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Catalytic Mechanism of the "Noncatalytic" Autooxidation of Sulfite

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Abstract—Iron ions are shown to play a special role among transition metal ions in the oxidation of sulfite by oxygen. The thermodynamically favorable formation of chain carriers $SO_3^{\bullet-}$: $FeOH^{2+} + HSO_3^- \longrightarrow Fe^{2+} + H_2O + SO_3^{\bullet-}$, $\Delta H^0_{r,\,298} \le -250$ kJ/mol accompanied by the regeneration of the active Fe(III) form in the reactions of Fe(II) with $SO_{3-5}^{\bullet-}$ and HSO_5^- provides the efficient catalytic mechanism for sulfite consumption even at $[Fe]_0 \ge 10^{-8}$ mol/l. Any aqueous solution contains iron ions in this amounts. Thus, the "noncatalytic" oxidation of sulfite is in fact the catalytic reaction involving unavoidable microadmixtures of iron ions. Other transition metal ions (Mn^{2+}, Co^{2+}, etc.) can only enhance the catalytic effect of iron admixture.

INTRODUCTION

In many papers and reviews [1–9] devoted to the kinetics of liquid-phase sulfite oxidation (henceforth, S(IV) or sulfite denotes the equilibrium mixture SO_2(aq)–HSO_3^-–SO_3^{2-}) and analysis of acid rain formation in the cloud moisture of the troposphere (see, e.g., [10, 11]), noncatalytic sulfite oxidation is usually considered to belong to noncatalytic transformations S(IV) ⟶ S(VI) with the participation O_3, H_2O_2, and HSO_5^- [8, 13]. This process attracts attention because its rate *w* determines the reference level for the evaluation of the influence additives of transition metal ions, inhibitors, UV radiation, penetrating radiation, and other factors on the sulfite oxidation dynamics of [8, 10]. The detailed kinetics of this reaction when [S(IV)] is changed from 10^{-7} to 0.1 mol/l and pH is changed from 2 to 12 was discussed in [4, 8, 14]. The papers on noncatalytic sulfite oxidation give special attention to water purification, purification of S(IV) salts or $SO_{2(g)}$ as sulfite sources, preparation of laboratory glassware for experiments [8], etc., because the assumption of the uncontrolled influence of various admixtures appeared at an early stage of the studies of this reaction [14]. The inhibition of noncatalytic sulfite oxidation by additives of easily oxidized organic substances (ethylamine, pyrocatechol, and others) found in the 1930s (see, e.g., [14, 15]) led the researchers to categorize this reaction as a radical-chain process involving $SO_{3-5}^{\bullet-}$, an intermediate product, and the strong oxidant HSO_5^- (see the table). This conclusion has been confirmed more recently in the experiments with UV, X-ray, and γ irradiation as initiating factors [16–18]. Although the effect of these radiations stimulates the development of long-chain sulfite oxidation [16–18] and the $SO_{3-5}^{\bullet-}$ radicals can be observed by ESR and UV spectroscopy in the flash photolysis/pulse radiolysis mode [12, 18], attempts to apply the radical chain mechanism (see the table) for the description of the noncatalytic sulfite oxidation dynamics face serious obstacles [14].

Phenomenological Description of Noncatalytic Sulfite Oxidation

The study of the noncatalytic sulfite oxidation kinetics is a thankless problem. It is one of the most inconstant reactions, with typically low reproducibility, which is often observed within the same study [7, 19]. The results obtained by other authors for the same or close conditions often do not coincide with previous data [8, 10, 14]. According to our experience on the influence of various factors on the noncatalytic sulfite oxidation rate, dust-removal from air fed to bubbling stirring of a sulfite solution results in a 2–2.5-fold decrease in *w*. According to our data, the reproducibility is better in alkaline solutions [19]. Since the rate constant of chain propagation for $SO_5^{\bullet-}$ with SO_3^{2-} is two orders of magnitude higher than that for the reaction with HSO_3^- [18], the reaction rate should increase with an increase in pH and remains unchanged at pH > $pK_{HSO_3^-}$. The experimental plot of *w* vs. pH is bell-shaped [14, 19], and the position of the rate maximum

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Radical chain mechanism of sulfite oxidation

No.	Reaction	Rate constant, l mol^{-1} s^{-1}	References
	Initiation of noncatalytic sulfite oxidation chains		
(i, I)	$Fe(OH)SO_3H^+ \longrightarrow Fe^{2+} + SO_3^{\bullet-} + H_2O$	0.2 s^{-1}	[35]
	Chain propagation:		
(II)	$SO_3^{\bullet-} + O_2 \longrightarrow SO_5^{\bullet-}$	2.5×10^9	[12]
(IIIa)	$SO_5^{\bullet-} + HSO_3^- \longrightarrow HSO_5^- + SO_3^{\bullet-}$	$(3.4–8.6) \times 10^3$	[16–18]
(IIIb)	$SO_5^{\bullet-} + HSO_3^- \longrightarrow SO_4^{2-} + SO_4^{\bullet-} + H^+$	$\leq(2–3.6) \times 10^2$	[16–18]
(IVa)	$SO_5^{\bullet-} + SO_3^{2-} \longrightarrow SO_5^{2-} + SO_3^{\bullet-}$	2.1×10^5	[16, 18]
(IVb)	$SO_5^{\bullet-} + SO_3^{2-} \longrightarrow SO_4^{2-} + SO_4^{\bullet-}$	5.5×10^5	[16, 18]
(V)	$SO_4^{\bullet-} + HSO_3^- \longrightarrow SO_4^{2-} + SO_3^{\bullet-} + H^+$	$(6.8–7.5) \times 10^8$	[12]
(VI)	$SO_4^{\bullet-} + SO_3^{2-} \longrightarrow SO_4^{2-} + SO_3^{\bullet-} + H^+$	$(3.1–5.7) \times 10^8$	[12]
(VIIa)	$SO_5^{\bullet-} + SO_5^{\bullet-} \longrightarrow SO_4^{\bullet-} + SO_4^{\bullet-} + O_2$	$(8.7–22) \times 10^7$	[18, 72]
	Chain termination:		
(VIIb)	$SO_5^{\bullet-} + SO_5^{\bullet-} \longrightarrow S_2O_8^{2-} + O_2$	$(1.3–4.8) \times 10^7$	[18, 72]
	Ion-molecular reaction:		
(VIII)	$HSO_5^- + HSO_3^- + H^+ \longrightarrow 2SO_4^{2-} + 3H^+$	$\approx 10^7 [H^+]$	[12]
	Reaction of noncatalytic sulfite oxidation chain carriers with Fe ions		
(IX)	$Fe^{2+} + SO_5^{\bullet-} \longrightarrow Fe^{3+} + SO_5^{2-}$	3.2×10^6	[12]
(X)	$Fe^{2+} + SO_4^{\bullet-} \longrightarrow Fe^{3+} + SO_4^{2-}$	$(3.0–9.9) \times 10^8$	[12]
(XI)	$Fe^{2+} + HSO_5^- \longrightarrow Fe^{3+} + SO_4^{\bullet-} + OH^-$	3×10^4	[74]
(XII)	$Fe^{2+} + S_2O_8^{2-} \longrightarrow Fe^{3+} + SO_4^{\bullet-} + SO_4^{2-}$	12	[63]

shifts toward higher pH with an increase in [S(IV)]. At pH 12, an aerated solution of sulfite is virtually stable [19].

In many experiments, $w \sim [S(IV)]$ [1, 7, 20], see also [8], which does not agree with the radical-chain mechanism: a higher reaction order with respect to sulfite would correspond to the participation of sulfite in the rate-limiting chain propagation step and in the initiation reaction.

In experiments of different authors at pH 3–4, $k_a = w/[SO_3^{2-}]$ differs for close pH by $\sim 10^4$ times [1, 2, 4–7].

