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Mechanism of the Reaction between the Aqua Complexes of Palladium(II) and Iron(II) in a Solution of $HClO_4$

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Abstract—The kinetics of the reaction of an aqua complex of iron(II) with a tetraaqua complex of palladium(II) in a perchloric acid solution was studied over the temperature range 20–55°C, and a reaction mechanism was proposed. It was found that the reaction is autocatalytic, and it occurs by a two-step one-electron transfer mechanism with the formation of iron(III) and palladium black. Based on the kinetic data, the nature of the autocatalysis in the test reaction was hypothesized.

INTRODUCTION

Electron transfer in redox reactions between *d*-metal complexes has been considered in a great number of publications [1–4].

Previously [5], we studied the oxidation of alcohols by iron(III) in the presence of a tetraaqua complex of palladium(II):

$$R^1R^2CHOH + 2Fe^{3+}_{aq} \xrightarrow{Pd^{2+}_{aq}} R^1R^2CHO + 2Fe^{2+}_{aq} + 2H^+. \quad (I)$$

We found that the rate of reaction (I) is independent of the initial concentration of Fe(III). At a degree of conversion of iron(III) approximately equal to 30%, palladium black rapidly precipitated from a homogeneous solution; this led to an increase in the concentration of Fe(III) and to the rupture of a catalytic cycle of alcohol oxidation (Fig. 1).

The shape of kinetic curves plotted as changes in the concentrations of Fe(III) and Pd(II) with time allowed us to assume that the following reaction rapidly occurs between the aqua ions of iron(II), which are accumulated in the course of reaction (I), and a tetraaqua complex of palladium(II):

$$2[Fe(H_2O)_6]^{2+} + [Pd(H_2O)_4]^{2+} \longrightarrow 2[Fe(H_2O)_6]^{3+} + Pd^0. \quad (II)$$

The use of the Pd(II)–Fe(III) catalytic system in the oxidation of organic and inorganic substances was reported [6–8]; however, we failed to find published data on the kinetics and mechanism of reaction (II). This work was devoted to studying the mechanism of Fe(II) oxidation by a tetraaqua complex of palladium(II).

EXPERIMENTAL

The reaction between a tetraaqua complex of palladium(II) and an aqua complex of iron(II) was performed in an aqueous $HClO_4$ solution with intense stirring in an argon atmosphere in a thermostatted reactor equipped with a sampler.

The $[Pd(H_2O)_4](ClO_4)_2$ complex was prepared in accordance with a published procedure [9]. Mohr's salt ($(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$) served as a source of iron(II). Iron(III) was introduced into the reaction solution as an $Fe_2(SO_4)_3 \cdot 9H_2O$ salt solution in perchloric acid.

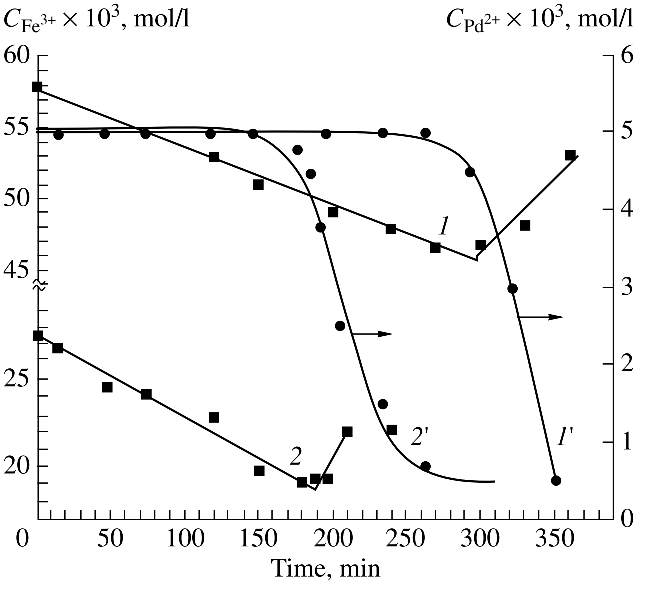

Fig. 1. Kinetic curves of (*1*, *2*) Fe^{3+} and (*1'*, *2'*) Pd^{2+} concentration changes in reaction (I): $[Fe^{3+}]_0$ = (*1*, *1'*) 0.06 or (*2*, *2'*) 0.03 mol/l; $[Pd^{2+}]_0 = 5 \times 10^{-3}$ mol/l; [MeOH] = 4 mol/l; $[HClO_4]$ = 0.7 mol/l; T = 55°C.

