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Iron(II) Sulfate Oxidation with Oxygen on a Pt/C Catalyst: A Kinetic Study

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Abstract—The kinetics of iron(II) sulfate oxidation with molecular oxygen on the 2% Pt/Sibunit catalyst was studied by a volumetric method at atmospheric pressure, $T = 303$ K, pH 0.33–2.4, $[FeSO_4] = 0.06$–0.48 mol/l, and $[Fe_2(SO_4)_3] = 0$–0.36 mol/l in the absence of diffusion limitations. Relationships were established between the reaction rate and the concentrations of Fe^{2+}, Fe^{3+}, H^+, and Cl^- ions in the reaction solution. The kinetic isotope effect caused by the replacement of H_2O with D_2O and of H^+ with D^+ was measured. The dependence of Fe^{2+} and Fe^{3+} adsorption on the catalyst pretreatment conditions was studied. A reaction scheme is suggested, which includes oxygen adsorption, the formation of a Fe(II) complex with surface oxygen, and the one-electron reduction of oxygen. The last step can proceed via two pathways, namely, electron transfer with H^+ addition and hydrogen atom transfer from the coordination sphere of the iron(II) aqua complex. A kinetic equation providing a satisfactory fit to experimental data is set up. Numerical values are determined for the rate constants of the individual steps of the scheme suggested.

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The oxidation of iron(II) salts is among the most important processes. Iron(III) compounds are valuable semiproducts used in the production of various iron-containing substances, pigments, and coatings. Furthermore, they are components of coagulants for water purification [1–4]. Conversion of dissolved iron into its highest oxidation state is a necessary step in a variety of commercial hydrometallurgical processes, such as purification of hydrometallurgical solutions and regeneration of Fe(III)-containing solutions that were used as an oxidizer in the processing of complex ores or in the removal of hydrogen sulfide from waste gas [5–11]. Iron(II) is known to be readily oxidizable in air in neutral and alkali media. However, iron (II) salt oxidation with oxygen proceeds via complicated multistep pathways and depends strongly on the composition of the reaction medium and other process conditions [12–21]. It is particularly difficult to oxidize Fe^{2+} in a sulfate solution. In this case, the oxidation rate may be inversely proportional to the squared concentrations of H^+ and Fe^{2+} [15–19].

In order to attain a higher Fe(II) conversion, it was suggested to use expensive oxidizers, such as the iodate ion [21, 22], the chlorate ion [23, 24], nitric acid [25, 26], ozonized air [26], hydrogen peroxide [26], chlorine dioxide [27], and pyrolusite [28], or to introduce various admixtures (alcohols [29], thyrone [30], and EDTA and related ligands [31–33]). There have been attempts to solve this problem by using homogeneous catalysts (copper salts [34, 35], porphyrins [30], nitrogen oxides, and nitrous acid [31, 36–41]). The heterogeneous catalysts that were used for this purpose are shales [42], cobalt phthalocyanine on a carbon cloth [43], and activated carbons [44–48], and all of them showed a very low efficiency. For example, in the oxidation of $FeSO_4$ (0.1 mol/l) with air in a 0.15 mol/l H_2SO_4 solution at 35°C in the presence of activated carbon (preheated in vacuo for higher activity), the conversion of Fe^{2+} into Fe^{3+} was as low as 25% in 3 days, even if it was 10 times higher than the conversion observed in the absence of a catalyst [44]. It was discovered that modification of the carbon surface with nitrogen-containing groups increases the reaction rate by one order of magnitude, but the absolute activity remains low and usually decreases with time [49, 50].

Earlier, we demonstrated that carbon loaded with 2 wt % noble metal (Pt, Pd, Ir) is 2–3 orders of magnitude more efficient in Fe(II) oxidation with oxygen than pure activated carbon [51]. Supported bimetallic systems appeared to be still more efficient [52]. Among the monometallic catalysts, the Pt/C systems are the most promising since they are cheaper than the palladium or iridium catalysts and, as distinct from the palladium catalysts, are resistant to active component washout in strong acid media. Supported platinum is sufficiently resistant to surface oxidation, which is possible after 100% Fe(II) conversion is reached. In our experiments, the activity of the initial Pd/C sample was reduced by 30% after several cycles (14 h on stream). The catalyst could be completely regenerated by reducing it with sodium formate directly in the reaction solution.

In order to reveal the factors affecting the efficiency of Pt/C catalysts in Fe(II) oxidation with oxygen, we

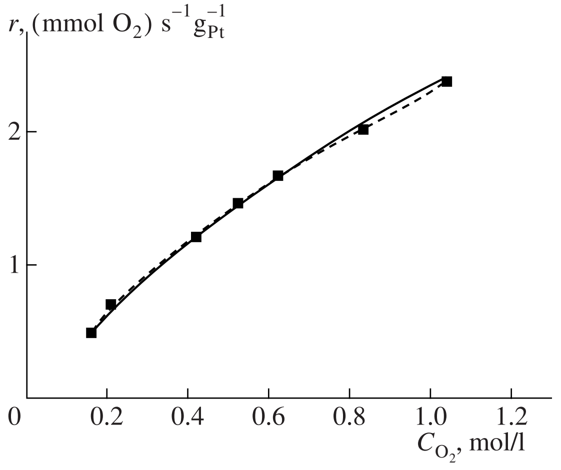


Fig. 1. Reaction rate as a function of the oxygen concentration at $[FeSO_4]$ = 0.36 mol/l and $[H_2SO_4]$ = 0.032 mol/l.

