

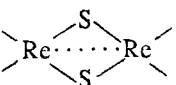
HYDROGENATION OF *m*-NITROCINNAMIC AND 3,5-DINITROBENZOIC ACIDS ON RHENIUM CLUSTERS

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UDC 541.128:542.941:547.
546:541.49:546.719

The catalytic properties of bi- and trinuclear rhenium thio complexes were investigated in liquid-phase hydrogenation of 3,5-dinitrobenzoic and m-nitrocinnamic acids. It was found that the selectivity of the processes for the corresponding amino acids and the efficiency of the clusters are higher if water, and not dimethylformamide, is used as the solvent. The catalytic efficiency of trinuclear rhenium thio complexes is higher than for binuclear complexes.

We previously showed in [1, 2] that mononuclear rhenium oxyhalide complexes with sulfur-containing ligands catalyze hydrogenation of monosubstituted nitrobenzenes only in conditions which promote formation of binuclear compounds with a

catalytically active site: . In liquid-phase reduction of *m*-nitrobenzoic acid (*m*-NBA) to *m*-aminobenzoic acid (*m*-ABA), trinuclear rhenium complexes are almost ten times more efficient [3].

We are continuing the study and comparison of the catalytic properties of bi- and trinuclear rhenium sulfide clusters in hydrogenation of more complex organic substances: 3,5-dinitrobenzoic (3,5-dNBA) and *m*-nitrocinnamic (*m*-NCA) acids. The presence of several functional groups capable of being reduced (two nitro groups in the molecule of 3,5-dNBA, a nitro group and double bond in the side chain of the benzene ring in the molecule of *m*-NCA) should introduce special characteristics in the hydrogenation of these substrates. We will assume that the results obtained in reduction of 3,5-dNBA and *m*-NCA can be compared with similar data for *m*-NBA and cinnamic acid (CA).

Re₂S₆Thio₃Cl₂, Re₂S₇, and Re₃S₇Cl₇ were used as the catalysts; MoS₂, Mo₂(S₂)₂Br₆ and Mo₃S₇Cl₄ were used in some experiments; dimethylformamide (DMF) and water were the solvents. The studies were conducted in the glass reactor of a volumetric setup at hydrogen pressure of 0.1 MPa. The products of hydrogenation of 3,5-dNBA were analyzed spectrophotometrically with the method we developed in [4]. Thin-layer chromatography (Silufol-254, mobile phase: mixture of methanol and chloroform in the ratio of 5:95) and methods of bromination and diazotization were used to monitor the evolution of reduction of *m*-NCA [5].

The studies showed that the rhenium thio complexes Re₂S₇, Re₂S₆Thio₃Cl₂, and Re₃S₇Cl₇, which we will call Re₂ and Re₃ for brevity, catalyze hydrogenation of nitro compounds to amino derivatives; the double bond in the side chain of cinnamic and *m*-nitrocinnamic acids is not reduced. The results of hydrogenation of the nitro groups of organic acids (*m*-nitrobenzoic, 3,5-dinitrobenzoic, and *m*-nitrocinnamic) in the presence of bi- and trinuclear rhenium clusters are reported in Fig. 1 and Table 1. The catalytic properties of the thio complexes are more effective if water, and not DMF, is used as the solvent.

Figure 1 shows that the rate of absorption of hydrogen by aqueous solutions of *m*-NBA and *m*-NCA in the presence of Re₂ and Re₃ (curves 1 and 3) changes in time in almost the same way, i.e., the presence of a double bond conjugated with a benzene ring has no marked effect on the rate of conversion of nitro groups in the molecule of *m*-NCA. A comparison of curves 1 and 2, 3, and 4, referring to hydrogenation of *m*-NBA and 3,5-dNBA, respectively, shows that reduction of the substrate

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TABLE 1. Catalytic Properties of Bi- and Trinuclear Rhenium Clusters (Re_2 and Re_3) in Hydrogenation of the Nitro Group in Organic Acids (solvent DMF/ H_2O)