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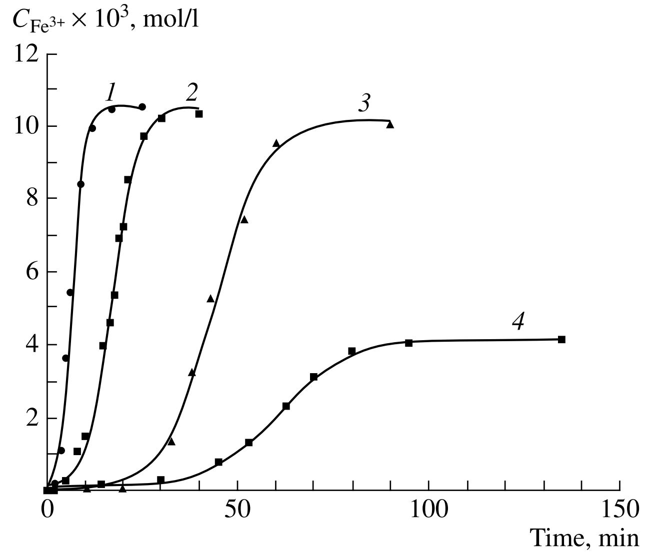

Fig. 2. Kinetic curves of Fe^{3+} formation in reaction (II) at various initial Fe^{2+} concentrations, mol/l: (*1*) 0.03, (*2*) 0.02, (*3*) 0.01, and (*4*) 0.005. $[Pd^{2+}]_0 = 5 \times 10^{-3}$ mol/l; $[HClO_4]$ = 0.7 mol/l; $T = 36°C$.

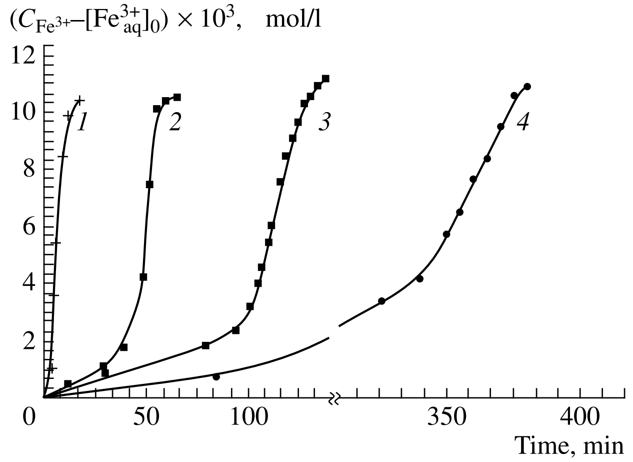

Fig. 3. Effect of the initial concentration of Fe^{3+} on the shape of the kinetic curves of Fe^{2+} formation according to the potentiometric data. $[Fe^{3+}]_0$, mol/l: (*1*) 0, (*2*) 0.004, (*3*) 0.008, and (*4*) 0.025. $[Pd^{2+}]_0 = 5 \times 10^{-2}$ mol/l; $[Fe^{2+}]_0 = 2.5 \times 10^{-2}$ mol/l; $[HClO_4]$ = 0.7 mol/l; $T = 36°C$.

The concentrations of the starting complexes and reagents were varied over the following ranges: from 0.001 to 0.005 mol/l for Pd(II), from 0.01 to 0.04 mol/l for Fe(II), from 0 to 0.04 mol/l for Fe(III), and from 0.3 to 3.6 mol/l for $HClO_4$. The concentration of Pd(II) was determined by spectrophotometry after the addition of an excess of an $SnCl_2$ solution to the test sample [10]. Iron(III) was determined by spectrophotometry as a complex with sulfosalicylic acid [11].

Freshly precipitated palladium black was prepared by the reduction of $[Pd(H_2O)_4](ClO_4)_2$ with potassium borohydride.

