Oxidation of Sulfite and Thiosulfate by the Cobalt(III) Complex of Dipicolinate in Aqueous Medium

Mahammad Ali, Swapan K. Saha, and Pradyot Banerjee*
Department of Inorganic Chemistry, Indian Association for the Cultivation of
Science, Jadavpur, Calcutta 700032, India

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The oxidation of sulfite and thiosulfate by $Co(dipic)_2^-$ (where H_2dipic=2,6-pyridinedicarboxylic acid) was studied in aqueous medium. The reactions were carried out by varying reagent concentrations, pH, and ionic strength. For thiosulfate oxidation, the rate is zero order in complex and second order in thiosulfate. The reaction rates were found to increase with the acidity and the general rate law is expressed as $k_{obs}=\{k_0'+k_1'[H^+]\}[S_2O_3^{2-}]^2$ where k_0' and k_1' denote the acid independent and dependent paths respectively. The values of rate parameters are $k_0'=(2.87\pm0.20)\times10^{-8}$ mol dm^{-3} s^{-1} and $k_1'=(0.57\pm0.02)$ mol^{-2} dm^6 s^{-1} at 30 °C. A plausible mechanism is suggested by considering the formation of an intermediate active species in the rate-determining step. The sulfite oxidation was, however, first order both in complex and reagent. An inverse dependence on $[H^+]$ was obtained for this reaction indicating a higher reactivity of the anionic species in solution. The general rate law is given by $k_{obs}=2(k_1[SO_2\cdot H_2O]+k_2[HSO_3^-]+k_3[SO_3^{2-}])$ and the evaluated second-order rate constants are: $k_1=(5.60\pm0.04)\times10^{-5}$ mol^{-1} dm^3 s^{-1}, $k_2=(3.02\pm1.21)\times10^{-3}$ mol^{-1} dm^3 s^{-1} and $k_3=(4.91\pm0.05)\times10^{-2}$ mol^{-1} dm^3 s^{-1} at 60 °C. The reactivity order $SO_3^{2-}>HSO_3^->SO_2\cdot H_2O$ has been explained successfully by considering the two isomeric structures for these species in solution. An overall rate law has been derived to interpret these results over the whole range of pH. The theoretical pH rate profile calculated from the different rate parameters shows an excellent agreement with the experimental one suggesting the validity of the proposed mechanism.

Very recently, we reported the oxidation of sulfite[1)] and thiosulfate[2)] with a substitution inert complex, dodecatungstocobaltate(III), in aqueous acidic solution. In the oxidation of sulfite, a mixed order dependence on sulfite concentration and a variable product distribution in accordance with stoichiometry was obtained. The thiosulfate oxidation was, however, a simple second-order reaction and in both these studies an alkali metal ion catalysis was observed. But these studies were limited to a pH range 1.5—5.5, as the complex was unstable beyond this pH and the reductants were unstable at low pH. Correspondingly, reactivities of the mono- and divalent anionic forms of the sulfite were determined. In the present study we have chosen a complex, $Co(dipic)_2^-$ (where H_2dipic=2,6-pyridinedicarboxylic acid), which is stable both in acidic and alkaline media and only one reactive species exists within the experimental pH range, and it has a standard reduction potential value[3)] ($E°=0.747$ V), little lower than the dodecatungstocobaltate(III)[2)] ($E°=1.00$ V). The choice of the complex is also significant because $Co(dipic)_2^-$ posseses a hydrophobic π-conjugated ligand and is much more reactive with the redox centers in metalloproteins than the redox reagents having hydrophilic electron transfer surfaces.[3—6)] The aim of this study is to determine and compare the reactivities of all the species of these reductants available in aqueous solution and also to obtain additional information regarding the mechanistic behavior of the complex towards the reaction.

