

EFFECT OF LIGANDS ON THE HYDROGENATION SELECTIVITY  
IN THE PRESENCE OF RHENIUM CATALYSTS

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It has been established that the catalytic activity of rhenium oxohalide complexes with phosphorus- or sulfur-containing ligands in hydrogenation of C<sub>6</sub>-C<sub>10</sub> olefins, nitrobenzene and p-nitrotoluene is primarily determined by the original ligand to rhenium ion bond. Chain length of olefins does not affect their hydrogenation rate.

Каталитическая активность рениевых оксогалогенидных комплексов с фосфор- или серосодержащими лигандами в реакциях гидрирования олефинов C<sub>6</sub>-C<sub>10</sub>, нитробензола и п-нитротолуола определяется прежде всего природой связи рений-лиганд в исходном комплексе. Длина цепи олефинов не влияет на скорость их гидрирования.

Hydrogenation of nitrobenzene and hexene-1 on metallic rhenium is known to proceed with comparable rates at temperatures above 373 K and  $P_{H_2} > 10^4$  kPa [1]. Soluble rhenium thio-complexes catalyze the reduction of nitrobenzene to aniline at atmospheric pressure and T=338 K, whereas under the same conditions hexene-1 is not hydrogenated [2]. We have established previously [3] that rhenium (V,VI) complexes with various

organophosphorus ligands are catalytically active in hydrogenation of hexene-1 at 338 K and  $P_{H_2} = 5.06 \times 10^3$  kPa.

The aim of the present study was to examine the effect of adding phosphorus- and sulfur-containing ligands on the catalytic properties of rhenium(V) oxohalide complexes in hydrogenation of  $C_6-C_{10}$  olefins, nitrobenzene and p-nitrotoluene.

$ReOHal_3(PPh_3)_2$  solutions (Hal=Cl or Br) in dimethylformamide become catalytically active in hydrogenation of  $C_6-C_{10}$  olefins at  $P_{H_2} = (1-20) \times 10^2$  kPa and  $T=354$  K. The dependence of conversion of the olefins examined on the time of their reduction on Cl- or Br-containing rhenium complexes with 8-fold excess of triphenylphosphine ( $PPh_3$ ) or 1-methyl-2-mercaptoimidazole (2-MI) and in their absence is illustrated in Fig. 1.

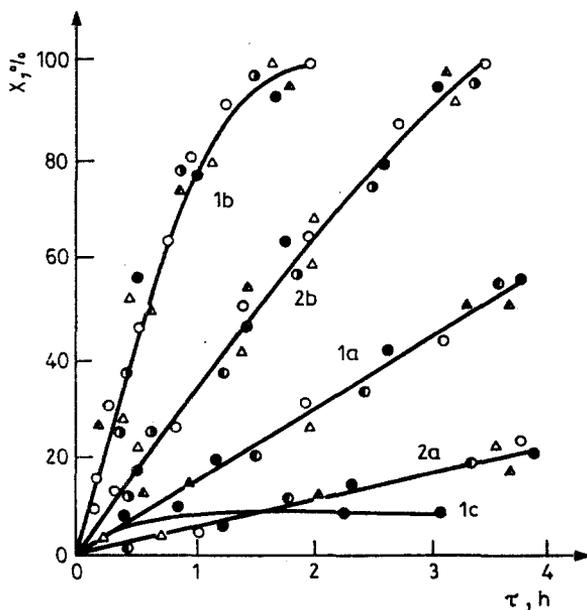


Fig. 1. Conversion of  $C_6-C_{10}$  olefins vs. hydrogenation time in the presence of  $ReOBr_3(PPh_3)_2$ , without ligands (1a), with an 8-fold excess of  $PPh_3$  (1b) or 2-MI (1c); in the presence of  $ReOCl_3(PPh_3)_2$ , without ligands (2a), with an 8-fold excess of  $PPh_3$  (2b)  
 -●-● - hexene, -○-○ - heptene, -△-△ - nonene,  
 -○-○ - octene, -△-△ - dodecene

It is seen that the chain length of these olefins does not affect their hydrogenation rate. Rhenium oxobromide complexes are 3-4 times more active than chlorine-containing analogs, an excess of  $\text{PPh}_3$  stabilizes the activity of rhenium complex, whereas the addition of excess 2-MI decreases the reaction rate. The latter phenomenon is apparently due to the partial formation of catalytically less active sulfur-containing fragments in hydrogenation of olefins [4].  $\text{ReOBr}_3(2\text{-MI})_2$  was found to be catalytically inactive.