The apparent activation energy of noncatalytic sulfite oxidation (E_a) on going from acidic (pH $\leq$ 4) to alkaline (pH $\geq$ 8) solutions varies from ~7 to 146 kJ/mol [20, 21], see also [8, 14].

A substantial influence of admixtures on noncatalytic sulfite oxidation is reflected in the correlation [9, 14] between the resistance of sulfite solutions to oxidation and the quality of water purification. For example, at pH 8.5 [9], noncatalytic sulfite oxidation is characterized by $k_a = 1.1 \times 10^{-3}$ in tap water, $k_a = 2.5 \times 10^{-4}$ in deionized water, $k_a = 1.7 \times 10^{-4}$ in triple distillate, and $k_a = 1.3 \times 10^{-5}$ s^{-1} in Milli-R/Q water. To remove traces of organic admixtures, Larson et al. [7] purified water by distillation with the addition of 30% H_2O_2 (0.1 ml) followed by the complete decomposition of hydrogen peroxide by UV irradiation (2–3 h). The efficiency of this purification is indirectly indicated by a multiple increase in the reproducibility of results in [7] and a threefold increase in k_a in experiments with the minor additives of Mn(II) [22, 23]. It is likely that unavoidable admixtures of transition metal ions (Fe(II/III), Co(II), Cu(I/II), etc.) can affect considerably the stability of sulfite solutions. This was known almost a century ago [14, 15]. These suspicions have found quantitative support as analytical methods become more sensitive. According to [6, 14, 24–26] and other papers, the residual concentration of iron ions $[\mathrm{Fe}]_0$ in deionized water with a resistivity of tens of mΩ/cm is characterized by values of $(2–50) \times 10^{-8}$ mol/l. A large amounts of iron are introduced into a solution with acidic and other additives [14, 26]. Despite this, no kinetic analysis was carried out that confirmed the participation of transition metal in noncatalytic sulfite oxidation. This is related to difficulties in the detection of low transition metal concentrations. The purpose of this work was to obtain evidence that the role of iron impurities is critical for this reaction and to prove its catalytic nature. We used published and our own experimental data on the noncatalytic sulfite oxidation dynamics and results of model experiments.

Thermodynamics of the Initiation Reactions of Sulfite Oxidation

Let us consider so-called “reactant” initiation, that is, the generation of free $\mathrm{SO}_3^{\dot{-}}$ radicals in one-electron processes of the interaction of sulfite with O_2: $\mathrm{HSO}_3^-/\mathrm{SO}_3^{2-} + \mathrm{O}_2 \longrightarrow \mathrm{SO}_3^{\dot{-}} + \mathrm{O}_2^{\dot{-}} + \mathrm{H}^+/$. Taking into account that $\Delta H^0_{f,\,298} \approx -500 \pm 5$ kJ/mol for $\mathrm{SO}_3^{\dot{-}}$ [27] and $\Delta H^0_{f,\,298}$ for other components [28, 29], we find $\Delta H^0_{r,\,298} \geq 135 \pm 5$ kJ/mol. Since $E_\mathrm{a} \geq \Delta H^0_{r,\,298}$, for the rate constants of both reactions we have $k \leq 10^{10}\exp(-135 \times 10^3/8.31 \times 298) \leq 3 \times 10^{-14}$ l mol^{-1} s^{-1}. Therefore, taking into account the characteristic values of $[\mathrm{O}_2(\mathrm{aq})]$ and [S(IV)], the initiation rates are negligible, $w_\mathrm{i} \leq 3 \times 10^{-19}$ mol l^{-1} s^{-1}. The formation of chain carriers in the reaction proposed in [7]: $\mathrm{O}_2 + \mathrm{OH}^- \longrightarrow \mathrm{O}_3^{\dot{-}} + \mathrm{OH}^\bullet$ ($\Delta H^0_{r,\,298} > 190$ kJ/mol) is characterized by still higher E_a and, correspondingly, lower w_i.

Consider the generation of $\mathrm{SO}_3^{\dot{-}}$ involving admixed transition metal ions, first of all, iron ions

$$\mathrm{Fe}^{3+} + \mathrm{HSO}_3^- \longleftrightarrow \mathrm{Fe}^{2+} + \mathrm{H}^+ + \mathrm{SO}_3^{\dot{-}};$$

$$\mathrm{Fe}^{3+} + \mathrm{SO}_3^{2-} \longleftrightarrow \mathrm{Fe}^{2+} + \mathrm{SO}_3^{\dot{-}}.$$

These reactions are noticeably endothermic ($\Delta H^0_{r,\,298} \approx$ 90–100 kJ/mol) and $k \leq 10^{10}\exp(-100 \times 10^3/8.31 \times 298) \leq 3 \times 10^{-8}$ l mol^{-1} s^{-1}. By contrast, the reaction of HSO_3^- with FeOH^{2+} ($\Delta H^0_{f,\,298}(\mathrm{FeOH}^{2+}) = 3.5$ kJ/mol [30])

$$\mathrm{FeOH}^{2+} + \mathrm{HSO}_3^- \longleftrightarrow \mathrm{Fe}^{2+} + \mathrm{H}_2\mathrm{O} + \mathrm{SO}_3^{\dot{-}}, \qquad \text{(i.I)}$$

is exothermic: $\Delta H^0_{r,\,298} \sim -250$ kJ/mol. The reaction

$$\mathrm{FeOH}^{2+} + \mathrm{SO}_3^{2-} \longleftrightarrow \mathrm{Fe}^{2+} + \mathrm{OH}^- + \mathrm{SO}_3^{\dot{-}}. \qquad \text{(i.II)}$$

is also thermodynamically favorable ($\Delta H^0_{r,\,298} \approx -180$ kJ/mol). Similar reactions of $\mathrm{SO}_3^{\dot{-}}$ generation involving Mn^{3+}, Co^{3+}, and Ni^{3+} ions are still more favorable (see, e.g., [25]). However, the redox potentials of the $\mathrm{Mn}^{3+}/\mathrm{Mn}^{2+}$, $\mathrm{Co}^{3+}/\mathrm{Co}^{2+}$, and $\mathrm{Ni}^{3+}/\mathrm{Ni}^{2+}$ pairs are so high (1.5–2.3 V) [31] that their stable forms in an aqueous solution are Mn^{2+}, Co^{2+}, and Ni^{2+}. The electron-withdrawing properties of these ions appear only in reactions with the strongest reducing agents such as $\mathrm{e}^{\dot{-}}_{\mathrm{aq}}$ or $\mathrm{H}^\bullet$.

The initiation process involving impure copper ions was considered to be the most probable in the earliest works on the mechanism of sulfite autooxidation [8, 15]. According to [6, 24], the residual concentration of copper ions in a solution is $(6–20) \times 10^{-8}$ mol/l. The thermodynamic analysis similar to that for iron ions gives for copper ions

$$\mathrm{Cu}^{2+} + \mathrm{HSO}_3^-/\mathrm{SO}_3^{2-} \longleftrightarrow \mathrm{Cu}^+ + \mathrm{H}^+/ + \mathrm{SO}_3^{\dot{-}},$$

$$\Delta H^0_{r,\,298} \approx (120/130)\ \text{kJ/mol};$$

$$\mathrm{CuOH}^+ + \mathrm{HSO}_3^-/\mathrm{SO}_3^{2-} \longleftrightarrow \mathrm{Cu}^+ + \mathrm{H}_2\mathrm{O}/\mathrm{OH}^- + \mathrm{SO}_3^{\dot{-}},$$

$$\Delta H^0_{r,\,298} \approx -(200/140)\ \text{kJ/mol}.$$

At first glance, it seems queer that copper ions, being a much weaker electron acceptor than the Fe(III) ions (E^0(Cu(II)/Cu(I)) = 0.153, E^0(Fe(III)/Fe(II) = 0.77 V [31]), can participate in the sulfite oxidation initiation step as thermodynamic analysis shows [1]. However, comparison of $\Delta(\Delta H^0_{r,\,298})$ on going from $\mathrm{Fe}^{3+} \longleftrightarrow \mathrm{FeOH}^{2+} + \mathrm{H}^+$ to $\mathrm{Cu}^{2+} \longleftrightarrow \mathrm{CuOH}^+ + \mathrm{H}^+$ shows a more pronounced change in $\Delta H^0_{r,\,298}$ for the hydrolysis of copper ions, that is, the worse electron-withdrawing properties of Cu^{2+} are compensated for its higher hydrolytic stability ($\mathrm{p}K_{\mathrm{Cu}^{2+}} = 8.12$ [32]). The presented values of $\Delta H^0_{r,\,298}$ show the negligible initiation rate for the first reaction. However, the thermodynamically favorable reaction of sulfite oxidation initiation involving CuOH^+ can occur only under the conditions of Cu^{2+}