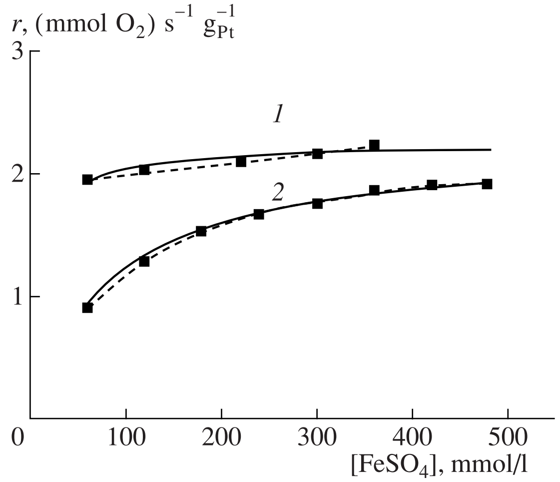


Fig. 2. Reaction rate as a function of the $FeSO_4$ concentration (*1*) in the absence of $Fe_2(SO_4)_3$ and (*2*) in the presence of 0.03 mol/l $Fe_2(SO_4)_3$. $[H_2SO_4]$ = 0.028 mol/l, and C_{O_2} = 1 mmol/l.

carried out a kinetic study of this reaction and optimized the reaction conditions.

EXPERIMENTAL

The chemicals used in this study were reagent-grade. Deuterated H_2O and H_2SO_4 contained 99 and 98% deuterium, respectively. In catalyst preparation, we used the carbon material Sibunit [53] with a particle size of 40–70 μm. The support was washed with hot 10% HCl. For removal of the chloride ion, it was then washed with water several times. An aqueous solution of H_2PtCl_6 with a platinum content of 9 mmol/l was added dropwise to a carbon suspension (10 ml of water per gram of carbon), an alkali solution (0.03 mol/l) was added, and platinum was then reduced with a sodium formate solution (0.04 mol/l) at 80°C for 1 h. Next, the catalyst was washed with water and was dried in air overnight. The metal content was determined by atomic absorption analysis after burning the sample.

The Fe(II) oxidation reaction was carried out in a vigorously shaken reactor at 303 K and atmospheric pressure. The reaction solution (40 ml) was placed in the reactor and was bubbled with oxygen for 3–5 min. After that, the catalyst was added and vigorous shaking was begun (more than 500 oscillations per minute). The oxygen uptake was measured as the change of the oxygen volume in the buret. The initial reaction rate was estimated from the oxygen uptake in the first three minutes of the reaction. The Fe(II) conversion was verified by titrating the reaction solution with a $KMnO_4$ solution (0.1 mol/l) before and after the reaction. The Fe(III) in the solution in adsorption measurements was determined by atomic absorption spectrometry.

Catalytic tests were made in the absence of external or internal diffusion limitations, so that the reaction rate was independent of the volume of the liquid phase or the agitation vigor.

Catalysts were thoroughly ground in an agate mortar. According to light microscopy data, the average particle size was thus reduced to 5–10 μm. The Thiele modulus was calculated to be $\Phi_{Fe(II)} = 0.5$, indicating that the reaction is kinetically controlled [54]. The $\Phi_{Fe(II)}$ calculation was based on the catalytic activity data presented in Fig. 1, the average particle size of 7.5 μm, and the assumptions that the catalyst particles are spherical and that the active phase is uniformly distributed. The tortuosity factor was taken to be 4. The porosity was taken to correspond to a mesopore volume of 0.6 cm^3/g.

RESULTS

The initial reaction rate increases linearly as the platinum content of the catalyst is increased from 0.5 to 3.0 wt %. The initial Fe(II) oxidation rate r as a function of the reactant concentrations is plotted in Figs. 1–5. In these figures, the points connected by dashed lines represent experimental data and the solid curves represent data calculated using Eq. (1) (see below). The numerical values of the constants of Eq. (1) are also presented below.

The order of the reaction with respect to oxygen ($\log r / \log C_{O_2}$ ratio, where C_{O_2} is the oxygen concentration) in the oxygen concentration range of 0.1–1.1 mol/l is 0.8 (Fig. 1). The reaction rate is independent of the iron(II) sulfate concentration between 0.06 and 0.36 mol/l (Fig. 2, curve *1*). Upon the addition of a small amount of iron(III) sulfate (0.03 mol/l), the order of the reaction with respect to iron(II) increases to 0.4 and the reaction rate decreases (Fig. 2, curve *2*). The order of the reaction with respect to $Fe_2(SO_4)_3$ is –0.4 (Fig. 3).

