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Kinetics of iron(III)-catalyzed autoxidation of sulfur(IV) in acetate buffered medium

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Abstract The kinetics of the environmentally important oxidation of sulfur(IV) by oxygen in acetate buffered medium in the presence of Fe(III) and the pH range 5.27–5.70 has been studied. The results were in agreement with the rate law:

$$-\mathrm{d[S(IV)]}/\mathrm{d}t = k_0[\mathrm{S(IV)}] + k_{\mathrm{Fe}}[\mathrm{Fe(III)}][\mathrm{S(IV)}][\mathrm{H}^+]^{-1}$$

The role of iron(III) appears to be that of production of SO_3^- radicals in $Fe(III)SO_3^{2-}$ complex by an internal 1-equivalent redox reaction. Subsequently, a radical mechanism involving oxysulfur radicals, viz., SO_3^-, SO_4^-, and SO_5^- operates. Addition of ethanol leads to the introduction of an induction period and decrease in reaction rate, most likely due to scavenging of SO_4^- radicals. The value of apparent energy of activation is 45.4 kJ mol^{-1}.

Introduction

Aqueous phase iron(III)-catalyzed autoxidation of sulfur(IV) is of great atmospheric importance and is implicated in acidification of atmospheric aqueous systems. The reaction has been studied [1–10] repeatedly and reviewed extensively [11–18]. However, most of the detailed studies pertain to low pH region (0–3) in which the kinetics obeys the rate law (1) [1–18]. For this reaction both radical and non-radical mechanisms have been proposed [1–10].

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$$-\mathrm{d[S(IV)]}/\mathrm{d}t = k[\mathrm{Fe(III)}][\mathrm{S(IV)}][\mathrm{H}^+]^{-1} \quad (1)$$

In the studies in pH range (>4), complications arise due to hydrolysis and polymerization of iron(III) and as a consequence due to reduced solubility of iron(III) [3, 7]. As a result, only few studies pertain to the region, pH > 5.0 [3, 4, 10]. The kinetics studies in this pH range are marred by widely different kinetic orders in iron(III), sulfur(IV) and pH [11, 13], obviously due to the choice of reaction conditions and pH in particular. Since the pH of atmospheric waters [19] such as cloud and rain water generally lies in the pH range 5–8 [13, 19], the study of this reaction under atmospheric pH conditions is important. Whereas, in earlier studies a buffer was not used, we selected acetate buffer to study the reaction at pH > 5 and to maintain constant pH. Since acetate is known to form strong complexes, it checks the hydrolysis, polymerization and reduction in solubility of iron(III), and allows the kinetics study using iron(III) concentrations of same order as in solutions of pH 1–2.

Experimental

The experimental procedure was exactly the same as described earlier [19–23] and is briefly given here. All chemicals used were of reagent grade and their solutions were prepared in double distilled water. The reactions were conducted in 0.15 L Erlenmeyer flasks, open to air, to allow the passage of atmospheric oxygen. The flask was placed in a beaker, which had an inlet at the lower part and an outlet at the upper part for circulating thermostatic water for maintaining desired temperature, 30.0 ± 0.1 °C. The reactions were initiated by adding the desired volume of standard Na_2SO_3 solution to the reaction mixture containing other additives such as buffer, Fe(III), etc. The reaction

mixture was stirred continuously and magnetically at 1600 ± 100 rpm to allow the passage of atmospheric oxygen and to save the reaction from becoming oxygen mass transfer controlled.

The kinetics was studied in buffered medium, in which the pH remained fixed throughout the entire course of reaction. For this purpose, 10 cm^3 of acetate buffer made from 1 M CH_3COOH and 1 M CH_3COONa in different proportions as per requirement were added to the reaction mixture (total volume 100 cm^3) for obtaining the desired pH.

The kinetics was followed by withdrawing the aliquot samples periodically and titrating the unreacted S(IV) iodometrically in slightly acidic medium as described earlier [19–23].

