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Catalytic Oxidation of Iron(II) Aqua Complex by Oxygen in the Presence of Palladium(II) Tetraaqua Complex

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Abstract—The catalytic oxidation of iron(II) with oxygen occurs along with an autocatalytic reaction between palladium(II) tetraaqua complex and iron(II) aqua complex in an oxygen atmosphere. The reaction is catalyzed by a compound of palladium in an intermediate oxidation state, presumably by a small palladium cluster formed in the course of the reduction of palladium(II) tetraaqua complex with iron(II) aqua complex.

Our previous kinetic study [1] established that oxidation of iron(II) aqua complex with palladium(II) tetraaqua complex occurs by an autocatalytic mechanism to give a small palladium cluster containing palladium in an intermediate oxidation state. The ability of the palladium cluster to catalyze oxidations with molecular oxygen is well known [2, 3]. In this context we might expect that in an oxygen atmosphere Fe(II) would undergo a catalytic oxidation with oxygen, initiated by products of a concurrent stoichiometric reaction between Fe(II) aqua ion and Pd(II) tetraaqua complex.

In the present work we studied the key role of the intermediate form of palladium, formed by reduction of Pd(II) tetraaqua complex with iron(II) aqua complex, in the activation of oxygen in aqueous solution.

The process in question represents a combination of two gross reactions (1) and (2).

$$2[\mathrm{FeH_2O})_6]^{2+} + [\mathrm{Pd(H_2O)_4}]^{2+} \longrightarrow 2[\mathrm{Fe(H_2O)_6}]^{3+} + \mathrm{Pd(0)}, \qquad (1)$$

$$4\mathrm{Fe}^{2+}_{\mathrm{aq}} + \mathrm{O_2} + 4\mathrm{H}^+ \xrightarrow{[\mathrm{Pd}]} 4\mathrm{Fe}^{2+}_{\mathrm{aq}} + 2\mathrm{H_2O}. \qquad (2)$$

It is known [4] that at 25–70°C and atmospheric pressure iron(II) aqua complex is not oxidized with oxygen at a noticeable rate in perchloric acid medium.

As is seen from Fig. 1, the kinetic curves of oxygen consumption are S-shaped, implying formation of an active species that promotes iron(II) oxidation with oxygen. The amount of reacted oxygen meets the stoichiometry of reaction (2). As the initial concentrations of Pd(II) and Fe(II) decrease, the induction period gets longer. It is important to note that the rate of oxygen consumption after completion of the induction period is constant up to complete conversion of iron(II) into iron(III). It is proportional to the initial concentration of Pd(II) tetraaqua complex and squared intial concentration of iron(II) aqua complex (Fig. 2) and takes form (3).

$$w_2 = k_{\mathrm{app}}[\mathrm{Pd}^{2+}_{\mathrm{aq}}]_0[\mathrm{Fe}^{2+}_{\mathrm{aq}}]^2_0. \qquad (3)$$

Here k_{app} is (0.9 ± 0.1) $\mathrm{l^2\,mol^{-1}\,s^{-1}}$ at 20°C.

With different initial concentrations of Pd(II) and iron(II) aqua complexes in reaction (1), similar kinetics of iron(II) formation are observed. This points to a genetic relation between reactions (1) and (2), i.e. reaction (1) generated such Pd(II) form that catalyzes both reaction between palladium(II) tetraaqua complex and iron(II) and oxidation of iron(II) aqua complex with oxygen.

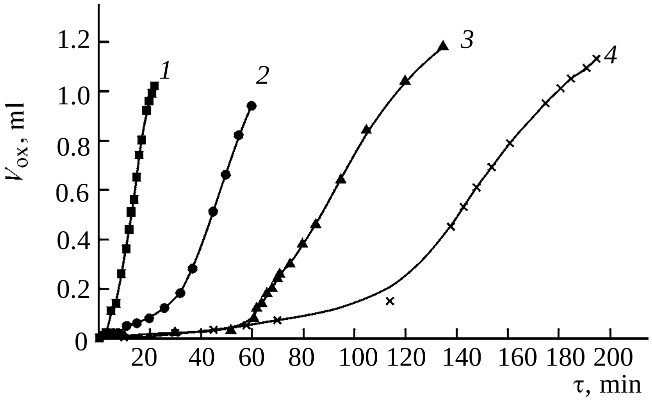


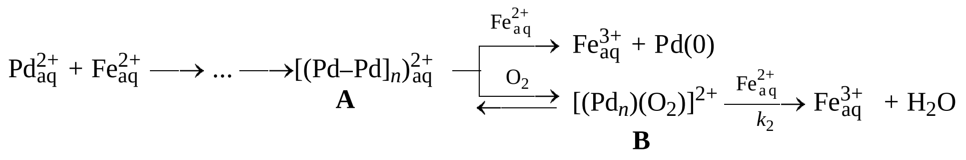
Fig. 1. Kinetic curves of oxygen consumption (V_{ox}). Initial concentration of Pd(II), mM: (*1*) 5, (*2*) 3.5, (*3*) 2, (*4*) 1 (20°C, p_{ox} 0.1 MPa, $[\mathrm{Fe}^{+2}]_0$ 2.5×10^{-2}, $[\mathrm{HClO_4}]$ 0.7 M).