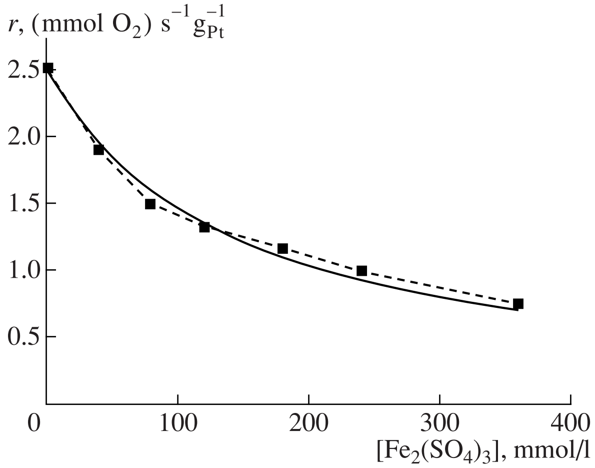


Fig. 3. Reaction rate as a function of the $Fe_2(SO_4)_3$ concentration at $[FeSO_4] = 0.36$ mol/l, $[H_2SO_4] = 0.050$ mol/l, and $C_{O_2} = 0.9$ mmol/l.

The addition of hydrochloric acid (Fig. 4) or lithium chloride reduces the reaction. The reaction rate as a function of $[H^+]$ is plotted in Fig. 5. In the absence of chloride ion admixtures, the order of the reaction with respect to the acid is 1.4 in the H^+ concentration range from 5 to 18 mmol/l and 0.5 at $[H^+] = 18–79$ mmol/l (Fig. 5, curve *1*). For $[H^+] > 79$ mmol/l, the reaction rate is independent of the acidity of the solution. Upon the addition of 0.09 mol/l HCl, the constant reaction rate remains independent of the acidity of the solution in the $[H^+]$ range of 8–174 mmol/l (Fig. 5, curve *2*).

Replacing H_2O and H_2SO_4 with D_2O and D_2SO_4, respectively, reduces the reaction rate: $r_H/r_D = 2.3$ ($r_H = 2.22$ (mmol O_2) s^{-1} g_{Pt}^{-1}, $r_D = 0.97$ (mmol O_2) s^{-1} g_{Pt}^{-1}). These experiments were performed under the following conditions: $[FeSO_4] = 0.31$ mol/l, pH 1.45, and $C_{O_2} = 1$ mmol/l. In the presence of chloride ions ($[Cl^-] = 0.09$ mol/l), the isotope effect is $r_H/r_D = 3$ ($r_H = 0.13$ (mmol O_2) s^{-1} g_{Pt}^{-1}, $r_D = 0.39$ (mmol O_2) s^{-1} g_{Pt}^{-1}). The kinetic runs in the presence of Cl^- were conducted under similar conditions, namely, $[FeSO_4] = 0.34$ mol/l, pH 1.48, and $C_{O_2} = 1$ mmol/l.

Our study of the dependence of Fe(II) and Fe(III) ion adsorption on the catalyst pretreatment conditions demonstrated the following. The starting support, as well as the catalyst held in flowing hydrogen at 420 K without air excess and transferred into the iron salt solution, does not adsorb Fe(II) or Fe(III) ions. Under the same conditions but in the presence of oxygen, the catalyst is capable of adsorbing Fe(III). In these experiments, the Fe(III) concentration in the solution was equal to the iron concentration at the initial stages (approximately in the third minute) of the reaction. As can be seen from the table, the amount of Fe(III) adsorbed increases with increasing the initial Fe(III) concentration.

DISCUSSION

The oxidation of alcohols and aldehydes with oxygen and the electrochemical reduction of oxygen on platinum catalysts have been studied in detail (see, e.g., [55, 56]). Although the mechanisms suggested for these reactions are much diversified, the role of the metal in all of them is that its surface activates molecular oxygen:

$$Z + O_2 \longrightarrow ZO_2, \qquad (I)$$

where Z is an empty site on the catalyst surface. In the next step, activated oxygen oxidizes the substrate.

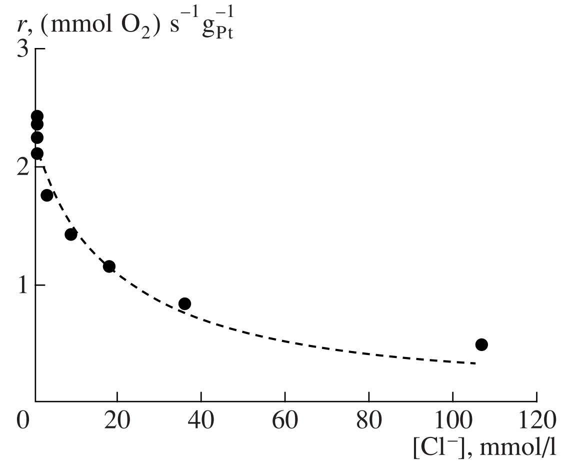


Fig. 4. Reaction rate as a function of the chloride ion concentration at $[FeSO_4] = 0.36$ mol/l, $[H_2SO_4] = 0.028$ mol/l, and $C_{O_2} = 1$ mmol/l.