Experimental

Materials and Reagents. The complex, ammonium salt of bis(dipicolinato)cobaltate(III), $NH_4[Co(dipic)_2]$, was prepared and standardized by the same procedure as reported earlier.[7)] Analytical grade reagents were used without further purification. Solutions were prepared in double distilled water and purged with dinitrogen before reaction. The sulfite solution was prepared by dissolving an appropriate amount of sodium sulfite in double distilled water which has been purged with dinitrogen adequately. In a similar fashion thiosulfate solution was prepared and standardized iodimetrically. All solutions were prepared just prior to use. Sodium perchlorate and potassium nitrate used in this study were of analytical grade and also recrystallized thrice before use. Sodium acetate–acetic acid and sodium borate–hydrochloric acid were used as buffers to maintain the pH of the solution as required.

Kinetic Measurements. The reactions were followed in a Pye-Unicam SP8-150 UV/VIS spectrophotometer equipped with thermostated cell compartments. Temperature was controlled using a Haake F3 thermostat. The pH measurements were carried out in a Systronics digital pH meter (model 335, India). Extra precautions were taken to eliminate the loss of sulfurous acid as SO_2 and to prevent air oxidation of thiosulfate. Reactions were carried out in air-tight stoppered quartz cells.

Test for Free Radicals. Both the reactions were tested for free radical generation during the reaction. For this purpose acrylonitrile (5 ml. 20% v/v, degassed with nitrogen) was added to a deaerated reaction mixture. Appearance of a heavy white precipitate within 10 min of reaction confirmed the presence of free radicals in the reaction mixture of sulfite. No polymerization was encountered when acrylonitrile was added to the deaerated solution of complex and reagents separately.

Stoichiometry and Reaction Products. For the thiosulfate oxidation, the reaction stoichiometry was determined iodimetrically by estimating the unreacted thiosulfate in reaction mixtures of thiosulfate and complex in different ratios. The stoichiometry thus obtained is 1 : 1 ($[Co(dipic)_2^-]$: $[S_2O_3^{2-}]$). The reaction product was tetrathionate and confirmed by the method of Kolthoff and Belcher[8)] using the reaction,

$$S_4O_6^{2-} + 3CN^- + H_2O \longrightarrow S_2O_3^{2-} + SO_4^{2-} + SCN^- + 2HCN \quad (1)$$

For the sulfite oxidation, the stoichiometry was determined spectrophotometrically by estimating the excess [Co(dipic)$_2^-$] in a Co(dipic)$_2^-$-sulfite reaction mixture. With excess sulfite, the stoichiometry was determined by estimating excess sulfite iodimetrically. Under both conditions, a 2 : 1 [(Co(dipic)$_2^-$]: [S(IV)] stoichiometry was obtained. The corresponding reaction product obtained was sulfate.

Results and Discussion

Oxidation of Thiosulfate by Co(dipic)$_2^-$. The reaction between Co(dipic)$_2^-$ and thiosulfate was followed at 510 nm (ε_{max}=630 mol^{-1} dm^3 cm^{-1}) by following the decrease in absorbance of the complex. Na$_2$edta (1.0×10^{-5} mol dm^{-3}) was used as the masking agent throughout the experiment to avoid any catalysis caused by the presence of foreign metal ions. A 30—35% decrease in rate was observed compared to that in the absence of EDTA. Variation of [EDTA] shows no further effect on the reaction rate. Under pseudo-first-order conditions, the plots of absorbance vs. time are all linear (80 to 90%, of total reaction) indicating a zero-order dependence of rate in complex. The corresponding k_{obs} are calculated from the slope of such plots. A plot of k_{obs} vs. [$S_2O_3^{2-}$] gives a curvature of increasing slope in the range of [$S_2O_3^{2-}$]=0.005—0.05 mol dm^{-3} at pH 4.5, I=0.60 mol dm^{-3} (NaClO$_4$), and temperature 30 °C. But a plot of k_{obs} vs. [$S_2O_3^{2-}$]^2 is a straight line passing through the origin indicating a second-order dependence of rate on [$S_2O_3^{2-}$] (Fig. 1). The effect of hydrogen ion concentration on the reaction rates was studied in the pH range 3.90—4.90 at [$S_2O_3^{2-}$]=0.03 mol dm^{-3}, I=0.60 mol dm^{-3} (NaClO$_4$) and temperature 30 °C. The reaction rates increase with the increase in [H$^+$] and the corresponding results are given in Table 1. A plot of k_{obs} vs. [H$^+$] gives a straight line with a positive intercept on the rate axis and follows a rate law of the type,