The reproducibility of the replicate measurements was generally better than ±10%. All calculations were performed in MS Excel.

Stoichiometry

The product analysis showed the recovery of sulfate to be 97 ± 2% in agreement with the Eq. 2.

$$S(IV) + 0.5O_2 \longrightarrow S(VI) \quad (2)$$

Results

In all kinetics runs, only catalytic concentrations of iron(III), (1–6) × 10^{-6} mol L^{-1}, were used. The disappearance of [S(IV)] followed a first order course and the first order rate constants, k_{obs}, were determined from log[S(IV)] versus time, plots, which were linear at least up to two half-lives. The plots of k_{obs} versus [Fe(III)] were linear as shown in Fig. 1 and in agreement with rate law (3),

$$k_{obs} = k_0 + k[Fe(III)] \quad (3)$$

where k_0 and k are the first order rate constants for uncatalyzed and Fe(III)-catalyzed reactions, respectively.

Table 1 The values of k_0 and k at 30 °C

pH	10^3 [S(IV)] (mol L^{-1})	k (L mol^{-1} s^{-1})	$10^5 k_0$ (s^{-1})
5.25	3	57.01	0.25
5.37	(3–6)	82.37	5.60
5.50	3	131.5	22.0
5.68	3	150.4	33.0

In the previous study [3], the uncatalyzed pathway, although small, was not noted. The values of k_0 and k at different [S(IV)] and pHs are given in Table 1. Equation 3 can be written as Eq. 4.

$$k_{cat} = k_{obs} - k_0 = k[Fe(III)] \quad (4)$$

Before studying the effect of pH, the combined effect of the concentration of buffer constituents, viz., CH_3COOH and CH_3COO^- was studied by varying both simultaneously in such a way that their ratio and hence pH remained fixed. These results indicated the reaction rate to be virtually independent of [buffer] and hence of acetate ion concentration. The values of k were determined at different pHs (Table 1) and from the log–log plot of k and $[H^+]$ an order of −1.0 was determined in $[H^+]$, which leads to the rate law (5) for Fe(III)-catalyzed pathway.

$$\{-d[S(IV)]/dt\}([S(IV)])^{-1} = k_{cat} = k_{Fe}[Fe(III)][H^+]^{-1.0} \quad (5)$$

where $k = k_{Fe}[H^+]^{-1.0}$. From the k^{-1} versus $[H^+]$ plot (Fig. 2), the value of 3.2 × 10^3 L mol^{-1} s^{-1} for k_{Fe} at 30 °C was found.

Ethanol is a well-known inhibitor for sulfur(IV) autoxidation reactions catalyzed by iron(III) and other metal ions [11, 24–27]. In this study, the presence of ethanol led to the introduction of an induction period and decrease in the reaction rate, so much so that at 8.5 × 10^{-3} mol L^{-1} ethanol, the reaction was completely seized (Table 2). The dependence of rate on [ethanol] was in accordance with the rate law (6) and accordingly the plot of $1/k_{cat}$ versus