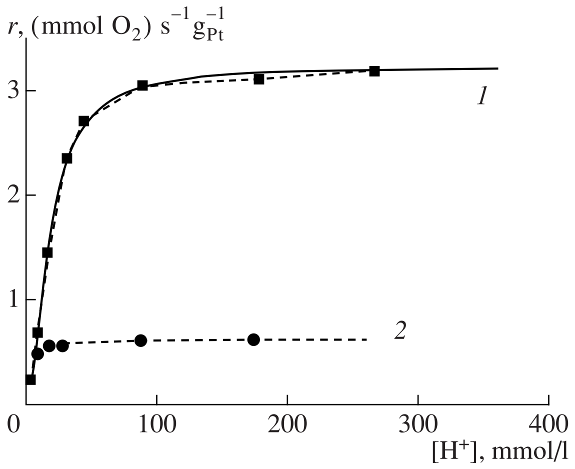


Fig. 5. Reaction rate as a function of acidity (*1*) in the absence of chloride ions and (*2*) in the presence of 0.09 mol/l HCl. $[FeSO_4] = 0.36$ mol/l, and $C_{O_2} = 1$ mmol/l.

Oxygen chemisorbed on platinum acquires a small negative charge, and, owing to this charge, the $Pt^{\delta+}$–$O_2^{\delta-}$ fragments can adsorb various cations. The specific adsorption of Zn^{2+}, Cd^{2+}, Ca^{2+}, and other cations was observed on platinum and palladium electrodes in the O_2 reduction reaction [57, 58]. The data listed in the table demonstrate that Fe(III) ions can be adsorbed by the platinum surface in the presence of oxygen:

$$ZO_2 + Fe^{3+}(H_2O)_6 \longrightarrow ZO_2\text{–}Fe^{3+}(H_2O)_6. \qquad \text{(II)}$$

We demonstrated in our earlier work [59] that the oxidation rate decreases over time. Furthermore, it was found that adding a small amount of Fe^{3+} reduces the order of the reaction with respect to Fe(II) (Fig. 2). These results can be explained by the inhibition of the reaction by its product. This inhibition is due to the competition between the initial reactant Fe(II) and the resulting Fe(III) for oxygen adsorbed on the platinum surface (reactions (II) and (III)).

$$ZO_2 + Fe^{2+}(H_2O)_6 \longrightarrow ZO_2\text{–}Fe^{2+}(H_2O)_6. \qquad \text{(III)}$$

Let us compare the data obtained in this study with the kinetic data that were obtained for the noncatalytic oxidation of Fe(II) complexes. The reaction order with respect to Fe(II) can be equal to unity, and this was actually observed in the oxidation of iron(II) pyrophosphate, phosphate, and chloride [12, 60]. A second-order kinetics was observed for the oxidation of iron(II) sulfate and perchlorate [15–17, 60]. As a rule, the bimolecular reaction is characterized by a higher activation energy and takes place at a higher temperature and in concentrated solutions [13, 60, 61]. At room temperature, the oxidation reaction can proceed via a bimolecular mechanism only in the presence of a strong Fe(II) complexing agent stabilizing the transition state [60]. Two trimolecular mechanisms have been reported, namely, (1) electron transfer from two iron(II) ions to oxygen in the μ-peroxo complex [17, 31, 60] and (2) the interaction of the superoxide with a second Fe(II)L ion [62, 63]. It was noted in some works that the rate of the rate-limiting step, which is the formation of a complex between Fe(II) and oxygen, can be increased by Fe(II)–O_2 complex stabilizers, such as multidentate ligands like ethylenediaminetetraacetate [31, 62] and the chloride ion [61]. Our finding that the reaction is zeroth-order with respect to Fe(II) suggests that, in the presence of a catalyst, the formation of the Fe(II)–O_2 complex is not the rate-limiting step. A similar kinetics of $FeSO_4$ oxidation with oxygen on a Pt/C catalyst was reported by Tabakova et al. [64], who described the mechanism of this process in electrochemical terms. In their opinion, platinum serves not only as a catalyst (oxygen activation on the Pt/C surface proceeds via a "peroxide" mechanism), but also as an electron conductor.

Fe(III) adsorption on the Pt/C catalyst

$[Fe_2(SO_4)_3]$, mmol/l	(mol Fe(III))/(mol Pt)
33	0.78
27	0.59
9.8	0.27
5.0	0.16
3.6	0.10
2.6	0.09

Note: Adsorption time, 10 min; $[H_2SO_4]$ = 0.032 mol/l; C_{O_2} = 1 mmol/l.