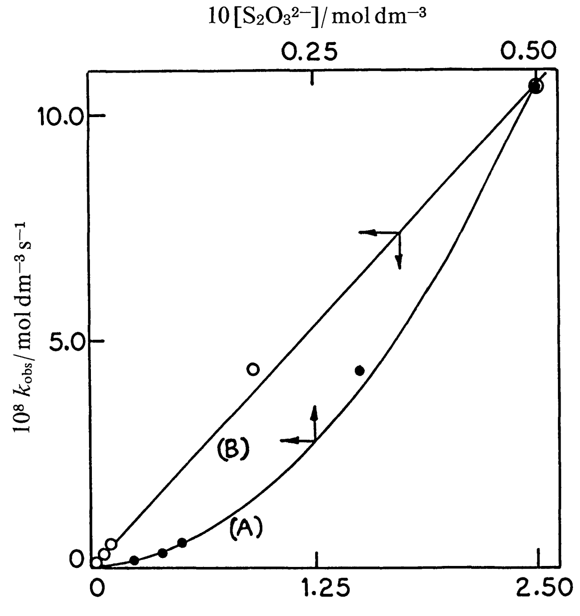

Fig. 1. Different plots showing the dependence of the observed rate on the reductant concentrations (A) k_{obs} vs. [$S_2O_3^{2-}$], (B) k_{obs} vs. [$S_2O_3^{2-}$]^2. Conditions are; [Co(dipic)$_2^-$]=4.0×10^{-4} mol dm^{-3}, I=0.60 mol dm^{-3}, pH=4.5, [EDTA]=1.0×10^{-5} mol dm^{-3}, and at 30 °C.

Table 1. Dependence of Rate on pH for the Oxidation of Thiosulfate by Co(dipic)$_2^-$ at [$S_2O_3^{2-}$]=0.03 mol dm^{-3}, [Na$^+$]=0.60 mol dm^{-3}, [Complex]=4.0×10^{-4} mol dm^{-3}, [EDTA]=1.0×10^{-5} mol dm^{-3}, and at 30 °C

pH	$10^8\,k_{obs}$ / mol dm^{-3} s^{-1}
3.90	9.24 (13.2)
4.01	7.90 (11.3)
4.25	6.05 (9.60)
4.50	4.35 (6.50)
4.90	3.45 (5.30)

The parenthetical values represent the k_{obs} in the absence of EDTA added externally. k_0'=(2.87±0.20)×10^{-8} mol dm^{-3} s^{-1}; k_1'=(0.57±0.02) dm^6 mol^{-2} s^{-1}.

$$\text{rate} = k_0'[S_2O_3^{2-}]^2 + k_1'[H^+][S_2O_3^{2-}]^2 \quad (2)$$

where k_0' represents the acid independent path and k_1', the acid dependent path. The values of k_0' and k_1' are evaluated and summarized in Table 1. Considering the stoichiometry of the reaction and the above rate dependence, the mechanism of the oxidation of thiosulfate by Co(dipic)$_2^-$ may be postulated as,

$$S_2O_3^{2-} + S_2O_3^{2-} \underset{k_{0-}''}{\overset{k_0''}{\rightleftharpoons}} [S_2O_3,S_2O_3]^{4-} \quad (3)$$

$$S_2O_3^{2-} + HS_2O_3^- \underset{k_{1-}''}{\overset{k_1''}{\rightleftharpoons}} [S_2O_3,HS_2O_3]^{3-} \quad (4)$$

$$[S_2O_3,S_2O_3]^{4-} + 2\,Co(dipic)_2^- \xrightarrow{\text{fast}} S_4O_6^{2-} + 2\,Co(dipic)_2^{2-} \quad (5)$$

$$[S_2O_3,HS_2O_3]^{3-} + 2\,Co(dipic)_2^- \xrightarrow{\text{fast}} S_4O_6^{2-} + 2\,Co(dipic)_2^{2-} + H^+ \quad (6)$$