Catalyst	Yield of amino acids, mole %	Selectivity, %	Efficiency 10^{-1} mole of product/mole of Re·h
<i>m</i> -NBA			
Re_2	20/64	60/70	1/14
Re_3	42/96	98/100	10/21
3,5-dNBA			
Re_2	33/58	77/86	2/8
Re_3	31/78	85/94	4/11
<i>m</i> -NCA			
Re_2	30/61	100/100	2/8
Re_3	34/81	100/100	5/11

Note. All indexes for Re_2 correspond to average values for Re_2S_7 and $\text{Re}_2\text{S}_6\text{Thio}_3\text{Cl}_2$.

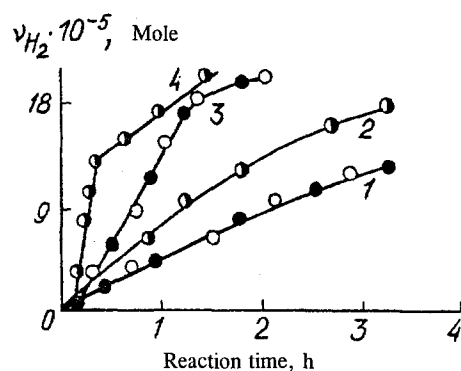


Fig. 1. Change in absorption of the amount of hydrogen (mole) vs. time of hydrogenation of the nitro group in organic acids *m*-NBA (●), 3,5-dNBA (○), and *m*-NCA (○) in aqueous solutions in the presence of bi- and trinuclear rhenium clusters Re_2 (1, 2) and Re_3 (3, 4). Concentration of rhenium $4.5 \cdot 10^{-3}$ M; concentration of acid $2.6 \cdot 10^{-2}$ M; volume of reaction mass 2.5 ml; temperature 343 K; hydrogen pressure 0.1 MPa.

with two functional groups takes place twice as rapidly. Accumulation of the intermediate product — nitroaminobenzoic acid — was not detected. In hydrogenation of 3,5-dNBA in the presence of Re_3 (curve 4), it was found that the reaction takes place in two stages: dinitrobenzoic acid is formed in the first stage. This is demonstrated by the fact that 2 moles of hydrogen are absorbed at the same rate for 25-30 min, and the reaction solution turns bright green, indicating accumulation of nitroso compounds. An inflection is then observed on the absorption curve: the second stage of the process is beginning — reduction of nitroso to amino groups, the rate decreases, and the solution gradually becomes colorless. The final product of the reaction is 3,5-diaminobenzoic acid (3,5-dABA). Curve 2 of absorption of hydrogen by aqueous solutions of 3,5-dNBA is smooth, although formation of nitroso compounds also cannot be excluded. These findings indicate that hydrogenation of 3,5-dNBA on rhenium clusters takes place via the stage of accumulation of nitroso derivatives, and both nitro groups are simultaneously transformed in the case of Re_3 .

The data in Table 1 show that in the presence of binuclear rhenium compounds, the selectivity for 3,5-dABA is 77% in DMF and 86% in water, while the selectivity is 85 and 94%, respectively for trinuclear complexes; both kinds of clusters have 100% selectivity for *m*-aminocinnamic acid. The efficiency of Re_3 clusters is 1.3-1.5 times higher in aqueous solutions than for Re_2 clusters.

The molybdenum analogs MoS_2 , $\text{Mo}_2(\text{S}_2)_2\text{Br}_6$, and $\text{Mo}_3\text{S}_7\text{Cl}_4$ do not exhibit catalytic activity in hydrogenation of these substrates in the hydrogen pressure range of 0.1-0.3 MPa at 343 K.

It was thus shown that sulfur-containing rhenium clusters are active catalysts of selective hydrogenation of the nitro groups in *m*-NCA and 3,5-dNBA to amino groups in aqueous solutions. Trinuclear rhenium thio complexes are probably more promising than mono- and binuclear complexes for more effective orientation of nitroaromatic acids in conducting one- and two-electron elementary events and for this reason are more promising in catalysis.

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