Because palladium(0) losses were unavoidable on sampling in the course of the reaction and the concentration of palladium(0) in solution could affect the rate of reaction, simultaneous kinetic measurements by potentiometry were performed in some cases without sampling the reaction solution. The potentiometric experiments were performed in a thermostatted reactor with a platinum electrode. A hydrogen electrode with an aqueous $HClO_4$ solution was used as a reference electrode. The concentrations of Fe(II) and Fe(III) were calculated from the Nernst equation.

As judged from the constants of hydrolysis [12], Pd(II), Fe(II), and Fe(III) occur as the corresponding aqua complexes in solutions over the perchloric acid concentration range tested (0.3–3.0 mol/l).

RESULTS AND DISCUSSION

Figure 2 demonstrates the kinetic curves of Fe(III) buildup in the course of oxidation of the iron(II) aqua complex by the tetraaqua complex of palladium(II) at various initial concentrations of Fe(II). The S-shaped kinetic curves suggest the autocatalytic character of the reaction. After an induction period, the rate of reaction remained constant up to the complete conversion of Pd(II) into palladium black. The duration of the induction period decreased with increasing initial concentration of palladium(II) ($[Pd^{2+}_{aq}]_0$), whereas the steady-state rate of Fe^{3+} formation in the developed step of oxidation increased.

As can be seen in Figs. 3 and 4, the duration of the induction period was directly proportional to the concentration of iron(III) added at the beginning of the reaction. At the same time, a change in the initial concentration of iron(III) ($[Fe^{3+}_{aq}]_0$) had an insignificant effect on the steady-state rate of the catalytic step of Fe(II) oxidation.

An increase in the duration of the induction period with the initial concentration of Fe^{3+} suggests that in the course of the reaction electron transfer takes place at the reversible step of the one-electron reduction of palladium(II) by iron(II):

$$Pd^{2+}_{aq} + Fe^{2+}_{aq} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Pd^{+}_{aq} + Fe^{3+}_{aq}. \qquad \text{(III)}$$

The resulting Pd^{+}_{aq} ion oxidizes the second iron(II) aqua ion:

$$Pd^{+}_{aq} + Fe^{2+}_{aq} \xrightarrow{k_2} Pd^0 + Fe^{3+}_{aq}. \qquad \text{(IV)}$$

However, reactions (III) and (IV) cannot explain the autocatalytic character of the oxidation of iron(II) by the tetraaqua complex of palladium(II), and the occurrence of palladium(I) as a mononuclear complex is unlikely [13].

The role of Pd(0) in redox processes with the participation of Pd(II) is well known. For example, the autocatalytic character of hydrogen [14, 15] and carbon monoxide [16] oxidation by palladium(II) complexes with anionic ligands are related to the above species.

It is well known that the colloidal particles of noble metals, such as gold, in contrast to bulk samples, exhibit enhanced reducing properties in aqueous solutions [17]. Therefore, we assumed that catalytically active colloidal particles of Pd(0) are formed in the course of reaction (IV). They react with the tetraaqua complex of palladium(II) to form a palladium(I) compound, the $[Pd_2]^{2+}$ cluster:

$$Pd^0 + Pd^{2+}_{aq} \rightleftharpoons [Pd_2]^{2+}_{aq}. \qquad (V)$$

To test this hypothesis, we performed experiments with the introduction of freshly prepared palladium black at the beginning of the reaction. In this case, the rate of the test reaction remained unchanged. Consistent kinetic data obtained using a sampling method and potentiometry are indicative of the absence of catalytic activity from palladium black formed in the course of the test reaction and of the homogeneity of the reaction phase.