The above mechanism thus accounts for both the zero-order dependence in complex and the second-order dependence in thiosulfate. Therefore, the rate law may be given as

$$-d[\text{complex}]/dt = k_0''[HS_2O_3^-][S_2O_3^{2-}] + k_1''[S_2O_3^{2-}][S_2O_3^{2-}] \quad (7)$$

Considering the dissociation of $HS_2O_3^-$ as

$$HS_2O_3^- \overset{K_2'}{\rightleftharpoons} H^+ + S_2O_3^{2-} \quad (8)$$

and [$S_2O_3^{2-}$]=[$S_2O_3^{2-}$]+[$HS_2O_3^-$], the above rate law may be modified as

$$-\frac{d[\text{complex}]}{dt} = 2\cdot\frac{(k_0''K_2'+k_1''[H^+])}{(K_2'+[H^+])^2}\cdot K_2'[S_2O_3^{2-}]^2 \quad (9)$$

The second dissociation constant⁹⁾ of sulfurous acid is $K_2'=1.0\times10^{-2}$ mol dm^{-3}. So under the experimental conditions, $K_2' \gg [H^+]$, and the above equation may be reduced to,

$$-\mathrm{d[complex]}/\mathrm{d}t = k_1 = 2(k_0''+k_1''K_2'^{-1}[H^+])[S_2O_3^{2-}]^2 \quad (10)$$

The equation (10) simplifies to the observed rate law (2) with $k_0'=2\,k_0''$ and $k_1'=2\,k_1''K_2'^{-1}$.

An attempt has been made to determine the effect of ionic strength on the reaction rate. Under the conditions, $[S_2O_3^{2-}]=0.03$ mol dm^{-3}, pH=4.50, $[Co(dipic)_2^-]=4.0\times10^{-4}$ mol dm^{-3} and at 30 °C, no effect of ionic strength is observed in the range, $I=0.2$—1.5 mol dm^{-3} ($NaClO_4$).

It is to be noted here that no sulfur deposition was observed in the experimental pH region during the course of reaction. However, at high acid, rapid sulfur deposition occurs and this phenomenon was studied by Dinegar et al.¹⁰⁾ The decomposition rate of thiosulfate thus obtained ($k=0.5$ mol^{-2} dm^6 s^{-1}) is of the same order as to the oxidation rate ($k_1'=0.57\pm0.02$ mol^{-2} dm^6 s^{-1}) in this study. The experimental rate constants for the oxidation of thiosulfate ions by $Fe(CN)_6^{3-}$,¹¹⁾ ($k=0.6$ mol^{-2} dm^6 s^{-1}) and $W(CN)_8^{3-}$,¹²⁾ ($k=0.30$ mol^{-2} dm^6 s^{-1}) are also of the same order as that in this study and favors the proposed mechanism. We have also studied the effect of cations and anions on the reaction rate for this system. Neither the charge nor the size of the cations or anions have appreciable effect on the reaction rate. A 30—35% decrease in rate in the presence of added EDTA was observed (Table 1) and may be attributed to the catalytic effect caused by the presence of trace amount of multivalent cations.