Note that the reaction scheme suggested by Tabakova et al. [64] does not explain the observed dependence of the reaction rate on the acid concentration (Fig. 5). It is interesting that, for the noncatalytic reaction, this dependence is quite different. For noncatalytic Fe(II) oxidation in acidic solutions at a low anion concentration, the reaction rate is independent of the proton concentration below pH 1 and decreases with increasing acidity above pH 1 [13, 15, 17, 60]. In the presence of a considerable amount of a ligand, the dependence of the reaction rate on pH is the opposite and is similar to the dependence observed in our study. For example, in concentrated chloride solutions of Fe(II) ([HCl] = 6–9 mol/l), the reaction rate increases with decreasing pH [15, 61]. For Fe(II) oxidation with oxygen in the presence of chelating ligands, the observed rate constant was found to be a linear function of $[H^+]$ above pH 2 and the reaction rate was observed to tend to some limit at high acidities [31]. The authors of that study concluded that protons catalyze iron(II) oxidation with oxygen through the formation of the intermediate $FeLO_2H$. The dependence of the catalytic oxidation rate on acidity observed in this study (Fig. 5, curve *1*) can be explained by protons being involved in the electron transfer step:

$$ZO_2\text{–}Fe^{2+}(H_2O)_6 + H^+ \longrightarrow Z + H\dot{O}_2 + Fe^{3+}(H_2O)_6. \qquad \text{(IV)}$$

The superoxide radical resulting from the one-electron reduction of oxygen reacts rapidly with Fe^{2+} in the solution via the Haber–Weiss mechanism [65].

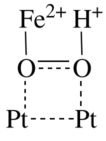
Investigation of the reaction in the presence of HCl has provided extra information about the reaction mechanism. The decrease of the activity of the catalyst caused by HCl would be expected a priori since there are many examples of the adverse effect of halide ions on the catalytic properties of platinum [56, 66, 67]. It is more interesting that, in the presence of chloride ions ($[Cl^-]$ = 0.09 mol/l), the reaction rate is independent of the acid concentration (Fig. 5, curve *2*) and shows a marked isotope effect ($r_H/r_D = 3$). It can be assumed that the oxygen reduction step in this case includes the transfer of a hydrogen atom from the coordination sphere of Fe(II), which is largely in the aqua complex state under the reaction conditions [17]:

$$ZO_2\text{–}Fe^{2+}(H_2O)_6 \longrightarrow ZO_2H\text{–}Fe^{3+}(H_2O)_5(OH^-). \qquad \text{(V)}$$

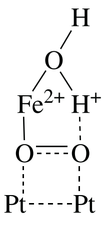
A similar mechanism of hydrogen atom transfer from an inner-sphere water molecule was suggested for electron exchange between Fe(II) and Fe(III) aqua ions in an aqueous perchlorate solution [68]. The k_H/k_D ratio in this case is 2.5. The hydrolyzed Fe(III) ion then reacts with a proton to yield an aqua complex:

$$\begin{aligned}&ZO_2H\text{–}Fe^{3+}(H_2O)_5(OH^-) + H^+\\ &\longrightarrow Z + H\dot{O}_2 + Fe^{3+}(H_2O)_6.\end{aligned} \qquad \text{(VI)}$$

Thus, Fe(II) oxidation can proceed via two pathways. In the first pathway, the one-electron oxygen reduction step involves protons (reaction (IV)); in the second, the formation of the superoxo radical $H\dot{O}_2$ involves water from the coordination sphere of Fe(II) aqua complexes (reaction (V)). It can be assumed that, when the reaction proceeds via the first pathway (reaction (IV)), the structure **A** is realized because the intermediate Pt–O_2–Fe(II) can be protonated. In the case of the second pathway, reaction (V) may proceed via the formation of a cyclic transition state (structure **B**). Oxygen reduction in this case is due to hydrogen atom transfer from the coordination sphere of Fe(II).



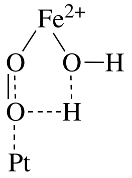
A



B

This assumption needs further investigation.

Oxygen can be adsorbed on platinum in linear and bridge forms [69]. Impurities blocking the platinum surface, such as chloride ions, will primarily diminish the probability of the reaction involving the bridging species because two adjacent platinum atoms should be available for the formation of a bridge. It is likely that, in the presence of chloride ions, Fe(II) oxidation takes place mainly on linear adsorption species, involving inner-sphere water of the Fe(II) aqua ions (reaction (V)). It is possible that the transition state has the following structure:



C

Thus, the oxidation of iron(II) sulfate with oxygen in acid solutions on the Pt/C catalysts is a complicated process and can proceed via two pathways. Initially, platinum adsorbs oxygen, and then Fe(II) and Fe(III) complexes with oxygen form on the oxygen-covered surface. The one-electron reduction of oxygen either involves protons of the medium or takes place through hydrogen atom transfer from the coordination sphere of the Fe(II) aqua complex. Suppose that, in the absence of chloride ions, oxygen is mainly adsorbed as bridging species on two-atom sites (Z_2). The mechanism of iron(II) sulfate oxidation with oxygen in acid solutions on the Pt/C catalysts in the absence of chloride ions via the pathways $N^{(1)}$ and $N^{(2)}$ will then be representable as