By the end of the induction period, a quasi-steady-stage concentration of $[Pd_2]^{2+}_{aq}$ ions was attained. It is likely that these ions were converted into other species in the course of iron(II) oxidation in a steady-state region (reactions (VI)–(XII)).

$$[Pd_2]^{2+}_{aq} + Fe^{2+}_{aq} \xrightarrow{k_6} [Pd_2]^{+}_{aq} + Fe^{3+}_{aq}, \qquad (VI)$$

$$[Pd_2]^{+}_{aq} + Fe^{2+}_{aq} \longrightarrow [Pd_2]^{0} + Fe^{3+}_{aq}, \qquad (VII)$$

$$[Pd_2]^{0}_{aq} + Pd^{2+}_{aq} \rightleftharpoons [Pd_3]^{2+}_{aq}, \qquad (VIII)$$

$$[Pd_3]^{2+}_{aq} + Fe^{2+}_{aq} \longrightarrow [Pd_3]^{+}_{aq} + Fe^{3+}_{aq}, \qquad (IX)$$

$$[Pd_3]^{+}_{aq} + Fe^{2+}_{aq} \longrightarrow [Pd_3]^{0}_{aq} + Fe^{3+}_{aq}, \qquad (X)$$

$$[Pd_3]^{0}_{aq} + Pd^{2+}_{aq} \rightleftharpoons [Pd_4]^{2+}_{aq}\text{ , etc.,} \qquad (XI)$$

$$[Pd_n]^{2+}_{aq} \xrightarrow{k_{12}} [Pd_2]^{2+}_{aq} + [Pd_{n-2}]^{0}_{aq} \longrightarrow Pd^{0}_{black}. \qquad (XII)$$

In general, the concentration of active Pd^0_{aq} and $[Pd_2]^{2+}_{aq}$ species remained unchanged, as indicated by the steady-state rate of the reaction.

In special experiments, we found that the introduction of iron(III) into the reaction solution after an induction period did not affect the rate of the reaction; that is, iron(III) did not react with the catalytically active palladium species. This allowed us to consider the set of reactions (III)–(XII) as a homogeneous catalytic chain process, in which reaction (III) is the rate-limiting step of the formation of catalytically active species, reactions (VI)–(XI) are the steps of a chain reaction, and reaction (XII) is the formation of palladium black with the regeneration of the catalyst and the cluster species in a catalytic cycle. This reaction scheme explains autocatalysis in the test reaction.

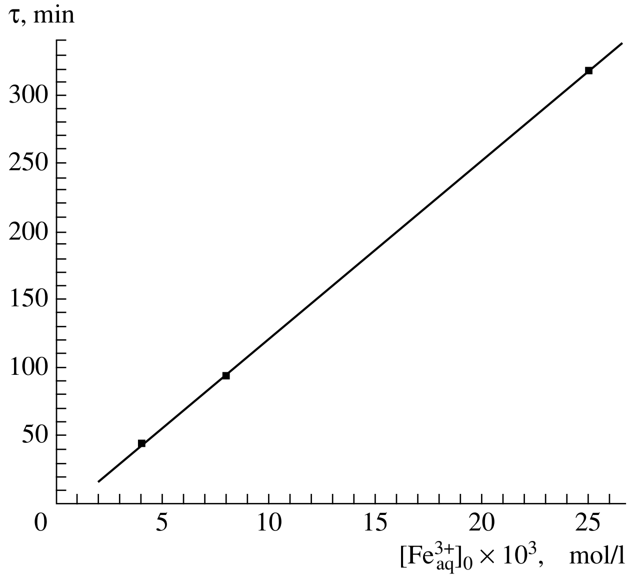

Fig. 4. Dependence of the length (τ) of an induction period on the initial concentration of Fe^{3+} at 36°C. $[Pd^{2+}]_0 = \times 10^{-3}$ mol/l; $[Fe^{2+}]_0 = 2.5 \times 10^{-2}$ mol/l; $[HClO_4] = 0.7$ mol/l.

Based on the experimental data, we can propose the following kinetic model for the test reaction: The rate of uncatalyzed Fe^{2+} oxidation by the tetraaqua complex of Pd^{2+} via reactions (III) and (IV) is equal to

$$w_{ind} = 1/2 w_{Fe^{3+}} = \frac{k_1 k_2 [Pd^{2+}_{aq}][Fe^{2+}_{aq}]^2}{k_{-1}[Fe^{3+}_{aq}] + k_2[Fe^{2+}_{aq}]}. \qquad (1)$$