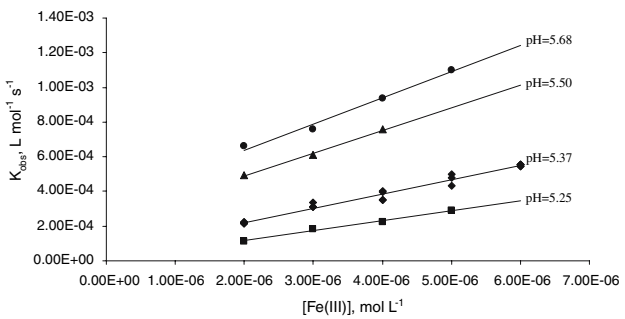

Fig. 1 The variation of k_{obs} with [Fe(III)] at 30 °C

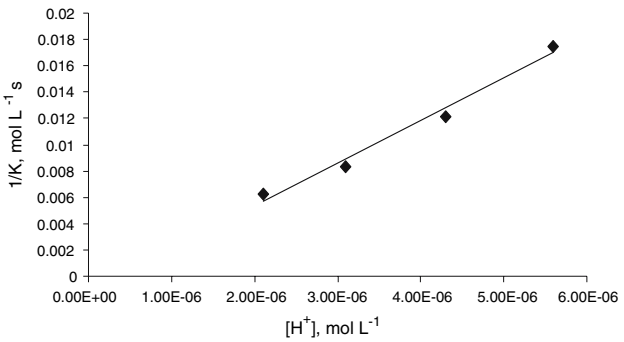

Fig. 2 The variation of k with $[H^+]$ at 30 °C

Table 2 Effect of ethanol on the rate of Fe(III)-catalyzed autoxidation of aqueous sulfur(IV) at $[S(IV)] = 3 \times 10^{-3}$ mol L^{-1}; $[Fe(III)] = 3 \times 10^{-6}$ mol L^{-1} ; pH = 5.37 and at 30 °C

10^4 [ethanol] (mol L^{-1})	Induction period (min)	$10^5 k_{cat}$ (s^{-1})
0	0	25.6
5.1	0	17.8
8.5	3	16.5
13.6	3	11.1
17	5	5.1
51	15	2.7
85	60	No reaction

Table 3 Values of R_{obs} showing iron(III)–manganese(II) synergism at $[S(IV)] = 3 \times 10^{-3}$, pH = 5.37 and at 30 °C

10^6 [Fe(III)] (mol L^{-1})	10^6 [Mn(II)] (mol L^{-1})	$10^7 R_{obs}$ (mol L^{-1} s^{-1})
3.0	–	8.3
–	3.0	6.3
3.0	3.0	22.2

[ethanol] was linear (Fig. 3). The values of slope (C/A) and intercept (B/A) were found to be 6.8×10^6 and 2.7×10^3, respectively at pH = 5.37 and at 30 °C.

$$k_{cat} = A/(B + C[\text{ethanol}]) \quad (6)$$

From k_{obs} values of 21.1×10^{-5} (25 °C), 31.1×10^{-5} (30 °C), 38.3×10^{-5} (35 °C) and 51.5×10^{-5} (40 °C) s^{-1} at $[Fe(III)] = 3 \times 10^{-6}$ and pH = 5.37, the apparent empirical energy of activation was found to be 45.4 kJ mol^{-1}.

Fe(III)–Mn(II) synergism is well known [13]. It is interesting to point out that even in the presence of complexing acetate ions, the Fe(III)–Mn(II) synergism was noted as shown in Table 3.

Discussion

The kinetics of this reaction has been studied in acetate buffered medium per force to avoid precipitation of iron(III) and formation of polymeric species. In spite of the fact that iron(III) is known to form acetate complexes (Table 4), a four-fold increase in concentrations of acetate and acetic acid both had no observable effect on the rate in the range of their concentrations used in this study. This suggests that iron(III) is fully liganded. A similar approach has been adopted by Cabelli and Bielski [28] in the study of the reaction of Mn(II)-formate with HO_2/O_2^- in the presence of higher concentrations of sodium formate such that the reaction became independent of [formate]. For this reason, in the presentation of the mechanism later, non-committal Fe(III) has been used to express iron(III) species. In the pH range of this study, sulfur(IV) would be largely present as HSO_3^- [13]. However, to be consistent with inverse first order dependence in $[H^+]$, SO_3^{2-} has been assumed to be the reactive species.