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[1] We estimated the unknown $\Delta H^0_{f,\,298}$ for CuOH^+ assuming that $\Delta H^0_{r,\,298} \approx 0$ for the reaction $\mathrm{Cu}^{2+} + \mathrm{OH}^- \longleftrightarrow \mathrm{CuOH}^+ + \mathrm{H}_2\mathrm{O}$. This approximate figure is based on the fact of a weak exothermicity of the similar complex formation reaction of ions $\mathrm{Fe}^{3+} + \mathrm{OH}^- \longleftrightarrow \mathrm{FeOH}^{2+} + \mathrm{H}_2\mathrm{O}$: $\Delta H^0_{r,\,298} \approx -5$ kJ [30]. In this approximation, for CuOH^+ we find $\Delta H^0_{f,\,298} \sim 120$ kJ/mol.

hydrolysis, that is, in alkaline solutions ($\mathrm{pH} > \mathrm{p}K_{\mathrm{Cu}^{2+}}$). Perhaps, this is responsible for a sharp increase in the catalytic activity of copper ions in the sulfite oxidation reaction at pH > 9 [33]. We assume that the initiation of sulfite oxidation ((i.I), (i.II)) in solutions with $\mathrm{pH} < \mathrm{p}K_{\mathrm{Cu}^{2+}}$ is the only possible and also occurs in the case of other transition metal ions, which inevitably include admixtures of iron ions. For example, the observed catalysis by Ni(II) ions is completely due to the contamination of the nickel preparations with iron admixtures [34]. In other words, the process of "iron initiation" is with a high probability responsible for the initiation step in the noncatalytic and catalytic sulfite oxidation processes by various transition metal ions in acidic solutions.

Kinetics of the Initiation of Sulfite Oxidation Involving Iron Ions

Thermodynamic analysis of the participation of admixed iron ions in $\mathrm{SO}_3^{\dot{-}}$ generation during noncatalytic sulfite oxidation was confirmed by recent kinetic experiments [35] on the reduction of Fe(III) by sulfite under anaerobic conditions at pH ≤ 3. To explain the results, Brandt et al. [35] proposed the rapid (~1 s) formation of the intermediate $\mathrm{Fe(OH)SO_3H^+}$ complex, which then slowly decomposes to form $\mathrm{SO}_3^{\dot{-}}$ and Fe(II). Later, Prinsloo *et al.* [36] used millisecond and scanning UV spectrophotometry ($\Delta\lambda = 5$ nm) and succeeded in finding evidence for the formation of the 1 : 2 and 1 : 3 Fe(III) complexes with HSO_3^-, measure the equilibrium constants of their formation ($K_{\mathrm{Fe(III)}:\mathrm{HSO}_3^-(1:2)} \le 200$, $K_{\mathrm{Fe(III)}:\mathrm{HSO}_3^-(1:3)} \le 200$ l/mol), and estimate the rate constants of their decomposition [37], see also [38]. Evidently, their contribution to the initiation of noncatalytic sulfite oxidation becomes substantial only at very high S(IV) concentrations. The rate constant of decomposition of $\mathrm{Fe(OH)SO_3H^+}$ complexes was determined ($k_\mathrm{i} \sim 0.2\ \mathrm{s}^{-1}$) in the study of the dynamics of Fe(III) reduction from a decrease in photoabsorption ($\lambda = 390$ nm) with time [35]. Despite $([\mathrm{HSO}_3^-]/[\mathrm{SO}_3^{2-}])_{\mathrm{pH} \le 3} \ge 10^4$, k_i found in these experiments could include the contribution of process (i.II) to $\mathrm{SO}_3^{\dot{-}}$ generation. This is related to a difference in the complex formation constants of $\mathrm{Fe(OH)SO_3H^+}$ and $\mathrm{Fe(OH)SO_3}$, which are $K_1 \approx 6 \times 10^2$ and $K_2 \approx 2 \times 10^7$ l/mol, respectively [39]. The ratio of the products of K_i and the rate constants of the decomposition of these complexes can thus be close to $[\mathrm{HSO}_3^-]/[\mathrm{SO}_3^{2-}]$ at pH ≤ 3.

The Influence of Concentration Conditions on w_i

The participation of $\mathrm{Fe(OH)SO_3H^+}$ and $\mathrm{Fe(OH)SO_3}$ in sulfite oxidation initiation can be distinguished by using the experimental plot of w_i vs. pH. No such data are available. However, we can obtain information on $w_\mathrm{i} = f(\mathrm{pH})$ from the fact that the plots of the rate constants of Fe(II) oxidation in oxygenated solutions of sulfite $k_\mathrm{ox} = w_{\mathrm{Fe(III)}}/([\mathrm{Fe}^{2+}][\mathrm{S(IV)}])$ [40, 41] and sulfite oxidation $k'_\mathrm{a} = w/([\mathrm{Fe}]_0[\mathrm{S(IV)}])$ [23, 33, 42, 43] in catalytic sulfite oxidation are uniform: they are bell-shaped with the "k_i" maximum at pH 3.3 ($[\mathrm{HSO}_3^-] \approx 2 \times 10^{-5}$–$2 \times 10^{-4}$ mol/l), where $w_{\mathrm{Fe(III)}}$ is the rate of formation of Fe(III) iron ions. This uniformity of the curves suggests a general mechanism of Fe(II) and S(IV) oxidation including slow steps of $\mathrm{SO}_3^{\dot{-}}$ generation ((i.I), (i.II)) and subsequent fast transformations of $\mathrm{SO}_3^{\dot{-}}$ into $\mathrm{SO}_4^{\dot{-}}$, $\mathrm{SO}_5^{\dot{-}}$, and HSO_5^-, as well as $\mathrm{Fe(II)} \longrightarrow \mathrm{Fe(III)}$ and $\mathrm{S(IV)} \longrightarrow \mathrm{S(VI)}$. The rate-limiting role of (i.I), (i.II) in Fe(II) oxidation is indirectly evidenced by the induction period τ_i during which $[\mathrm{SO}_4^{\dot{-}}]$, $[\mathrm{SO}_5^{\dot{-}}]$, and $[\mathrm{HSO}_5^-]$ increase in solutions to their stationary level [40]. Minor additives of Fe(III) ($[\mathrm{Fe(III)}]_0 \ll [\mathrm{Fe(II)}]$) result in the disappearance of τ_i, but has no effect on the stationary rates of the transformations $\mathrm{Fe(II)} \longrightarrow \mathrm{Fe(III)}$ and $\mathrm{S(IV)} \longrightarrow \mathrm{S(VI)}$ [40]. This proves the rate-limiting role of $\mathrm{SO}_3^{\dot{-}}$ generation steps in both processes (see also [40]).[2]