	$N^{(1)}$	$N^{(2)}$	
(1) $Z_2 + O_2 \longrightarrow Z_2O_2$	1	1	k_1
(2) $Z_2O_2 + Fe^{2+}(H_2O)_6 \longrightarrow Z_2O_2\text{–}Fe^{2+}(H_2O)_6$	1	1	k_2
(3) $Z_2O_2\text{–}Fe^{2+}(H_2O)_6 + H^+ \longrightarrow Z_2 + H\dot{O}_2 + Fe^{3+}(H_2O)_6$	1	0	k_3
(4) $Z_2O_2\text{–}Fe^{2+}(H_2O)_6 \longrightarrow Z_2O_2H\text{–}Fe^{3+}(H_2O)_5(OH^-)$	0	1	k_4
(5) $Z_2O_2H\text{–}Fe^{3+}(H_2O)_5(OH^-) + H^+ \longrightarrow Z_2 + H\dot{O}_2 + Fe^{3+}(H_2O)_6$	0	1	k_5
(6) $Z_2O_2 + Fe^{3+}(H_2O)_6 \rightleftarrows Z_2O_2\text{–}Fe^{3+}(H_2O)_6$	0	0	$K_6 = k_6/k_{-6}$

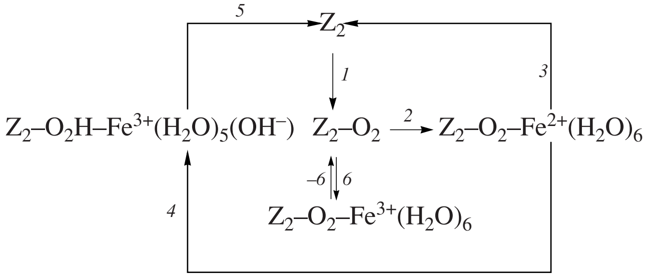
$Fe^{2+}(H_2O)_6 + O_2 + H^+ = Fe^{3+}(H_2O)_6 + H\dot{O}_2$

If, in the presence of chloride ions, oxygen is mainly adsorbed as linear species on single sites (Z_1), then the following scheme may be valid:

(7) $Z_1 + O_2 \longrightarrow Z_1O_2$	1	k_7
(8) $Z_1O_2 + Fe^{2+}(H_2O)_6 \longrightarrow Z_1O_2\text{–}Fe^{2+}(H_2O)_6$	1	k_8
(9) $Z_1O_2\text{–}Fe^{2+}(H_2O)_6 \longrightarrow Z\text{–}O_2H\text{–}Fe^{3+}(H_2O)_5(OH^-)$	1	k_9
(10) $Z_1O_2H\text{–}Fe^{3+}(H_2O)_5(OH^-) + H^+ \longrightarrow Z_1 + H\dot{O}_2 + Fe^{3+}(H_2O)_6$	1	k_{10}
(11) $Z_1O_2 + Fe^{3+}(H_2O)_6 \rightleftarrows Z_1O_2\text{–}Fe^{3+}(H_2O)_6$	0	$K_{11} = k_{11}/k_{-11}$
(12) $Z_1 + Cl^- \rightleftarrows Z_1Cl^-$	0	$K_{12} = k_{12}/k_{-12}$

$Fe^{2+}(H_2O)_6 + O_2 + H^+ = Fe^{3+}(H_2O)_6 + H\dot{O}_2$

The graph of the reaction in the absence of chloride ions appears as



After choosing spanning trees, we obtain the following expression for the reaction rate in the absence of chloride ions [70]:

$$r = \frac{k_1 k_2 [\mathrm{Fe}^{2+}] C_{\mathrm{O}_2}(k_3[\mathrm{H}^+] + k_4)}{k_2[\mathrm{Fe}^{2+}](k_3[\mathrm{H}^+] + k_4) + k_1 C_{\mathrm{O}_2}\left(k_3[\mathrm{H}^+] + k_4 + k_2[\mathrm{Fe}^{2+}]\left(1 + \frac{k_4}{k_5[\mathrm{H}^+]}\right) + k_6[\mathrm{Fe}^{3+}](k_3[\mathrm{H}^+] + k_4)\right)}, \quad (1)$$

where k_i is the rate constant of the ith reaction step; $[\mathrm{Fe}^{2+}]$, $[\mathrm{Fe}^{3+}]$, and $[\mathrm{H}^+]$ are the iron (II) sulfate, iron(III) sulfate, and acid concentrations, respectively; and $K_6 = k_6/k_{-6}$.