The rate law (6) for the inhibition is same as reported by Alyea and Backstrom [27], Pasiuk-Bronikowska et al. [9], Manoj et al. [26] and Mudgal et al. [29] for inhibition of sulfur(IV) autoxidation with different types of inhibitors. To explain the inhibition, the operation of a radical mechanism [3, 11, 13] involving oxysulfur radicals, viz., SO_3^-, SO_5^-, SO_4^- has been proposed. Although for Fe-catalyzed reactions both radical [1, 3, 11–13] and non-radical [6] mechanisms have been proposed, the recent work strongly favors the former, which involves a number of possible pathways as discussed by Ziajka et al. [8], Brandt et al. [1], Conklin and Hoffman [6] and others [11–13]. The relative importance of different pathways in Fe(III)-catalyzed reactions has been discussed recently by Warneck [30]. Based on this and the mechanisms proposed previously [6, 11–13], the following mechanism is proposed.

$$HSO_3^- \overset{K_d}{\rightleftharpoons} SO_3^{2-} + H^+ \quad (7)$$

$$Fe(III) + SO_3^{2-} \overset{K_1}{\rightleftharpoons} [Fe(III)(SO_3^{2-})] \quad (8)$$

$$[Fe(III)(SO_3^{2-})] \xrightarrow{k_1} Fe(II) + SO_3^- \quad (9)$$

$$SO_3^- + O_2 \xrightarrow{k_2} SO_5^- \quad (10)$$

$$SO_5^- + Fe(II) + H_2O \xrightarrow{k_3} HSO_5^- + Fe(III) \quad (11)$$

$$HSO_5^- + Fe(II) \xrightarrow{k_4} SO_4^- + Fe(III) + OH^- \quad (12)$$

$$SO_4^- + SO_3^{2-} \xrightarrow{k_5} SO_4^{2-} + SO_3^- \quad (13)$$

$$SO_4^- + X \xrightarrow{k_6} \text{non chain products} \quad (14)$$

$$SO_4^- + C_2H_5OH \xrightarrow{k_7} \text{non chain products} \quad (15)$$

In the above mechanism, X represents an impurity or wall-surface.

In his modeling study, Warneck [30] found the reactions (16–17) to be less significant than the other competing reactions. Hence, these reactions have been ignored. The first order termination, as in reaction (14), has been proposed by Martin et al. [3] and might represent termination on a wall surface. Reaction (15) becomes operative when ethanol is also present.

Table 4 The values of selected rate/overall stability constants at 25 °C

Reaction	Rate/stability constants	Value	Reference
$Fe^{3+} + SO_3^{2-} \rightleftharpoons [Fe(SO_3)]^+$	K	1.99×10^7	[6]
$Fe^{3+} + OAc^- \rightleftharpoons [Fe(OAc)]^{2+}$		$\log \beta_1 = 4.0$	
$Fe^{3+} + 2OAc^- \rightleftharpoons [Fe(OAc)_2]^+$		$\log \beta_2 = 7.6$	[11]
$Fe^{3+} + 3OAc^- \rightleftharpoons [Fe(OAc)_3]$		$\log \beta_3 = 9.6$	
$Fe^{2+} + SO_5^- (+H_2O) \longrightarrow FeOH^{2+} + HSO_5^-$	k_3	1.0×10^6 L mol^{-1} s^{-1}	[8]
$SO_4^- + SO_3^{2-} \longrightarrow SO_4^{2-} + SO_3^-$	k_5	3.1×10^8 L mol^{-1} s^{-1}	[31]
$SO_4^- + CH_3CH_2OH \longrightarrow SO_4^{2-} + CH_3CHOH + H^+$	k_7	1.6×10^7 L mol^{-1} s^{-1}	[32]

$$SO_4^- + Fe(II) \longrightarrow Fe(III) + SO_4^{2-} \quad (16)$$

$$HSO_5^- + SO_3^{2-} \longrightarrow 2S(VI) \quad (17)$$

By assuming long chain hypothesis and the setting $d[SO_3^-]/dt$, $d[SO_4^-]/dt$, $d[SO_5^-]/dt$ and $d[HSO_5^-]/dt$ equal to zero, it can be shown that the rate of initiation is equal to the rate of termination, i. e.,

$$k_1[Fe(III)(SO_3^{2-})] = k_6[SO_4^-][X] + k_7[SO_4^-][ethanol] \quad (18)$$

The rate of reaction is given by the rate of the chain propagation step (13), as in Eq. 19.