Oxidation of S(IV) by $Co(dipic)_2^-$. The stoichiometric equation for the oxidation of S(IV) by $Co(dipic)_2^-$ both in acidic and alkaline medium may be written as

$$2\,Co(dipic)_2^- + S(IV) \longrightarrow 2\,Co(dipic)_2^{2-} + SO_4^{2-} \quad (11)$$

Table 2. Dependence of Rate on the [S(IV)] for the Oxidation of Sulfite by $Co(dipic)_2^-$ at Different pH, Conditions are [Complex]=4.0×10^{-4} mol dm^{-3}, $I=0.50$ mol dm^{-3}, and at 60 °C

[S(IV)]		$10^3\,k_{obs}/s^{-1}$		
mol dm^{-3}	pH	2.0	4.5	8.0
0.01			0.10	1.00
0.03			0.24	2.50
0.05		0.12	0.36	4.76
0.07		0.16	0.53	5.70
0.10		0.22	0.71	8.90
0.15		0.33		

$k_1=(5.60\pm0.04)\times10^{-5}$ dm^3 mol^{-1} s^{-1}, $k_2=(3.02\pm1.21)\times10^{-3}$ dm^3 mol^{-1} s^{-1}, and $k_3=(4.91\pm0.05)\times10^{-2}$ dm^3 mol^{-1} s^{-1}; $K_1=(5.03\pm0.01)\times10^{-3}$ mol dm^{-3}, and $K_2=(4.26\pm0.10)\times10^{-7}$ mol dm^{-3}.

where S(IV) indicates all type of the reacting sulfite species (e.g. $SO_2\cdot H_2O$, HSO_3^-, and SO_3^{2-}). Sulfate was only the reaction product as confirmed by the usual tests.

The spectral change for the reaction between $Co(dipic)_2^-$ and S(IV) was noted at pH 3.0, 4.5, and 8.0 with $I=0.50$ mol dm^{-3} ($NaClO_4$) and at 25 °C. All the spectral scannings gave an isosbestic point near 450 nm and indicated the absence of an appreciable amount of stable intermediate formed during the course of reaction. Measurement of the reaction rate was accomplished by monitoring the decrease in optical density at 510 nm (the absorption maximum of $Co(dipic)_2^-$ species). All the experiments were carried out under pseudo-first-order conditions keeping S(IV) concentration at least tenfold in excess over $Co(dipic)_2^-$ concentration. The plots of $-\log(A_t-A_\infty)$ against time (where A_t and A_∞ have their usual significance) are all linear upto 85% of the total reaction and thus ensures a first-order dependence on complex concentration. Dependence of rate on S(IV) is first order and is shown by the linearity of the plot of k_{obs} vs. [S(IV)] at pH 2.0, 4.5, and 8.0 at $I=0.50$ mol dm^{-3} ($NaClO_4$) and temperature 60 °C. The corresponding data are listed in Table 2.

The effect of hydrogen ion concentration on the oxidation rate was investigated in the pH range 2.0—8.0 at a constant temperature (60 °C) and ionic strength ($I=0.50$ mol dm^{-3}, $NaClO_4$). The dissociation constants of sulfurous acid¹²⁾ are reported to be $K_1=1.05\times10^{-2}$ mol^{-1} dm^3 and $K_2=4.36\times10^{-7}$ mol^{-1} dm^3 at 25 °C. Therefore, all the molecular and both mono- and divalent anionic species of the reductant would be present in

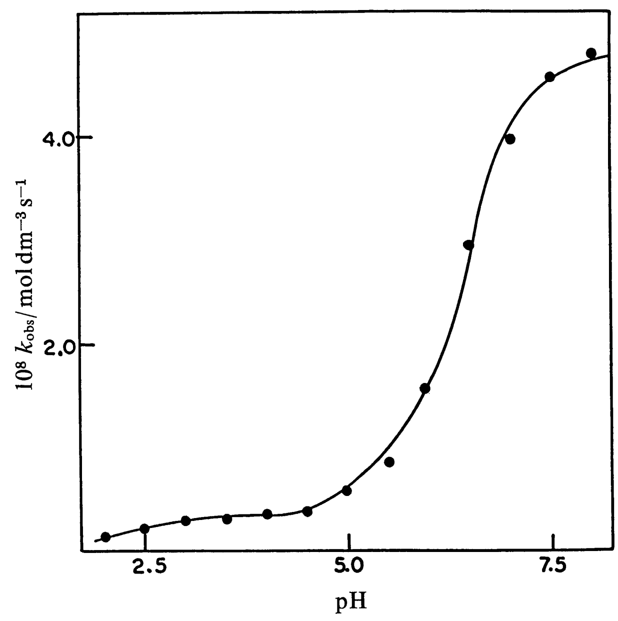

Fig. 2. Plot of k_{obs} vs. pH for the oxidation of sulfite with $Co(dipic)_2^-$ at [complex]=4.0×10^{-4} mol dm^{-3}, [S(IV)]=0.05 mol dm^{-3}, $I=0.50$ mol dm^{-3} ($NaClO_4$) and at 60 °C. Bold line represents the experimental graph and the theoretical values are shown by ●.