Equation (1) provides a good explanation for the observed kinetics. For the initial moment of the reaction, when Fe(III) ions are absent and the Fe(II) concentration is high, rate equation (1) takes the following form (if $k_2[\mathrm{Fe}^{2+}] \gg k_1 C_{\mathrm{O}_2}$):

$$r = \frac{k_1 C_{\mathrm{O}_2}(k_3[\mathrm{H}^+] + k_4)}{k_3[\mathrm{H}^+] + k_4 + k_1 C_{\mathrm{O}_2}\left(1 + \frac{k_4}{k_5[\mathrm{H}^+]}\right)}. \quad (2)$$

Equation (2) is in agreement with the observed zeroth order of the reaction with respect to Fe(II). At high acidities, the reaction rate reaches its limit and is independent of the proton concentration if $k_3[\mathrm{H}^+] \gg k_4$, $k_3[\mathrm{H}^+] \gg k_1 C_{\mathrm{O}_2}$, and $k_3 k_5[\mathrm{H}^+]^2 \gg k_1 k_4 C_{\mathrm{O}_2}$:

$$r = \frac{k_1 C_{\mathrm{O}_2} k_3 k_5 [\mathrm{H}^+]^2}{k_3 k_5 [\mathrm{H}^+]^2 + k_1 k_4 C_{\mathrm{O}_2}} = k_1 C_{\mathrm{O}_2}. \quad (3)$$

The dependence of the reaction rate on acidity at low $[\mathrm{H}^+]$ concentrations is expressed as

$$r = \frac{k_1 C_{\mathrm{O}_2}(k_3 k_5 [\mathrm{H}^+]^2 + k_4 k_5 [\mathrm{H}^+])}{k_3 k_5 [\mathrm{H}^+]^2 + k_4 k_5 [\mathrm{H}^+] + k_1 C_{\mathrm{O}_2}(k_4 + k_5[\mathrm{H}^+])}. \quad (4)$$

According to Eq. (4), the order of the reaction with respect to acid at low H^+ concentrations cannot be above unity, and this was actually observed experimentally at $[\mathrm{H}^+] = 4.5–18.2$ mmol/l. In the presence of Fe(III), if $k_2[\mathrm{Fe}^{2+}] \gg k_1 C_{\mathrm{O}_2}$, the rate equation will appear as

$$r = \frac{k_1 C_{\mathrm{O}_2}(k_3[\mathrm{H}^+] + k_4)}{(k_3[\mathrm{H}^+] + k_4) + k_1 C_{\mathrm{O}_2}\left(1 + \frac{k_4}{k_5[\mathrm{H}^+]} + \frac{K_6[\mathrm{Fe}^{3+}]}{k_2[\mathrm{Fe}^{2+}]}(k_3[\mathrm{H}^+] + k_4)\right)}. \quad (5)$$

Equation (5) accounts for the observations that the addition of Fe(III) increases the order of the reaction with respect to Fe(II) and that the order of the reaction with respect to Fe(III) is negative.

Likewise, after constructing the graph of the reaction and choosing spanning trees, we obtain the following expression for the reaction in the presence of chloride ions:

$$r = \frac{k_7 k_8 k_9 [\mathrm{Fe}^{2+}] C_{\mathrm{O}_2}}{k_8 k_9 [\mathrm{Fe}^{2+}](1 + K_{12}[\mathrm{Cl}^-]) + k_7 C_{\mathrm{O}_2}\left(k_9 + k_8[\mathrm{Fe}^{2+}]\left(1 + \frac{k_9}{k_{10}[\mathrm{H}^+]}\right) + k_9 K_{11}[\mathrm{Fe}^{3+}]\right)}, \quad (6)$$

