_i} \qquad (21)$$

On rearranging Eq. (21), we get:

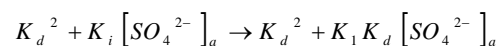$$\frac{1}{k'_{obs}} = \frac{K_i}{k\,K_1 K_d} \qquad (22)$$

$$\frac{1}{k'_{obs}} = \frac{K_1 + \left[H^+\right]_a (K_2 + K_1 K_3)}{k\,K_1} + \frac{\left[SO_4^{\,2-}\right]_a \left(K_4\left[H^+\right]_a^2\right)(K_2 + K_1 K_3)}{k\,K_1 K_d} \qquad (23)$$

Equation (23) can be simplified as:

$$\frac{1}{k'_{obs}} = \left(\frac{1}{k} + b\right) + \frac{K_4 b \left[H^+\right]_a \left[SO_4^{\,2-}\right]_a}{K_d} \qquad (24)$$

$$b = \frac{K'\left[H^+\right]_a}{k\,K_1} \ and \ K' = (K_2 + K_1 K_3)$$

The excess of sulfate ions is small when:

$$K_d^{\,2} + K_i \left[SO_4^{\,2-} \right]_a \rightarrow K_d^{\,2} + K_1 K_d \left[SO_4^{\,2-} \right]_a$$

and

$$k'_{obs} = \frac{k\,K_1 K_d\left[SO_4^{\,2-}\right]_a}{K_d^{\,2} + K_1 K_d\left[SO_4^{\,2-}\right]_a} \qquad (25)$$

Equation (25) can be simplified by taking the reciprocal, which gives:

$$\frac{1}{k'_{obs}} = \frac{K_d}{k\,K_1\left[SO_4^{\,2-}\right]_a} + \frac{1}{k} \qquad (26)$$

According to Eq. (26), a plot of $1/k'_{obs}$ vs. $1/[SO_4^{2-}]_a$ should be linear with a positive slope equal to $K_d/k\,K_1$, and a y-intercept of $1/k$. As shown in Fig. 4, this plot is linear, with an intercept of 30.926×10^{-5} M s and a slope of 31.05×10^{-5} M^2 s, which are equal to $1/k$ and equal to $K_d/k\,K_1$, respectively. These values confirm the proposed mechanism. From the intercept and slope of this plot, the value of the second-order rate constant, k, and K_1 are derived and found to be $k = 32.335$
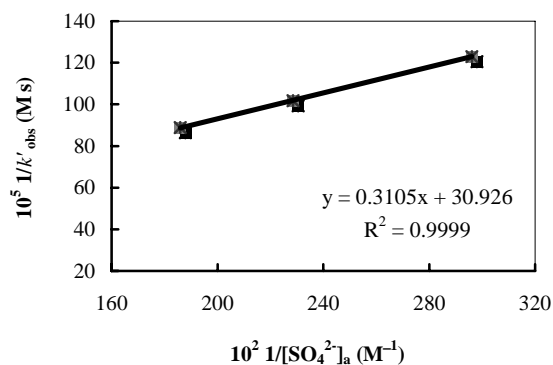
Fig. 4. Plot of $1/k'_{obs}$ vs. $1/[SO_4^{2-}]_a$, showing the catalytic effect of added sulfate ions in the redox reaction.
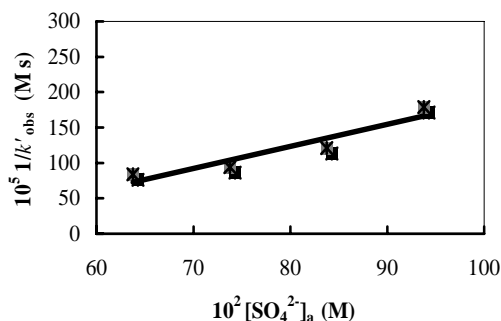
Fig. 5. Plot of $1/k'_{obs}$ *vs*. $[SO_4^{2-}]_a$, showing the retarding effect of added sulfate ions in the redox reaction between tris(2,2′-bipyridine)iron(II) sulfate and ceric sulfate.

$\times 10^2$ M^{-1} s^{-1} and $K_1 = 11.653 \times 10^{-3}$, with $K_d = 1.17 \times 10^{-2}$ M at 28 °C.

However, a linear correlation between the inverse of the rate constant, $1/k'_{obs}$, and the $[SO_4^{2-}]_a$ is consistent with the rate law Eq. (24) (Fig. 5). The agreement is qualitative only, however, because the extent of the retardation produced by the sulfate and hydrogen ions might not be similar (Eqs. (1-4)), such that the plot in Fig. 5 actually shows a negative intercept $= (1/k) + b = -126.25 \times 10^{-5}$ M s and a positive slope $= K_4 b[H^+]_a/K_d = 31.202 \times 10^{-4}$ s, resulting in negative mathematical values for K' and K_4, respectively. The issue here is, of course, that negative mathematical values for equilibrium constants have no physical or quantitative existence.

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