$$R_{obs} = k_5[SO_4^-][SO_3^{2-}] \quad (19)$$

By substituting the value of $[SO_4^-]$ from Eq. 18 in Eq. 19, we get the rate law (20) for Fe(III)-catalyzed pathway.

$$R_{obs} = k_5k_1[Fe(III)(SO_3^{2-})][SO_3^{2-}]/\{k_6[X] + k_7[ethanol]\} \quad (20)$$

or

$$k_{cat} = k_5k_1\,[Fe(III)(SO_3^{2-})][SO_3^{2-}]/\{k_6[X] + k_7[ethanol]\} \quad (21)$$

Assuming that iron(III) is present as Fe(III) and $[Fe(III)(SO_3^{2-})]$ only, the total iron(III) concentration, $[Fe(III)]_T$, would be given by Eq. 22 and the rate law (20) would become Eq. 23.

$$[Fe(III)]_T = [Fe(III)] + [Fe(III)(SO_3^{2-})] \quad (22)$$

$$R_{obs} = \frac{k_5k_1K_dK_1[[Fe(III)]_T[SO_3^{2-}][S(IV)]}{(k_6 + k_7[ethanol])(1 + K_1[SO_3^{2-}])(K_d + [H^+])} \quad (23)$$

The stability constant of $FeSO_3^+$ complex is reported to be high [6] (Table 4). In the present study, a clean-cut first order in [S(IV)] requires the inequality $K_1[SO_3^{2-}] >> 1$ to be valid, which would be true only if K_1 in the present case is also high. The value of K_d is reported to be 6.4×10^{-8} (25 °C) [11] and so in the pH range of this study $[H^+] >> 1$ shall hold. Based on these assumptions, the rate law (21) reduces to Eqs. 24–25, which fully explains the observed experimental rate laws (5) and (6).

$$-d[S(IV)]/dt = \frac{k_5k_1K_d[Fe(III)]_T\,[S(IV)]}{(k_6 + k_7[ethanol])[H^+]} \quad (24)$$

$$k_{Fe} = k_5k_1K_d/\{(k_6 + k_7[ethanol])[H^+]\} \quad (25)$$

In the absence of ethanol, the rate law (26) shall be valid for the catalyzed pathway.

$$-d[S(IV)]/dt = \frac{k_5k_1K_d[Fe(III)]_T\,[S(IV)]}{k_6[X][H^+]} \quad (26)$$

which is equivalent to rate law (5) though $k_{Fe} = k_5k_1K_d/k_6$ [X].

A comparison of the rate laws (6) and (24) shows $B/A = k_6[X]\,[H^+]/(k_1k_5K_d[Fe(III)]_T)$, and $C/A = k_7[H^+]/(k_1k_5K_d\,[Fe(III)]_T)$. From C/A value of 6.4×10^6 and B/A value of 2.7×10^3, determined from Fig. 3 at pH 5.37, the value of k_7 was found to be $(2.37 \times 10^3 k_6[X])$. The reported value of $k_7(1.6 \times 10^7$ L mol^{-1}s^{-1} at pH 7.8; Table 1) requires the value of $k_6[X]$ to be about 6.7×10^3, which appears to be reasonable. In the absence of inhibitors, the rate law (26) is applicable and a comparison with experimental law (5) shows $k_{Fe} = k_5k_1K_d/k_6[X]$. Using $k_5 = 3.1 \times 10^8$ L mol^{-1} s^{-1}[27] and $K_d = 6.4 \times 10^{-8}$ [13], from the values of 6.7×10^3 L mol^{-1}s^{-1} and 3.2×10^3 determined for $k_6[X]$ and k_{Fe}, respectively in this work, from Eq. 24, value of k_1 was found to be about 1.1×10^6 L mol^{-1} s^{-1} at 30 °C, which is in good agreement with the k (Eq. 1) value of $(1.2 \pm 0.3) \times 10^6$ L mol^{-1} s^{-1}