In this case, increase in the partial pressure of oxygen should enhance the role of reaction (2) in iron(III) formation, and, therewith, the amount of palladium(II) reacted by reaction (1) will decrease. Actually, as follows from the table, the higher is the partial pressure of oxygen, the more reaction (2) contributes to iron(III) formation.

Temperature also affects the contribution of reaction (2) to iron(II) oxidation. As the temperature increases from 8 to 55°C, the role of reaction (2) becomes less and less essential (see table).

The latter circumstance is defined by the fact that the activation energy of iron(II) oxidation with Pd(II) tetraaqua complex is higher than the activation energy of reaction (2). In the present work we could not determine these activation energies, but their difference can be estimated on the basis of the following reasoning.

Analysis of our present and published data [1] shows that iron(II) oxidation both with palladium(II) tetraaqua complex and with oxygen is catalyzed by the same low-valence form of palladium, i.e. by a "small" palladium cluster, according to the following scheme.



According to this scheme, the rates of concurrent reactions (1) and (2) are w_1 and w_2, respectively [Eqs. (4) and (5)].

$$w_1 = k_1[\mathbf{A}][Fe^{2+}_{aq}], \tag{4}$$

$$w_2 = k_2[\mathbf{A}O_2][Fe^{2+}_{aq}]. \tag{5}$$

Here k_1 is the rate constant of reaction (1), k_2 is the rate constant of reaction (2), [A] is the concentration of active form **A** of palladium, and [$\mathbf{A}O_2$] is the concentration of palladium complex **B** with oxygen. Equilibrium (6) is established between **A** and **B**.

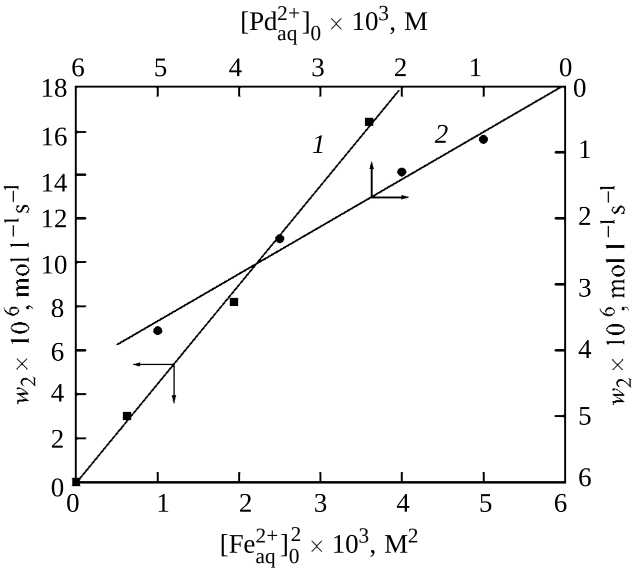


Fig. 2. Rate of reaction (2) vs. (*1*) squared initial concentration of Fe(II) ($[Pd^{2+}_{aq}]_0$ 5×10^{-3} M) and (*2*) initial concentration of Pd(II) ($[Fe^{2+}_{aq}]_0$ 2.5×10^{-2} M] (20°C, p_{ox} 0.1 MPa, [$HClO_4$] 0.7 M).

$$\mathbf{A} + O_2 \overset{K}{\rightleftarrows} \mathbf{B}. \tag{6}$$

The equilibrium concentration of complex **B** is related to the equilibrium concentrations of **A** and oxygen by Eqs. (7.1) and (7.2).

$$[\mathbf{A}]_\Sigma = [\mathbf{A}] + [\mathbf{B}], \tag{7.1}$$

$$[\mathbf{B}] = \frac{K[\mathbf{A}]_\Sigma[O_2]}{1 + K[O_2]}. \tag{7.2}$$

Substituting Eq. (7.2) into Eq. (5), we obtain Eq. (8) for the rate of iron(II) oxidation with oxygen.

$$w_2 = k_2[\mathbf{B}][Fe^{2+}_{aq}] = \frac{k_2K[\mathbf{A}]_\Sigma[O_2][Fe^{2+}_{aq}]}{1 + K[O_2]}. \tag{8}$$

Dividing Eq. (4) by Eq. (8) gives the required ratio (9) that is invariable at a particular temperature.

$$\frac{[Fe^{2+}_{aq}]_1}{[Fe^{2+}_{aq}]_2} = \frac{w_1}{w_2} = \frac{k_1}{k_2}\frac{1}{K[O_2]}. \tag{9}$$

The natural logarithm of the ratio between the concentrations of iron(III) formed by reactions (1) and (2) at a specified temperature will be proportional to the difference between the activation energies of reactions (1) and (2). Actually, the series of $Fe(III)_1/Fe(III)_2$ ratios makes a straight line in the ln $[Fe(III)_1/Fe(III)_2]$–$1/(RT)$ coordinates. Its slope corresponds to the difference between the activation energies and the enthalpy of formation of the palladium oxygen complex, $(E_{a(1)} - E_{a(2)} - \Delta H_0)$, which is equal to 50 ± 5 kJ/mol.