Let us compare the plot of k'_a vs. pH with the calculated plot of the equilibrium concentration $[\mathrm{Fe(OH)SO_3H^+}]_\mathrm{eq}$ vs. pH. With this purpose, we present the experimental points [23, 33, 40, 42, 43] as the plot of $k'_\mathrm{a}/k'_{\mathrm{a}\,(\mathrm{pH_{max}})}$ vs. pH, see points in Fig. 1. The calculated curve in this figure will also be presented as the plot of the ratio $\beta = \chi/\chi_{\mathrm{pH_{max}}}$ vs. pH, where $\chi = [\mathrm{Fe(OH)SO_3H^+}]_\mathrm{eq}/[\mathrm{Fe(III)}]_0$ and $[\mathrm{Fe(III)}]_0$ is the overall concentration of all forms of iron(III) in the solution. The calculations of $[\mathrm{Fe(OH)SO_3H^+}]_\mathrm{eq}$ were based on data on the equilibrium constants of complex formation of Fe(III) with OH^-, HSO_3^-, and SO_3^{2-} [39] and dissociation constants of $\mathrm{SO}_{2(aq)} \longleftrightarrow \mathrm{H}^+ + \mathrm{HSO}_3^-$ ($K_3 = 1.4 \times 10^{-2}$ mol/l [39]) and $\mathrm{HSO}_3^- \longleftrightarrow \mathrm{H}^+ + \mathrm{SO}_3^{2-}$ ($K_4 = 6.24 \times 10^{-8}$ mol/l [39]). As can be seen from Fig. 1, the pH 3–4

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[2] The conclusion on the unified nature and, as a consequence, on the equality of k_ox and k'_a in aerated sulfite solutions at specified pH and [S(IV)] disagree with conclusions made in [40] where these constants were mistakenly referred to as different processes.

range where the maxima in the pH plots for $k'_a / k'_{a(pH_{max})}$ are arranged is favorable for $Fe(OH)SO_3H^+$ formation. This coincidence of the plots is not accidental and shows that reaction (i.I) is the only channel of initiation by iron ions in the pH 1–7 range, that is, reaction (i.II) is insignificant compared to (i.I). The maximum on the curve $\beta = f(pH)$ is explained by the achieving the maximum degree of $FeOH^{2+}$ binding into $Fe(OH)SO_3H^+$ at a specified value of [S(IV)] [39]. A decrease in β at $pH < 3$ is related to the shift of the equilibrium of Fe^{3+} hydrolysis to the left: $Fe^{3+} + H_2O \longleftrightarrow FeOH^{2+} + H^+$ ($K_5 \approx 6 \times 10^{-3}$ mol/l [39] and transition HSO_3^- to $SO_{2(aq)}$. At $pH \geq 4$ the subsequent hydrolysis becomes substantial: $FeOH^{2+} + H_2O \longleftrightarrow Fe(OH)_2^+ + H^+$ ($K_6 \leq 7 \times 10^{-5}$ mol/l [44]).

The region of homogeneous noncatalytic sulfite oxidation at $[Fe]_0 = 5 \times 10^{-8}$ mol/l calculated by us from thermodynamic data on the complex-formation equilibria in the S(IV)/Fe(III) system [39] is presented in Fig. 2. This region shown in the [S(IV)]–pH coordinates lies to the left and higher than curve *1* (Fig. 2), which demarcates the homogeneity and heterogeneity regions of the system.[3] At $[S(IV)] \times 10^{-3}$ mol/l the region of homogeneous noncatalytic sulfite oxidation is somewhat extended, that is, $Fe(OH)_3$ is not precipitated even at $pH \geq pH_{cr}$. This is due to the formation of the $Fe(OH)SO_3$ and $FeSO_3^+$ complexes, which prevent the formation of insoluble $Fe(OH)_3$ (see also [45]). The points shown in Fig. 2 reflect the concentration conditions used in [1, 4–7, 19–21, 46–55], see also [14]. Most of them were obtained under the conditions where the transition of some iron ions to insoluble $Fe(OH)_3$ should be taken into account. In analysis below, we consider only the homogeneous region of the noncatalytic sulfite oxidation reaction.

The Interrelation of w and [Fe]₀ in Noncatalytic Sulfite Oxidation

The presented kinetic and thermodynamic data on the participation of Fe(III) ions in initiation (i.I) and the plot $w \sim [Fe]_0$ observed for catalytic sulfite oxidation [23, 24, 26, 43, 45, 56] force us to search for the same proportionality for the noncatalytic reaction. According to [1, 2, 4–7], in the range of pH 2.0–4.3 and $[S(IV)] \geq 10^{-4}$ mol/l, k_a varies within 4×10^{-4} to 0.3 s^{-1}. Using for further estimates $k_a \geq 0.07$ s^{-1} found by us at $[Fe]_0 \approx 5 \times 10^{-7}$ mol/l, $pH \approx 3$, and $[S(IV)] \approx 10^{-2}$ mol/l (see also [26]), we find $k''_a = k_a/[Fe]_0 \approx 1.4 \times 10^5$ l mol^{-1} s^{-1}. Then accepting the above-mentioned proportionality between *w* and $[Fe]_0$, the concentration of admixed iron in [1] is $[Fe]_0 \approx k_a/k''_a \approx 0.013/(1.4 \times 10^5) \approx 9 \times 10^{-8}$ mol/l. Similar calculation for the conditions used in [4] gives $[Fe]_0 \approx k_a/k''_a \approx 3 \times 10^{-9}$, for experiments in [5] we find $[Fe]_0 \approx k_a/k''_a \approx 1.4 \times 10^{-8}$, and for [6] $[Fe]_0 \geq 2 \times 10^{-8}$ mol/l, which virtually coincides with the estimates of $[Fe]_0$ made by Brimblecomb and Spedding [6]. These estimates seemingly confirm the hypothesis that noncatalytic sulfite oxidation is related to sulfite oxidation catalysis by microadmixtures of iron ions. However, an attempt to estimate similarly $[Fe]_0$ from data of [7], which are characterized by anomalously high $k_a \approx 0.3$ s^{-1} at pH 4.3 gives $[Fe]_0 \approx k_a/k''_a \approx 2 \times 10^{-6}$ mol/l.[4] Let us compare the data of these experiments with those on the dynamics of catalytic processes with the controlled $[Fe]_0$ level. Considering, for example, data from [23] (pH ~ 4.2, $[Fe]_0 = 1 \times 10^{-6}$ and $[S(IV)] = 2 \times 10^{-5}$ mol/l), we find $k_a \approx 2$ s^{-1}, which is almost an order of magni-

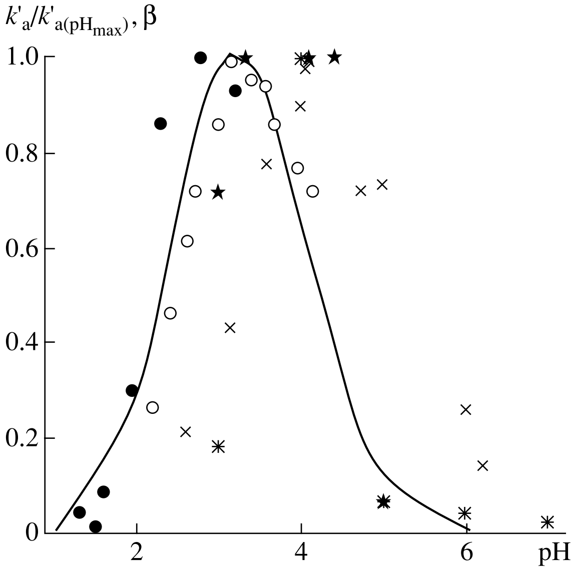

Fig. 1. Experimental and calculated pH plots of the $k'_a / k'_{a(pH_{max})}$ (points) and $\beta = \chi/\chi_{pH(max)}$ ratios (calculated curve). $\chi = [Fe(OH)SO_3H^+]_{eq}/[Fe(III)]_0$. Experimental points from the works: × [23], ★ [33], ○ [40], ● [42], and ✳ [43].