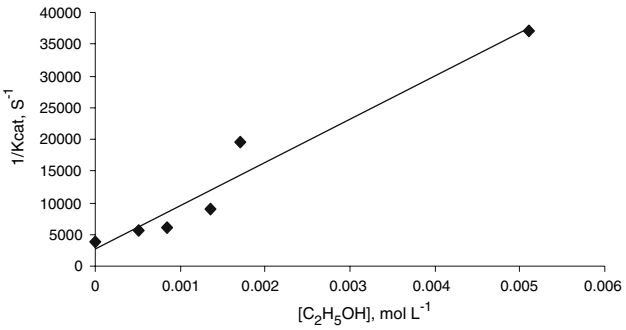

Fig. 3 Variation of k_{cat} with $[C_2H_5OH]$ at $[Fe(III)] = 3 \times 10^{-6}$ mol L^{-1}, $[S(IV)] = 3 \times 10^{-3}$ mol L^{-1}, pH 5.37 and at 30 °C

Table 5 Comparison of rate constants for Fe(III) catalyzed oxidation of S(IV)

Rate constants	Value	Conditions	References
k	3.9×10^2 L mol^{-1} s^{-1}	t = 22–44 °C [formate] = 1×10^{-3} mol L^{-1}; pH = 5	[24]
k	0.57×10^2 L mol^{-1} s^{-1}	pH = 5.25, t = 25 °C; [acetate] = 0.062 mol L^{-1}	This work
k_{obs}	3.3×10^{-4} s^{-1}	t = 25 °C; [acetate] = 3×10^{-4} mol L^{-1}; added iron(III) = 3×10^{-7} mol L^{-1}	[3]
k_{obs}	2.1×10^{-4} s^{-1}	t = 25 °C; [acetate] = 0.08 mol L^{-1}; [Fe(III)] = 3×10^{-6} mol L^{-1}; pH = 5.37	This work

estimated at 20 °C [6] for the reaction (9) from a large number of studies reported in the literature [2–6]. This inspires confidence in the proposed mechanism.

Martin et al. [3] have shown that when pH $<$ 3, the non-complexing inhibitors have no significant effect on the rate and a non-radical mechanism operates with reaction (9) being rate-determining and the subsequent steps involving radicals being fast, as proposed by Brandt et al. [1] and discussed by Kuo et al. [11]. On the other hand, when pH $>$ 5, the reaction is strongly inhibited by free radical scavengers and a radical mechanism operates, as in the present case. It is of interest to compare the results of this study with those of Martin et al. [3] and Sedlak and Hoigne [24] included in Table 5. Looking at the difference in temperature and concentrations of formate and acetate ions, our values of k and k_{obs} are compatible with the values reported [3, 24]. The value of inhibition parameter, C/B, reported by Martin et al. [3] is 2.4×10^4, which is higher by an order of magnitude than the value of 2.5×10^3, is determined from Fig. 3, in this work. For complicated reactions like this, such a difference is not uncommon.

A critical examination of the proposed mechanism (7–15) shows the k_1-path to be the most important in both low and high pH solutions. Whereas, in the former path, this acts as the rate-determining step, in the latter it acts as an initiator of the reaction [6, 11, 13, 33, 34]. Inclusion of SO_4^- in the k_5-path is necessary to explain the inhibition by ethanol in the k_7-path. The first order chain termination in the k_6-path has been included by us and others [3, 35] to be consistent with the observed kinetics. However, this path is not unique and it should be possible to write a different termination step leading to the observed rate law. The k_7-path is important to explain ethanol inhibition of the reaction rate. It must be pointed out that SO_3^- and SO_5^- radicals react too slowly [32] to account for inhibition through their scavenging by reaction with ethanol.

The results of this study clearly suggest that both in low and high pH aqueous solutions, the nature of the rate law in respect of the catalysis of sulfur(IV) autoxidation by dissolved iron(III) ions remains the same provided there is no precipitation/polymerization of iron(III).

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