Comparison of the rate equation for reaction (2) [Eq. (8)] with the empirical dependence of the rate of this reaction on Fe(II) concentration [Eq. (3)] makes evident that the concentration of the catalytic-active form of palladium is a function of the initial concentrations of Fe(II) aqua complex and Pd(II) tetraaqua complex. Then Eq. (8) can be brought to form (10).

$$w_2 = \frac{k'_2 K[Pd^{+}_{aq}]_0 [O_2][Fe^{2+}_{aq}]^2_0}{1 + K[O_2]}. \qquad (10)$$

Hence the apparent rate constant k_{app} in Eq. (3) is defined by Eq. (11).

$$k_{app} = \frac{k'_2 K[O_2]}{1 + K[O_2]}. \qquad (11)$$

To obtain evidence showing that palladium black is not a catalyst of oxidation of Fe(II) aqua complex with oxygen, we performed the following experiment. After complete reduction of Pd(II) tetraaqua complex to Pd(0) by reaction (1) in an argon atmosphere at 20°C, we quickly replaced argon with oxygen. In this case, oxygen was not absorbed. Palladium black freshly formed by reduction of Pd(II) tetraaqua complex with potassium boron hydride, too, did not catalyze iron(II) oxidation with oxygen.

Oxidation of transition metal ions, in particular iron(II) perchlorate, with oxygen in aqueous solutions has been thiroughly [5, 6]. The reaction is believed to occur by the Fenton mechanism which includes formation of hydrogen peroxide and hydroxyl radical, i.e. is radical in nature.

When methanol is oxidized with oxygen in the Pd(II) tetraaqua complex–Fe(III) catalytic complex, about 40% of oxygen is consumed for iron(II) oxidation and 60%, for alcohol oxidation. Therewith, selective formation of the corresponding carbonyl compound, formaldehyde, is observed. This result suggests lack of free-radical formation of the carbonyl compound in this catalytic system.

Had the oxidation of iron(II) aqua complex with oxygen in the system under study followed a radical pathway, formaldehyde introduced into the initial solution would has been consumed to form formic acid, CO, and CO_2, like what is observed in the reaction of formaldehyde with Fenton reagent. However, the concentration of formaldehyde does not change in the course of iron(II) oxidation with oxygen in the presence of Pd(II) tetraaqua complex.

Effect of temperature and oxygen pressure on the rate of iron(II) oxidation ($[Pd^{2+}_{aq}]_0$ 5×10^{-3} M, $[Fe^{+2}]_0$ 2.5×10^{-2}, $[HClO_4]$ 0.7 M; p_{tot} 0.1 MPa)

T, °C	p_{ox}, MPa	$\Delta[Pd^{2+}_{aq}]$, mM[a]	$[Fe^{3+}_{aq}]$, mM[b]	$[Fe^{3+}_{aq}]_1/[Fe^{3+}_{aq}]_2$[c]
20	0.02	5	14	2.5
20	0.05	3.9	20	0.7
20	0.075	3.3	25	0.35
20	0.1	3	25	0.3
8	0.1	2	25	0.2
25	0.1	4	21	0.6
35	0.1	5	18	1.2
55	0.1	5	12	4

[a] Change in the concentration of palladium(II) tetraaqua complex. [b] Total concentration of iron(III) formed. [c] Ratio between the concentrations of iron(III) formed by reactions (1) and (2).

Thus, the reduction of palladium(II) tetraaqua complex with iron(II) aqua complex gives rise to an active form of palladium, where palladium is in an intermediate oxidation state. This form exhibits a high catalytic activity and a high affinity to oxygen. The activation of oxygen followed by reaction of palladium oxygen complex with iron(II) ions does not yield radical particles (hydroxyl radical). The oxidation occurs by a molecular (heterolytic) mechanism. This explains the observed high selectivity of the partial oxidation of lowest aliphatic alcohols and benzyl alcohol with oxygen in the palladium(II) tetraaqua complex–iron(II)/(III) system [1].

EXPERIMENTAL

The initial reaction solution was prepared by dissolving a batch of Mohr salt in a solution of palladium(II) tetraaqua complex. The iron(II) concentration was varied from 0.02 to 0.1 M. The concentration of perchloric acid was always 0.7 M.

The kinetics of iron(II) oxidation with oxygen in the presence of Pd(II) tetraaqua complex were followed by the consumption of oxygen, using a volumetric installation and a temperature-controlled shaken reactor. The reaction rate did not depend on the frequency of shaking. The volume of the reaction solution was 10 ml in all experiments. The partial pressure of oxygen was varied by diluting oxygen with argon.

The concentrations of palladium(II), iron(II), and formaldehyde were determined spectrophotometrically. Palldium (II) was analyzed in the form of a solution of a green complex obtained by adding excess tin(II) chloride solution to a sample to be analyzed [7], iron(III), in the form of a complex with sulfosalicylic acid [8], and formaldehyde, in the presence of sodium salt of chromotropic acid [9].

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