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[3] $[H^+]_{cr} > [Fe]_0 K_w^3 / SP_{Fe(OH)_3} K_5 K_6$, where $K_w \approx 10^{-14}$ is the ion product of water and $SP_{Fe(OH)_3} \approx 4 \times 10^{-38}$ is the solubility product for $Fe(OH)_3$, $K_5K_6 \approx 4 \times 10^{-7}$ [44]. For the characteristic level of admixed iron in sulfite solutions $[Fe]_0 = 5 \times 10^{-8}$ mol/l, we find $pH_{cr} \approx 5.5$ (see Fig. 2).

[4] Note that $k_a = 0.3$ s^{-1} according to [7], which is the result of the extrapolation of the expression (obtained in this work) for $k_a = f(pH, [O_2]_{aq})$ to pH 4. Using the same experimental value $k_a(pH\ 4.3) \approx 6.9 \times 10^{-2}$ s^{-1}, we find the more realistic value $[Fe]_0 \approx 5 \times 10^{-7}$ mol/l.

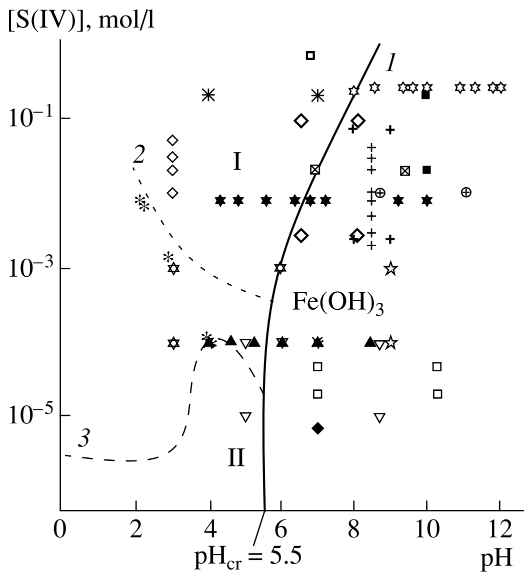

Fig. 2. Regions of (to the left from curve *1*) homogeneous and (to the right of curve *1*) heterogeneous noncatalytic sulfite oxidation reactions (see text). Room temperature, $[Fe]_0 = 5 \times 10^{-8}$ mol/l. Points in figure reflect the concentration conditions under which noncatalytic sulfite oxidation was studied. ◇ [1], ✡ [4], ∗ [5], ▲ [6], ✶ [7], ✡ [19], ☆ [20], ◇ [21], ▫ [46], ⊞ [47], ◇ [48], ⊠ [49], ▪ [50], ◆ [51], ⊕ [52], ✳ [53], ▽ [54], and + [55]. Region *I*: $[Fe(II)] \approx [Fe]_0$, region *II*: $[Fe(III)] \approx [Fe]_0$ (see text and Fig. 3).

tude higher than the experimental k_a value for the noncatalytic reaction [7]. Why do k_a values disagree at seemingly close $[Fe]_0$? The disagreement of k_a seems to be due to the difference in unavoidable $[Fe]_0$ impurity leading to different catalyst/substrate concentration ratios, $\alpha = [Fe]_0/[S(IV)]$. This relation between the concentration parameter α and *w* can be confirmed by our comparison of kinetic data on noncatalytic [1, 4–7] and catalytic sulfite oxidation [10, 23, 26, 33, 41–43, 70] for pH 3, which exhibits inconstancy of k_a'' when α is varied (Fig. 3).[5] Most of the presented data (points in Fig. 3) correspond to $T = 298$ K and to the ion strength of a sulfite solution close to zero ($\mu \approx 0$). To complete the picture, Fig. 3 also presents the experimental data [42] referred to $T = 283$ K and $\mu = 1.2$ and those obtained at $T = 293$ K and $\mu \longrightarrow 0$ [43]. To match these results with the main body of data, the experimental k_a'' values for these conditions were recalculated to k_a'' at $T = 298$ K. With this purpose, we used the temperature coefficient of the reaction ($E_a \approx 91.3$ kJ/mol) found in [57]. Correction to differences in μ were not applied. Figure 3 shows that, despite ignoring the μ factor, the recalculation of the experimental rate constants (points in parentheses) gives k_a'', which agrees satisfactorily with those obtained for close α ($\geq 10^{-2}$) and at $\mu \longrightarrow 0$. Despite information deficiency, a similar interrelation of k_a'' and α can qualitatively be revealed for other pH. This data show that the curves $k_a'' = f(\alpha)$ at pH ≤ 5 have a general feature: the pronounced *S*-like shape (Fig. 3). This uniformity of the curves suggests a hypothesis about two regimes of catalytic sulfite oxidation. Their common feature is the first reaction order with respect to iron. The distinction is related to the difference in the apparent rate constants, which is clearly illustrated by the pH plots of k_a'' for low ($\ll 10^{-3}$) and high ($\geq 10^{-2}$) values of the α parameter (Fig. 4, curves *1* and *2*). We see that the differences in k_a'' are especially high $k_a''(\alpha \geq \alpha_{cr})/k_a''(\alpha \ll \alpha_{cr}) \approx 10^3$ at low pH. Their values for α decrease with an increase in pH. Note that at low pH (≤1.5) the k_a'' values show a pronounced tendency toward saturation. This suggests that data from [10] for these conditions most likely require some correction.

The sulfite oxidation regime corresponding to the lower plateau for k_a'' (Fig. 3) is only possible for low α ($\ll 10^{-3}$, low $[Fe]_0$, high [S(IV)]; noncatalytic sulfite oxidation regime), and the regime corresponding to the higher plateau for k_a'' (Fig. 3) is characterized by high α ($\geq 10^{-2}$, high $[Fe]_0$ and low [S(IV)]; controlled catalytic sulfite oxidation regime). Two sulfite oxidation regimes at a specified pH can reasonably be related to a change in the iron ion distribution over valent forms when α is varied. As follows from Fig. 3, we can distinguish a narrow zone of values $\alpha \approx 5 \times 10^{-4}$–$10^{-3}$ at which the ratio between concentrations of the oxidized and reduced forms of iron ions $\zeta = [Fe(III)]/[Fe(II)]$ changes jumpwise from $\ll 1$ to $\gg 1$. This α value denoted henceforth as α_{cr} equals $\approx 10^{-3}$ at pH 3.

In the framework of the above data, we can isolate the regions of the presence of iron ions predominantly in the form of Fe(II) or Fe(III) in the [S(IV)]–pH coordinates as applied to noncatalytic sulfite oxidation with the concentration of admixed iron ions in the solution $[Fe]_0 = 5 \times 10^{-8}$ mol/l. Based on data on the noncatalytic sulfite oxidation dynamics obtained at pH 2.0–5.5 [4–7, 26] under the conditions of lower plateau, we may estimate the minimum sulfite concentration: $[S(IV)]_{min} = [Fe]_0/\alpha$ when $\zeta \ll 1$. This plot $[S(IV)]_{min} = f(pH)$ is presented in Fig. 2 (curve *2*). Similar estimates along with data on catalytic sulfite oxidation dynamics obtained under the conditions the higher plateau [10, 23] give the pH plot of the maximum sulfite concentra-

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[5] Data in [41] were obtained assuming that the concentration [S(IV)] in the solution is at equilibrium. As before, data in [42], [43], and [57] are presented in Fig. 4 for $T = 298$ K without correction to μ. Data from [45] for pH ≥ 4 correspond to the maximum $[Fe]_0 \geq 10^{-6}$ mol/l used in the work, that is, the conditions where the square law with respect to iron $w \sim [Fe]_0^2$ breaks. We made an assumption on $w \sim [Fe]_0$ to describe the dynamics of the reaction under these conditions.