the experimental pH range. We made an attempt to find out the reactivities of individual species separately. For this purpose, we have chosen two different pH regions (i) pH 2.0—5.0, around the pK_1, where only molecular ($SO_2 \cdot H_2O$) and monovalent anionic (HSO_3^-) species are present and (ii) pH 5.5—8.0, around the pK_2, where only monovalent (HSO_3^-) and divalent (SO_3^{2-}) anionic species are only reactive. The corresponding equilibria are described later (in Eqs. 13 and 14). Under both the conditions the plot of k_{ox} vs. $[H^+]^{-1}$ gives the limiting curves of decreasing slope with non-zero intercept on the rate axis. This involves the necessity of three parameters leading to the equation of the form

$$k_{ox} = \frac{a + b[H^+]}{c + [H^+]} \tag{12}$$

where $k_{ox} = k_{obs}/2[S(IV)]$ and 2 is the stoichiometric factor. Data were fit to this equation using a non linear least-squares computer-fit program with each point weighed as k_{ox} and corresponding values of *a, b, c* under the two conditions are given as (i) a=$(1.64 \pm 0.01) \times 10^{-5}$; $b = (5.60 \pm 0.04) \times 10^{-5}$; $c = (5.03 \pm 0.01) \times 10^{-3}$ and (ii) $a = (2.09 \pm 0.04) \times 10^{-8}$; $b = (3.02 \pm 1.21) \times 10^{-3}$; $c = (4.26 \pm 0.09) \times 10^{-7}$.

It is well-known that sulfurous acid exists as hydrated sulfur dioxide in aqueous solution but both HSO_3^- and SO_3^{-2} do exist in aqueous media. The dissociation of sulfurous acid in aqueous solution may be given as[13]

$$SO_2 \cdot H_2O \xrightleftharpoons{K_1} HSO_3^- + H^+ \tag{13}$$

$$HSO_3^- \xrightleftharpoons{K_2} SO_3^{2-} + H^+ \tag{14}$$

where K_1 and K_2 are the first and second dissociation constants of sulfurous acid. Considering the stoichiometry and above observations, the possible mechanism corresponding to the oxidation of S(IV) by $Co(dipic)_2^-$ may be proposed as

$$Co(dipic)_2^- + SO_2 \cdot H_2O \xrightarrow{k_1} SO_3^{\cdot -} + Co(dipic)_2^{2-} + 2H^+ \tag{15}$$

$$Co(dipic)_2^- + HSO_3^- \xrightarrow{k_2} SO_3^{\cdot -} + Co(dipic)_2^{2-} + H^+ \tag{16}$$

$$Co(dipic)_2^- + SO_3^{2-} \xrightarrow{k_3} SO_3^{\cdot -} + Co(dipic)_2^{2-} \tag{17}$$

$$S(V)(H\dot{S}O_3 \text{ or } SO_3^{\cdot -}) + Co(dipic)_2^- + H_2O \xrightarrow{\text{fast}} SO_4^{2-} + Co(dipic)_2^{2-} \tag{18}$$