With the constraint $k_2[Fe^{2+}_{aq}] \gg k_{-1}[Fe^{3+}_{aq}]$, we obtain

$$w_{Fe^{3+}} = 2k_1[Pd^{2+}_{aq}][Fe^{2+}_{aq}]. \qquad (2)$$

The rate of reaction in the catalytic (steady-state) process developed, which depends on the rate of reaction (VI), can be represented in the form

$$w_{cat} = k_6[Pd^{2+}_2][Fe^{2+}_{aq}]. \qquad (3)$$

On the assumption that the rate of formation of the $[Pd_n]^{2+}_{aq}$ species is equal to the rate of its decay

$$k_1[Pd^{2+}_{aq}][Fe^{2+}_{aq}] = k_{12}[Pd^{2+}_n],$$

$$[Pd^{2+}_n] = [Pd^{2+}_2] = \frac{k_1[Pd^{2+}_{aq}][Fe^{2+}_{aq}]}{k_{12}}$$

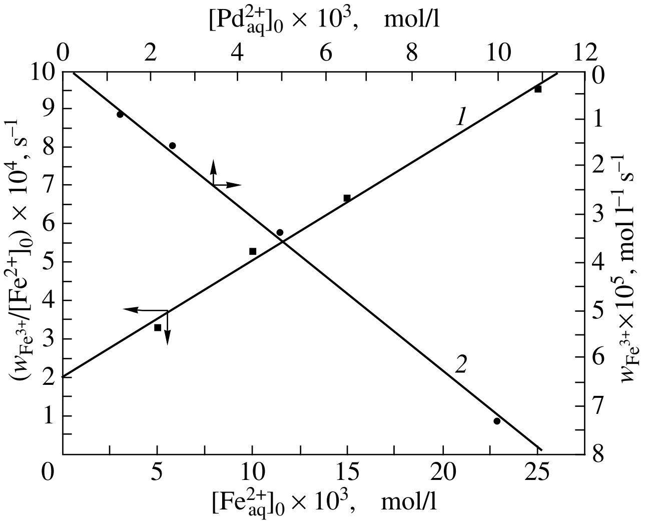

Fig. 5. Dependence of the apparent rate of Fe^{3+} formation on the initial concentrations of (*1*) Fe^{2+} and (*2*) Pd^{2+} at T = 36°C. $[HClO_4]$ = 0.7 mol/l; (*1*) $[Pd^{2+}_{aq}]_0 = 5 \times 10^{-3}$ mol/l; (*2*) $[Fe^{2+}_{aq}]_0 = 2.5 \times 10^{-2}$ mol/l.

Eq. (3) can be rearranged to the following form:

$$w_{cat} = k_{cat}[Pd^{2+}_{aq}][Fe^{2+}_{aq}]^2, \quad (4)$$

where $k_{cat} = k_1k_6/k_{12}$.

Then, the rate of reaction (II) is equal to

$$w_{Fe^{3+}} = 2k_1[Pd^{2+}_{aq}][Fe^{2+}_{aq}] + 2k_{cat}[Pd^{2+}_{aq}][Fe^{2+}_{aq}]^2. \quad (5)$$

Upon substituting experimental data in Eq. (5), the dependence of $w_{Fe^{3+}}/[Fe^{2+}]_0$ on $[Fe^{2+}]_0$ is expressed as a straight line (Fig. 5, line *1*). The slope of this straight line is proportional to the rate constant k_{cat}, and the intercept on the ordinate axis makes it possible to find the rate constant k_1. The rate constants at 36°C were calculated to be equal to $k_{cat} = (3.0 \pm 0.5)$ l^2 mol^{-2} s^{-1} and $k_1 = (2.0 \pm 0.3) \times 10^{-2}$ l mol^{-1} s^{-1}.

The above data allowed us to conclude that the redox reaction between the Fe^{2+} aqua ion and the tetraaqua complex of Pd^{2+} in an $HClO_4$ solution occurs by a chain one-electron mechanism with palladium autocatalysis. The rate of formation of iron(III) is proportional to the squared concentration of Fe^{2+}. The experimental data provide support for our previous hypothesis [5] on the participation of palladium in an intermediate oxidation state in the catalysis of alcohol oxidation by the palladium(II) tetraaqua complex–iron(III) aqua complex system.

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