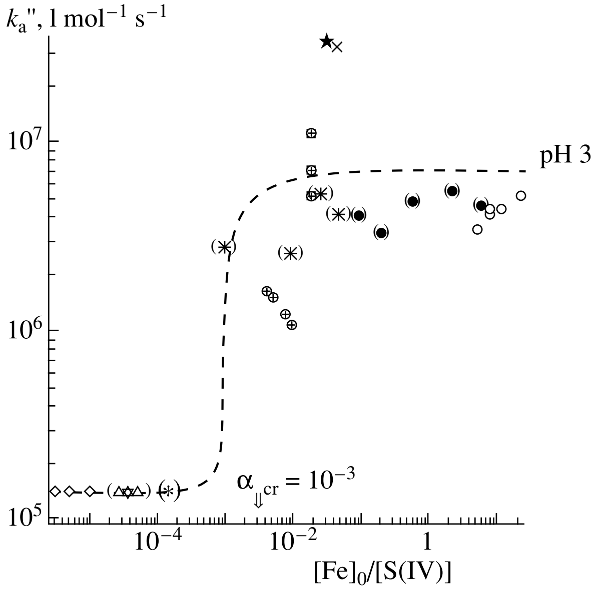

Fig. 3. Apparent rate constant of sulfite oxidation $k_a'' = k_a'/[Fe]_0$ (dotted line) for noncatalytic sulfite oxidation and catalytic sulfite oxidation as a function of the α parameter; pH 3, $T = 298$ K, see text. Points in parentheses, the $[Fe]_0$ values in a solution were estimated by the authors, see text. ◇ [1], ✡ [4], ⁎ [5], ▲ [6], ⊞ [10], △ [26], × [23], ★ [32], ○ [40], (●) [42], (✳) [43], and ⊕ [70].

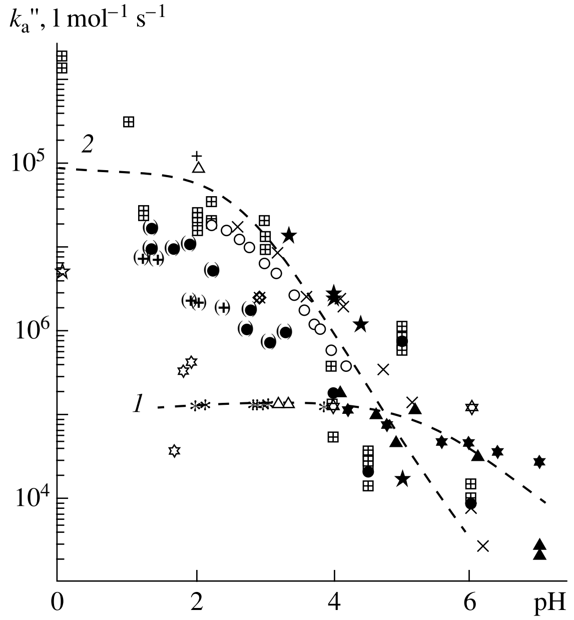

Fig. 4. Apparent rate constant of sulfite oxidation $k_a'' = k_a'/[Fe]_0$ (dotted line) as a function of pH. Curve *1*: $\alpha \ll \alpha_{cr}$ ($[Fe(II)] \approx [Fe]_0$), curve *2*: $\alpha \gg \alpha_{cr}$ ($[Fe(III)] \approx [Fe]_0$), see text. Points reflect published data. ✡ [4], ⁎ [5], ▲ [6], ✶ [7], ⊞ [10], × [23], ✡ [24], [25], △ [26], ★ [33], ○ [40], ☆ [41], (●) [42], (✳) [43], ● [45], + [57], and + [73].

tion $[S(IV)]_{max}$ when $\zeta \gg 1$ (curve *3* in Fig. 3). Figure 2 shows that curves *2* and *3* along with curve *1* make it possible to isolate the islands of Fe(II) (region *I*) and Fe(III) (region *II*) stability in aerated sulfite solutions containing admixed iron ions. In the intermediate (between curves *2* and *3*) region, both forms of iron atoms coexist in a solution. The interrelations $[S(IV)] = f(pH)$ thus obtained reflect a change in the redox properties of aerated sulfite solutions with respect to iron ions and are in accordance with the concepts in [40, 58]. These changes in the redox properties of solutions with variation of the concentration parameters α or pH can reasonably be related to a change in the concentration of the strong oxidant HSO_5^-. The authors of [7] report that at elevated pH the conversion of S(IV) into HSO_5^- during noncatalytic sulfite oxidation reaches ten percentage, whereas at low pH and high [S(IV)] the HSO_5^- concentration is beyond detectable limits. The high $[HSO_5^-]$ at elevated pH are due to the retardation of autocatalytic reaction (VIII) (table), which occurs rapidly only at low pH or high [S(IV)]. At high pH or low S(IV) this reaction is retarded and the role of reaction (XI) increases. This is precisely the competition of reactions (VIII) and (XI) which is a reason for the plot of k_a'' vs. α revealed in our work (see Fig. 3). The significance of reaction (XI) even under the conditions of the lowest pH (≤1.7) is indicated by an increase in *w* when minor [Mn(II)] are added to the sulfite solution ($[S(IV)] \geq 10^{-3}$ mol/l) [24]. Since catalysis of sulfite oxidation by Mn(II) ions in the absence of impure Fe is impossible (see above), the role of additives of manganese ions is catalysis of the limiting step of reaction (III): $SO_5^{\dot{-}} + Mn(II) \xrightarrow{H^+} HSO_5^- + Mn(III)$, $k \geq 2 \times 10^8$ l mol^{-1} s^{-1} [59] and $Mn(III) + HSO_3^- \longrightarrow Mn(II) + SO_3^{\dot{-}} + H^+$, $k = 1.3 \times 10^6$ l mol^{-1} s^{-1} [25]. The related increase in $[HSO_5^-]$ accelerates the regeneration of Fe(III) in reaction (XI) and thus increases ζ [60]. This has recently been found experimentally [61] when the authors showed that additives of Mn(II) ions change basically the ζ value. Thus, reactions (VIII) and (XI) can be classified as key, determining, along with the initiation reaction, the sulfite oxidation dynamics in the presence of iron ion microadditives.