Now considering the pH region 2.0—5.0, as in condition (i), where k_1 and k_2 paths are operative, the corresponding rate law may be given as

$$k_{obs} = 2\frac{k_2K_1 + k_1[H^+]}{K_1 + [H^+]}[S(IV)] \tag{19}$$

$$k_{ox} = \frac{k_2K_1 + k_1[H^+]}{K_1 + [H^+]} \tag{20}$$

where k_{obs} is the pseudo-first-order rate constant. Similarly in the pH region 5.5—8.0, as in the condition (ii), where the HSO_3^- and SO_3^{2-} are the reactive species, the rate expression can be given as

$$k_{ox} = \frac{k_3K_2 + k_2[H^+]}{K_2 + [H^+]} \tag{21}$$

and both Eqs. 19 and 20 are consistent to Eq. 11 with a=K_1k_2, $b = k_1$ and $c = K_1$ in Eq. 19 and with $a = K_2k_3$, $b = k_2$ and $c = K_2$ in Eq. 20. The values of k_1, k_2, k_3, and dissociation constants K_1 and K_2 thus obtained are listed in Table 2. There is an excellent agreement between the reported values of K_1 and K_2 and those obtained from the computer-fit program for the experimental data.

Considering the reaction of all the species in the pH range 2.0—8.0, the general rate expression for the reaction between $Co(dipic)_2^-$ and S(IV) can be given as

$$k_{obs} = 2\frac{k_1[H^+]^2 + K_1k_2[H^+] + K_1K_2k_3}{[H^+]^2 + K_1[H^+] + K_1K_2}[S(IV)] \tag{22}$$

Using the above values of k_1, k_2, and k_3 and the values of first and second dissociation constants of sulfurous acid the values of k_{obs} are calculated from the above expression at different $[H^+]$. An excellent agreement between the calculated and observed rate (Fig. 1) provides further support in favor of the proposed mechanism.

A comparison of the reactivities of the different S(IV) species obtained in solution shows the reactivity order $SO_2^{2-} > HSO_3^- > SO_2 \cdot H_2O$. In fact SO_3^{2-} is 16 times more reactive than HSO_3^- and HSO_3^- is 53 times more reactive than $SO_2 \cdot H_2O$. This difference in reactivity may be explained by considering the following equilibria,[14]

$$HSO_3^- + H^+ \rightleftarrows \underset{(A)}{H:SO_3:H} \rightleftarrows \underset{(B)}{HO\text{–}S\text{–}OH}$$

$$SO_3^{2-} + H^+ \rightleftarrows \underset{(C)}{H:SO_3} \rightleftarrows \underset{(D)}{HO:SO_2}$$

In the acidic medium (pH 2.0) an appreciable amount of $SO_2 \cdot H_2O$ is believed to exist in solution. In the (A) form the lone pair is tied up with proton whereas in (B) the electron density will be withdrawn from the sulfur atom by the two OH groups. Similar phenomenon may occur for (C) and (D) also but the electron density will be more on the sulfur atom since the electrons on the sulfur atom are tied up by one proton in (C) or pulled up by one OH group in (D). For SO_3^{2-}, no such consideration occurs and thus electron density will be more available and consequently would show the highest reactivity which actually we found.

The present study provides a systematic approach to the oxidation of sulfur dioxide and thiosulfate in aqueous medium. This study constitutes a rare example where the reactivities of all the species of sulfur dioxide available in aqueous solution have been determined and compared.

The zero-order rate in complex for the thiosulfate oxidation also is one of the very few examples of thiosulfate oxidation where the rate-determining step is the formation of some active intermediate which in turn reacts with the complex in a fast step. This study has some special importance. Generally in the oxidation reactions of thiosulfate by metal ions and complexes, a zero-order dependence on [complex] is encountered for oxidants having $E^\circ \leqslant 0.54$ V and a first-order dependence for oxidants[2,15–17] having $E^\circ \geqslant 0.80$ V. The present study, therefore, cites a unique example where zero-order rate in complex is obtained though the oxidation potential is sufficiently high ($E^\circ=0.75$ V). Possibly π-donating character of the dipicolinate ligand makes the metal-center reluctant to electron transfer and thus follows a zero-order rate in complex. Our experimental results are comparable to the reported k_2 values with other oxidants in the presence of added EDTA. But none has reported the acid independent k'_0 path which we found significant in the present study.

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