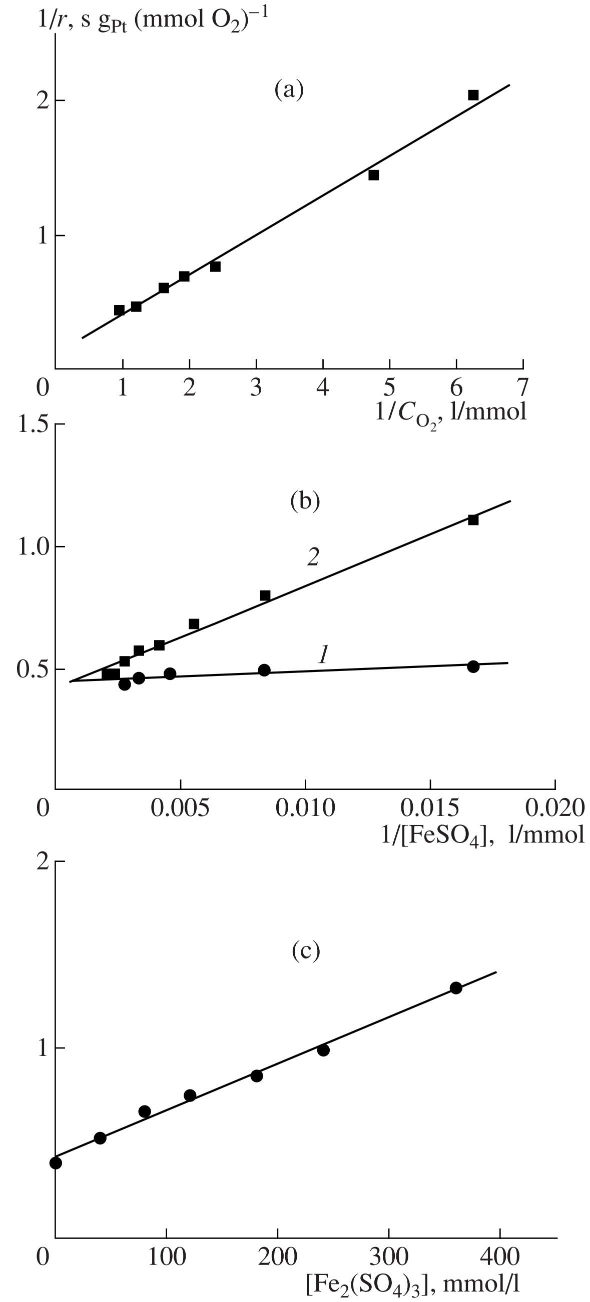


Fig. 6. $1/r$ versus (a) $1/C_{O_2}$, (b) $1/[Fe^{2+}]$, and (c) $[Fe^{3+}]$. (a) $[Fe^{2+}] = 0.36$ mol/l and $[H^+] = 0.032$ mol/l; (b) $[H^+] = 0.028$ mol/l, $C_{O_2} = 1$ mmol/l, and $[Fe^{3+}]$ = (*1*) 0 and (*2*) 0.03 mol/l; (c) $[Fe^{2+}] = 0.36$ mol/l, $[H^+] = 0.05$ mol/l, and $C_{O_2} = 0.9$ mmol/l.

where $K_{11} = k_{11}/k_{-11}$ and $K_{12} = k_{12}/k_{-12}$. It follows from Eq. (6) that chloride ions reduce the reaction rate and that, at high acidities, when $k_{10}[H^+] \gg k_9$, the reaction rate is independent of pH, and this is actually observed in experiments.

The rate equation (1) provides a quantitative description for the observed kinetics at the following values of the constants:

$$k_1 = 0.66 \text{ l mmol}^{-1} \text{ s}^{-1}, \quad k_2 = 0.041 \text{ l mol}^{-1} \text{ s}^{-1},$$

$$k_3 = 0.25 \text{ l mol}^{-1} \text{ s}^{-1}, \quad k_4 = 0.32 \text{ s}^{-1},$$

$$k_5 = 0.002 \text{ l mol}^{-1} \text{ s}^{-1}, \quad \text{and} \quad K_6 = 0.21 \text{ l/mmol}.$$

The coefficients of the rate equations were fitted so as to minimize the χ^2 criterion. In the minimization of χ^2, we used the Levenberg–Marquardt algorithm. The initial values were the coefficients determined graphically by linearizing Eq. (1):

$$\begin{aligned}\frac{1}{r} = {} & \frac{1}{k_1 C_{O_2}} + \frac{1}{k_2[Fe^{2+}]} + \frac{1}{k_3[H^+] + k_4} \\ & + \frac{k_4}{k_5[H^+](k_3[H^+] + k_4)} + \frac{K_6[Fe^{3+}]}{k_2[Fe^{2+}]}.\end{aligned} \tag{7}$$

The relationships thus obtained are plotted in Fig. 6. In order to illustrate the fit between the calculated and experimental data, we present the data calculated using the rate equation (1) (solid lines in Figs. 1–3; Fig. 5, curve *1*). The discrepancy between the experimental and calculated data does not exceed 10%; that is, it is within the experimental error.

Note the following aspect of the above reaction mechanism: this mechanism is consistent with the concept of the structural sensitivity of reactions [59]. According to the literature, fine metal particles differ in electronic properties from the bulk metal [71]. For example, the heat of adsorption of oxygen on fine particles is larger. Since the reactivity of adsorbed oxygen depends on the heat of adsorption, the specific activity of the Pt/C catalysts must depend on the particle size.

Thus, this kinetic study afforded practically important results. Firstly, we discovered that the Pt/C catalysts are highly active in strong acid media, in which noncatalytic oxidation with oxygen is negligible. While the rate of noncatalytic iron(II) sulfate oxidation decreases in proportion to the squared H^+ concentration, the oxidation rate in the presence of Pt/C increases as the solution pH is decreased down to 1.1. Therefore, the Pt/C catalysts are usable in strong acid solutions. Secondly, the rate of the reaction on Pt/C is nearly independent of the Fe(II) concentration. In the other cases, the order of the reaction at the same Fe(II) sulfate concentration is 1 to 2. This makes it possible to use the platinum catalysts in the oxidation of dilute iron(II) sulfate solutions. The platinum catalysts can be used in Fe(II) oxidation in media with a high ionic strength, including the oxidation of iron(II) in 20% zinc sulfate solutions. In view of this, the most promising application of these catalysts is obtaining high-purity Fe(III) compounds. At the same time, these catalysts can be used in hydrometallurgy, specifically, in the oxidative treatment of the solutions resulting from the oxidative leaching of ores.

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