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LETTERS TO THE EDITOR

Influence of Aromatic Compounds on Catalytic Oxidation of Alcohols in the System Pd(II) Tetraaqua Complex–Fe(III) Aqua Ion

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We have found previously [1] that aliphatic alcohols C_1–C_3 are catalytically oxidized to the corresponding carbonyl compounds in the system palladium(II) tetraaqua complex–iron(III) aqua ion. In the course of oxidation, palladium is reduced to the intermediate oxidation state Pd(I), which precedes formation of a small palladium cluster, an actual catalytic species [1, 2].

It is known that aromatic compounds, via π electrons of the ring, form complexes with palladium in lower oxidation state [3, 4].

Here we report that addition of a benzene derivative (nitrobenzene, acetophenone, benzonitrile, phenylacetonitrile) to the reaction system containing methanol, Pd(II) tetraaqua complex, and Fe(III) aqua ion ([MeOH] 4, $[Fe^{3+}]_0$ 0.03, $[Pd^{2+}]_0$ 5×10^{-3}, $[HClO_4]$ 0.7 M) in the temperature range 40–70°C increases the degree of Fe(III) conversion and the yield of the carbonyl compound. In all the cases, the concentration of the aromatic compound was 12×10^{-3} M. It is important that no palladium black formed during the time in which the Fe(III) concentration decreased.

The aromatic compounds do not affect the maximal rate of alcohol oxidation; it remains the same as in the reaction performed without these additives. In the presence of acetophenone, the conversion of Fe(III) was 67%, and with nitrobenzene, benzonitrile, and phenylacetonitrile it was 95%. Without these additives, the conversion of Fe(III) was as low as 30%.

Related compounds containing no phenyl group (i.e., nitromethane, acetone, or acetonitrile) exert no effect on the degree of Fe(III) conversion.

The capability of the carbonyl group in acetophenone for coordination with Pd is considerably lower than that of the functional groups of the other aromatic compounds studied. Therefore, the effect of acetophenone on the degree of Fe(III) conversion was the weakest.

Oxidation of alcohols with Fe(III) in the presence of Pd(II) tetraaqua complex is accompanied by accumulation of Fe(II) aqua ions, which, on reaching certain critical concentration, start to react with the initial Pd complex to form palladium black [1]. This breaks the catalytic cycle of alcohol oxidation. As we showed in [2], the catalytic species in autocatalytic oxidation of Fe(II) aqua ions with Pd(II) tetraaqua complex is low-valence Pd. Apparently, this state of Pd is stabilized by complexation with an aromatic compound, inhibiting the reaction between Pd(II) tetraaqua complex and Fe(II) ions formed under the conditions of alcohol oxidation. Therefore, the degree of Fe(II) conversion and the selectivity of alcohol oxidation with respect to formation of the carbonyl compound increase in the above catalytic system.

With benzonitrile and phenylacetonitrile, palladium black precipitates only after complete reduction of Fe(III), which is due to occurrence of a stoichiometric reaction between Pd(II) and alcohol. This fact indicates that, in the presence of the above nitriles, Fe(II) is not noticeably oxidized with Pd(II) tetraaqua complex.

Thus, the effect of the aromatic derivatives on the catalytic oxidation of alcohols in the system Pd(II) tetraaqua complex–Fe(III) aqua ion is due to the capability of the substituent in the benzene ring and of the aromatic ring itself for coordination with palladium in the intermediate oxidation state (small palladium cluster).

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REFERENCES

1. Potekhin, V.V., Solov’eva, S.N., and Potekhin, V.M., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2003, no. 12, p. 2420.
2. Potekhin, V.V., Matsura, V.A., Solov’eva, S.N., and Potekhin, V.M., *Kinet. Katal.*, 2004, vol. 45, no. 3, p. 629.
3. Allegra, G., Immirzi, A., and Porri, L., *J. Am. Chem. Soc.*, 1965, vol. 87, no. 6, p. 1394.
4. Allegra, G., Tettamant, G., Immirzi, A., Porri, L., and Vitulli, G., *J. Am. Chem. Soc.*, 1970, vol. 92, no. 2, p. 289.