On the Distribution of Admixed iron Ions over the Fe(II) and Fe(III) Forms

The significant variation of the redox properties of aerated sulfite solutions in noncatalytic sulfite oxidation with changes in pH and [S(IV)] (Fig. 3) forces us to concentrate in more detail on the available experimental data on the [Fe(III)]/[Fe(II)] ratio in these solutions. We consider only several publications [62–64], which report quantitative determinations of ζ at analytically detected $[Fe]_0$. In [62, 63] at pH 3, $[Fe]_0 = 10^{-5}$ and $[S(IV)] \geq 2 \times 10^{-3}$ mol/l ($\alpha \approx 5 \times 10^{-3}$), the authors found that $\zeta \approx 0.15$. Data from [64] show that $\zeta \geq 9$ at pH 4, $[Fe]_0 = 10^{-6}$ and $[S(IV)] = 10^{-4}$ mol/l ($\alpha \approx 10^{-2}$). Such a dramatic change in ζ with a simultaneous increase in pH and a decrease in [S(IV)] is in accordance with a change in the ratio of rates of the key reactions w_8/w_{11}. The agreement between the pH plots of β and $k'_a/k'_{a(pH_{max})}$ observed by us (Fig. 1) indicates indirectly that Fe(III) prevails over Fe(II) in dilute sulfite solutions with $\alpha \geq 4 \times 10^{-2}$ [23, 33, 42, 43]. The existence of a sulfite solution with pronounced reductive properties ($\zeta \longrightarrow 0$) has been shown in [26] by the experiments with $S_2O_8^{2-}$ additives to a sulfite solution. In these experiments (pH ≥ 3, $[S(IV)] \approx 10^{-2}$ mol/l, $\alpha \approx 5 \times 10^{-5}$) the authors observed a multiple ($w_{S_2O_8^{2-}}/w \gg 1$) increase in w_i and w, and the saturation effect was observed at $[S_2O_8^{2-}] \geq 10^{-2}$ mol/l, that is, a weak increase in w_i and w with $[S_2O_8^{2-}]$. The slow ion reaction $HSO_3^- + S_2O_8^{2-}$ does not explain the strong effect of noncatalytic sulfite oxidation acceleration [12]. The latter is due to reaction (XII), which accelerates Fe(III) regeneration and increases ζ compared to experiments in the absence of $S_2O_8^{2-}$ additives. In the saturation zone $k_{i,1}\chi[Fe(III)][HSO_3^-] = k_{12}[S_2O_8^{2-}][Fe^{2+}]$. The estimates show [26] that at $[S_2O_8^{2-}] = 2 \times 10^{-2}$ mol/l, $\zeta \approx 10$, that is, more than 90% iron ions exist in the Fe(III) form and, correspondingly, only 10% are in the Fe^{2+} form. (As detected spectrophotometrically, $[FeOH^{2+}] \approx [Fe]_0$ when $[Fe]_0$ increases to 10^{-4} mol/l.) Similar experiments were described in [65, 66], but additives of H_2O_2 or HSO_5^- were used as potential redox initiators of noncatalytic sulfite oxidation. Unlike $S_2O_8^{2-}$, both H_2O_2 and HSO_5^- [12] react with HSO_3^- rather rapidly to form SO_4^{2-}, but, like $S_2O_8^{2-}$, react with Fe(II) to regenerate $\dot{SO_4^-}$ in the case of HSO_5^- (XI). An interpretation of these experiments is very difficult due to a decrease in HSO_5^- in the reaction with sulfite (VIII). An increase in the radical concentration in these solutions and, hence, w_i, was proved by the observation [66, 67] of an increase (by approximately an order of magnitude) in the rate of phenol formation w_{ph} when HSO_5^- was added. Analysis of these data allows us to estimate the upper boundary of w_i in noncatalytic sulfite oxidation. A sulfite excess and low pH suggest that $\zeta \approx 0$, that is $[Fe(II)]_0 \approx [Fe]_0$, in the absence of HSO_5^- additives. Taking into account that $[HSO_5^-]_0/[HSO_3^-] \ll 1$ and assuming that (VIII) is the main reaction involving HSO_5^- under these conditions, we find that $\zeta_{HSO_5^-} \approx w(–Fe(II))\tau/[Fe]_0 \approx k_{11}[HSO_5^-][Fe]_0/(k_8[HSO_3^-][Fe]_0)$, where $w(–Fe(II))$ and τ are the oxidation rate of Fe(II) ions and characteristic time of this reaction, respectively. Taking into account $[HSO_5^-]_0$ and pH 3, we find finally $\zeta_{HSO_5^-} \leq 0.1$. Considering the difference in w_{Ph} in the absence and presence of HSO_5^- and the proportional concentrations of chain carriers, we obtain for the "pure" system $\zeta \approx \zeta_{HSO_5^-}$, $w_{ph}/w_{ph(HSO_5^-)} < 10^{-2}$. The use of the linear relationship between w_{ph} and the concentration of chain carriers provides the estimate of $[Fe]_0$ in these experiments. Comparison of w_{ph} in the experiments with the admixture level ($w_{ph} \approx 1 \times 10^{-10}$ mol l^{-1} s^{-1}) and controlled level of $[Fe]_0 = 8.5 \times 10^{-7}$ mol/l ($w_{ph(Fe)} \leq 1.7 \times 10^{-9}$ mol l^{-1} s^{-1} [67]) gives $[Fe]_0 \approx 8.5 \times 10^{-7}$ mol/l, $w_{ph}/w_{ph(Fe)} \approx 5 \times 10^{-8}$ mol/l, and $\alpha \approx 5 \times 10^{-8}/2 \times 10^{-3} \approx 2.5 \times 10^{-5}$ ($\ll \alpha_{cr}$)). Therefore, for [Fe(III) and w_i under the experimental conditions [66], we have $[Fe(III)] \approx [Fe]_0\zeta \approx 5 \times 10^{-10}$ mol/l and $w_i \approx k_{i,I}\chi[Fe]_0\zeta \approx 2 \times 10^{-11}$ mol l^{-1} s^{-1}. This w_i value is more than three orders of magnitude higher than the w_i value characteristic of the experiments with external UV or radiation initiation [16–18]. Perhaps, this difference in w_i is the main reason why the canonical radical chain mechanism is inapplicable to the description of the noncatalytic sulfite oxidation dynamics because of a small role of square chain termination (VIIb) in this reaction compared to the experiments with external initiation.

Kinetics of Noncatalytic Sulfite Oxidation

Let us discuss some unusual features of noncatalytic sulfite oxidation kinetics when pH and [S(IV)] are varied using. We will use the relations of these parameters with the differences in conditions of HSO_5^- formation and consumption. For example, the fact (shown in experiments with $S_2O_8^{2-}$ [26] and HSO_5^- [66] additives) that the oxidative properties of sulfite solutions are minimal at $\alpha \ll \alpha_{cr}$ and pH < pH$_{cr}$ (that is, $\zeta \ll 1$) allows us to relate this to the intense consumption of HSO_5^- in the reaction with HSO_3^- (VIII) because $w_8/w_{11} = k_8/k_{11}\alpha \gg 1$. In this case, the Fe(II) $\longrightarrow$ Fe(III) transition occurs mainly in the reaction with $\dot{SO_5^-}$ (IX). (At pH 3, for example, $w_9/w_{11} = k_8k_9/k_{3a}k_{11} \gg 1$). By contrast, the significance of reaction (IX) in the formation of the final sulfite oxidation products in reductive solutions is low: $w_9/w \approx w_9/w_8 = \alpha k_9/k_{3a} \ll 1$. The reaction of $\mathrm{SO}_5^{\dot{-}}$ with Fe(II) and accompanying fast reaction (VIII) ($w_9/w_8 \ll 1$) efficiently result in chain termination. This conclusion follows from the comparison of the regeneration rates of $\mathrm{SO}_5^{\dot{-}}$ in the cycles involving Fe(II) and HSO_3^-, which include reactions (i.I), (II), (IV), (IX), (XI) and (II), (IIIa) (see the table). Comparison of the slowest units of these cycles (III) and (IX) gives $w_{3a}/w_9 = k_{3a}/k_9\alpha \gg 1$, that is, $\mathrm{SO}_5^{\dot{-}}$ regeneration in the cycle involving HSO_3^- is in fact faster. Despite the relatively low rate of reaction (IX) ($w_9/w \ll 1$), the $\mathrm{SO}_5^{\dot{-}}$ decay in it is much faster than that in the second-order reaction $\mathrm{SO}_5^{\dot{-}} + \mathrm{SO}_5^{\dot{-}}$ (VIIb). This is due to very low w_i. Using sample data from [67], we find $\tau_{7b} = (2w_\mathrm{i}k_{7b})^{-1.2} \geq (2 \times 10^{-11}\, 2.6 \times 10^7)^{-1/2} \geq 40$ s, whereas $\tau_9 = (k_9[\mathrm{Fe}]_0)^{-1} \geq (3.2 \times 10^6 4 \times 10^{-8}) \leq 8$ s. The estimate $\tau_{7b} \gg \tau_9$ also agrees with the conclusion on the small contribution of the chain propagation reaction (VIIb) to $\mathrm{SO}_4^{\dot{-}}$ formation [67] and, hence, a low rate of square termination (VIIb)! Thus, reaction (IX) under the conditions $\zeta \ll 1$ ($\alpha \ll \alpha_\mathrm{cr}$) is *pseudo-linear chain termination*.