The reduction rate of the nitro group of aromatic hydrocarbons, nitrobenzene and *p*-nitrotoluene in the presence of  $\text{ReOBr}_3(\text{PPh}_3)_2$  is lower compared with that of the olefins tested (Fig. 2). In the absence of complex forming additives (2-MI or  $\text{PPh}_3$ ) the process proceeds with an induction period. For nitrobenzene and *p*-nitrotoluene this period is 2 and 1 h, respectively. The 12 % conversion of nitrobenzene is observed after 6.5 h instead of 4.5 h for nitrotoluene, which indicates the higher reactivity of the latter. In the presence of 2-MI or  $\text{PPh}_3$  no induction period is observed. The nature of complexing ligands practically does not change the reaction rate. Nitrocompounds are hydrogenated on the rhenium triphenylphosphine oxobromide catalyst a thousand times faster than olefins (Figs 1,2). Nitrobenzene hydrogenation on  $\text{ReOBr}_3(2\text{-MI})_2$  has no induction period and its rate is 40 times greater than on  $\text{ReOBr}_3(\text{PPh}_3)_2$ .

Thus in hydrogenation of olefins and nitro-compounds a decisive role in the catalytic activity of rhenium contacts is played by the nature of the Re-S or RE-P bonds in the initial complex. The nature of substrate ligand is also important. In the case of  $\text{ReOHal}_3(\text{PPh}_3)_2$ , the chain length of  $\text{C}_6\text{-C}_{10}$  olefins does not affect the process rate, whereas in hydrogenation of aromatic hydrocarbons an activating action of the  $\text{CH}_3$ -group is observed. The addition of complex formation ligands (2-MI or  $\text{PPh}_3$ ) exerts a much weaker influence on the catalytic properties of rhenium complexes.

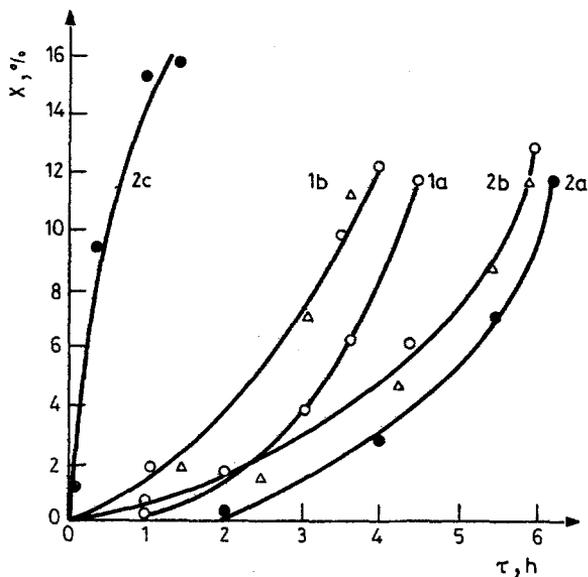


Fig. 2. Conversion of nitro-compounds vs. hydrogenation time in the presence of  $\text{ReOBr}_3(\text{PPh}_3)_2$ : for p-nitrotoluene without ligands (1a), with an 8-fold excess of 2-MI and  $\text{PPh}_3$  (1b); for nitrobenzene without ligands (2a), with an 8-fold excess of 2-MI and  $\text{PPh}_3$  (2b); on  $\text{ReOBr}_3(2\text{-MI})_2$  without ligands (2c)

-Δ-Δ- 2MI      -o-o-  $\text{PPh}_3$   
 $C_{\text{Re}} = 1.6 \times 10^2 \text{ M}$ ,       $P_{\text{H}_2} = 18 \times 10^2 \text{ kPa}$ ,  $T = 354 \text{ K}$

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