Taking into account that $k_{3a}/k_9 \approx 10^{-3}$, we conclude that the concentration parameter α_cr used in our consideration plays the role of a criterion for the differentiation of noncatalytic sulfite oxidation regimes. In the chain noncatalytic sulfite oxidation regime, that is, at $\alpha \ll \alpha_\mathrm{cr}$, the Fe(III) ions act as an initiator of chain process (i.I), and the active Fe(III) form is regenerated in reaction (IX). The additives of substances, which affect $[\mathrm{Fe(OH)SO_3H^+}]_\mathrm{eq}$ (complex formation of Fe(III) with SO_4^{2-}, Cl^- [14, 68, 69], and substances of buffer additives) decrease w_i and w (inhibition of noncatalytic sulfite oxidation), thus changing the k_a value. The inhibition of noncatalytic sulfite oxidation also occurs when additives of radical acceptors (pyrocatechol, ethylamine, benzene, and others) are added [15, 62, 70, 71].

Thus, the $w/2w_9$ ratio can be considered as the chain length of noncatalytic sulfite oxidation (ν): $\nu = \alpha_\mathrm{cr}/\alpha$. Using our experimental data [26] ($\alpha \approx 5 \times 10^{-5}$), we have $\nu = k_3[\mathrm{HSO_3}]/k_9[\mathrm{Fe}]_0 \approx 30$. A similar estimate using data from [4, 5] gives $\nu \approx 6$ ($\alpha \approx 3 \times 10^{-4}$) [4] and $\nu \approx 5 \times 10^4$ ($\alpha \approx 2 \times 10^{-6}$) [5]. Taking into account that $w \approx 5 \times 10^{-8}$ mol l^{-1} s^{-1} measured by us and the evident ratio $w_\mathrm{i} = w/2\nu$, we find $w_\mathrm{i} \approx 10^{-9}$ mol l^{-1} s^{-1}. Taking into consideration the experimental value $k_{\mathrm{i},1}\chi \approx 7 \times 10^{-2}$ s^{-1} (see above), we obtain $[\mathrm{Fe(III)}] = w_\mathrm{i}/k_{\mathrm{i},1}\chi \approx 1.5 \times 10^{-8}$ mol/l and $\zeta \approx 3 \times 10^{-2}$. Based on data from [5] ($[\mathrm{Fe}]_0 \approx 2.2 \times 10^{-8}$, $[\mathrm{S(IV)}] \approx 10^{-2}$ mol/l, pH ≈ 3, see above) and experiments in a sulfite excess ($\chi \approx 1$ and $k_{\mathrm{i},1}\chi \approx 0.2$ s^{-1}), we have $(w_\mathrm{i})_{\mathrm{pH}\,3} = w/2\nu \approx 2 \times 10^{-12}$ mol l^{-1} s^{-1}, $[\mathrm{Fe(III)}] \approx 1 \times 10^{-11}$ mol l^{-1} and $\zeta \approx 4 \times 10^{-4}$. Comparing the estimates of w_i at pH 3 obtained from the following data

$[\mathrm{Fe}]_0$, mol/l	$W_\mathrm{i} \sim [\mathrm{Fe(III)}]$, mol l^{-1} s^{-1}
$\approx 3.5 \times 10^{-9}$ [4]	$\approx 3 \times 10^{-14}$
$\approx 2 \times 10^{-8}$ [5]	$\approx 2 \times 10^{-12}$
$\approx 5 \times 10^{-7}$ [26]	$\approx 10^{-9}$

we conclude that, in the reductive sulfite solutions, an increase in $[\mathrm{Fe}]_0$ is accompanied by the nonlinear increase in w_i and, correspondingly, [Fe(III)]! Such an unexpected result agrees with the noninterpreted experimental data [67] on the square increase in w_ph (and, hence, w_i) in the experiments with benzene additives to sulfite solutions containing iron ions. The presented comparison of $[\mathrm{Fe}]_0$ and w_i allows us to assume that $[\mathrm{Fe(III)}] \sim [\mathrm{Fe}]_0^2$. This relation combined with the expression for $\nu = k_3[\mathrm{HSO}_3^-]/k_9[\mathrm{Fe}]_0$ (see above) clarifies the experimental linear plot of the catalytic sulfite oxidation rate vs. $[\mathrm{Fe}]_0$: $w = w_\mathrm{i}\nu$; that is, $w \sim [\mathrm{Fe}]_0$.

Let us consider data on the reaction order of noncatalytic sulfite oxidation with respect to sulfite and the pH plot of k_a for solutions with $\alpha \ll \alpha_\mathrm{a}$ ($\zeta \ll 1$). Let us rearrange the equation for the noncatalytic sulfite oxidation rate into the form $w = 2k_3[\mathrm{SO}_5^{\dot{-}}][\mathrm{HSO}_3^-] = 2k_3k_{\mathrm{i}.1}\chi[\mathrm{Fe(III)}][\mathrm{HSO}_3^-]2k_3k_{\mathrm{i}},.../k_9[\mathrm{Fe}]_0)$. Since $[\mathrm{Fe(III)}] \approx \zeta[\mathrm{Fe}]_0$, $w \approx 2k_3\zeta k_{\mathrm{i}.1}\chi[\mathrm{HSO}_3^-]/k_9$. Taking into account that $[\mathrm{SO}_3^{2-}]/[\mathrm{HSO}_3^-] = K_4/[\mathrm{H}^+]$, find $w = 2k_3\zeta k_{\mathrm{i}.1}\chi[\mathrm{H}^+][\mathrm{SO}_3^{2-}]/k_9K_4$ and, finally, $k_\mathrm{a} = 2k_3\zeta k_{\mathrm{i}.1}\chi[\mathrm{H}^+]/k_9K_4$. Inserting our data on the ζ and $k_{\mathrm{i}.1}\chi$ values into this equation, we find $k_\mathrm{a} \approx 7 \times 10^{-2}$ s^{-1}, which coincides exactly with the experimental k_a value. This expression demonstrates that k_a weakly depends on pH ($\chi \sim [\mathrm{H}^+]^{-1}$, see above) in the range from 2 to 4. Available experimental data [5] show that $k_\mathrm{a} = 3 \times 10^{-3}$ s^{-1} remains virtually unchanged when pH varies in these limits. The above data on the sharp difference in k_a for slight distinctions of the concentration parameters can qualitatively be explained by a change in the ratio of rates of the key reactions $w_8/w_{11} = k_8[\mathrm{HSO}_3^-]/k_{11}[\mathrm{Fe(II)}]$ at minor differences in $[\mathrm{Fe}]_0$, $[\mathrm{H}^+]$, and $[\mathrm{HSO}_3^-]$.

The quantitative correspondence of the calculated and experimental k_a values and qualitative agreement between the analytical and experimental plots of k_a along with the parameters of unavoidable contamination of water and reagents with iron ions allow us to conclude that noncatalytic sulfite oxidation is in fact the process of homogeneous catalysis of sulfite oxidation by microadditives of iron ions. The question about the noncatalytic sulfite oxidation mechanisms under the conditions of deep iron ion hydrolysis and disturbance of the homogeneity of the system (see Fig. 2) is of separate interest. Note that many papers on noncatalytic oxidation by oxygen and hydrogen peroxide in aqueous solutions did not consider the role of iron ions microadmixtures.

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