

INFLUENCE OF SUBSTITUENTS ON HYDROGENATION OF NITRO GROUPS  
IN AROMATIC HYDROCARBONS CATALYZED BY RHENIUM THIOCOMPLEXES

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Homogeneous hydrogenation studies of  $(\text{NO}_2)_{1-2}\text{-C}_6\text{H}_3\text{-4-L}$  nitro compounds (where L = -H,  $-\text{NH}_2$ ,  $-\text{COOH}$ ,  $-\text{CHO}$ ,  $-\text{OH}$ ,  $-\text{CH}_3$  and  $-\text{CH}=\text{CH}-\text{COOH}$ ) catalyzed by  $\text{Re}_2\text{S}_6\text{Thio}_3\text{Cl}_2$  in dimethylformamide solutions at  $P_{\text{H}_2} = 0.1$  MPa and  $T = 343$  K, have revealed that the reaction is enhanced by electron-acceptor substituents and hindered by electron-donor ones.

Исследовано гомогенное гидрирование нитросоединений типа  $(\text{NO}_2)_{1-2}\text{-C}_6\text{H}_3\text{-4-L}$ , где L = -H,  $-\text{NH}_2$ ,  $-\text{COOH}$ ,  $-\text{CHO}$ ,  $-\text{OH}$ ,  $-\text{CH}_3$ ,  $-\text{CH}=\text{CH}-\text{COOH}$ , в присутствии тиокомплекса рения  $\text{Re}_2\text{S}_6\text{Thio}_3\text{Cl}_2$  в диметилформамидных растворах при  $P_{\text{H}_2} = 0,1$  МПа и 343 К. Установлено, что реакция ускоряется электроноакцепторными и тормозится электронодонорными заместителями.

Aromatic amines are produced largely by the reduction of the appropriate nitro compounds on various catalysts. But the literature data on the reduction of aromatic nitro compounds by molecular hydrogen under homogeneous catalytic conditions are scarce [1]. In the hydrogenation of nitrobenzoic acids homogeneous platinum catalysts lose their catalytic activity [2]. Here we present the results of our hydrogenation studies for several aromatic nitro compounds on a soluble  $\text{Re}_2\text{S}_6\text{Thio}_3\text{Cl}_2$  catalyst [3].

Chemical grade nitroanilines (NA), p-nitrophenol (p-NPh), analytical grade nitrobenzene (NB), p-, o-nitrobenzaldehydes (p-, o-NBd), p-, o-nitrotoluenes (p-, o-NT), m-nitro- and m-dinitrobenzoic acids (m-NBA and m-dNBA), m-dinitrobenzene (m-dNB), m-nitrocinnamic acid (m-NCA), and o- and p-nitrobenzoic acids (o-NBA and p-NBA) synthesized like in Ref. [4] and purified by recrystallization from water, were used.

Hydrogenation rate of nitro groups was measured according to the rate of hydrogen consumption. The content of benzene amino derivatives in the reaction products was determined using the nitrosation method [5]. Accumulation of aniline and toluidines in the reaction mixture with time was followed chromatographically.

Data on the hydrogenation of aromatic nitrocompounds are listed in Table 1 and illustrated in Fig. 1.

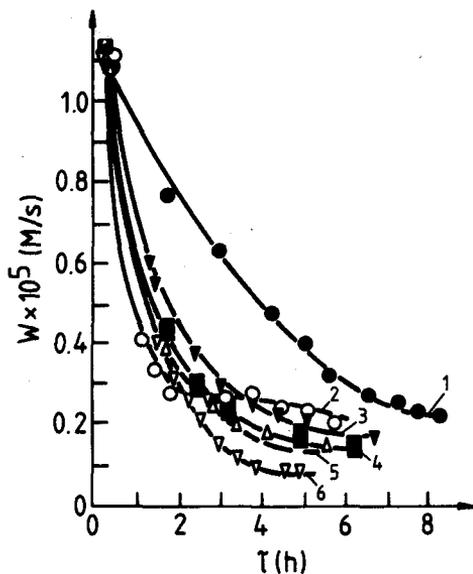


Fig. 1. Time dependence of hydrogenation rate for aromatic nitro compounds on  $\text{Re}_2\text{S}_6\text{Thio}_3\text{Cl}_2$ : 1 - m-dNBA, 2 - o-NBA, 3 - n-NBA, 4 - NB, 5 - m-NCA, 6 - m-NBA

Table 1

Hydrogenation of aromatic nitro compounds on the rhenium thiocomplex.  $[Re] = 4.5 \times 10^{-3} M$ ,  $[substrate] = 2.8 \times 10^{-2} M$ , solvent - dimethylformamide,  $T = 343 K$ ,  $P_{H_2} = 0.1 MPa$ ;  
 $W_C = W_O = 1.1 \times 10^{-5} \text{ mol/dm}^3 \text{ s}$  ( $t=0.5 \text{ h}$ )

Substrate	Time	$W \times 10^6$	Amine yield	Selectivity
	(h)	( $\text{mol/dm}^3 \text{ s}$ ) ( $t=1 \text{ h}$ )	(mol %)	(%)
NB	5	3.3	22	55
p-NT	4	4.2	36	89
o-NT	3	4.6	33	68
p-NPh	7.5	2.4	36	88
m-NA	4	2.6	10	39
p-NA	3	0.9	0	0
o-NA	3	1.6	3	22
p-NBd	8	2.6	44	74
o-NBd	4	5.9	70	99
m-dNB	14.5	4.2	51	97
m-NBA	7	2.6	16	37
p-NBA	7	3.8	35	49
o-NBA	8	2.8	82	90
m-NCA	7	2.8	34	100
m-dNBA	7	6.4	34	74

For the first half hour, the rate of hydrogen consumption ( $W_O$ ) remains unchanged, irrespective of the substrate. It is also equal to the rate of hydrogen consumption by the catalytic solution ( $W_C$ ) during the formation of active species. For this period of time, the molar ratio of the gas consumed and the rhenium charged was found to be 1:1. In the case of nitroanilines, one can observe catalyst deactivation by accumulated semiproducts and the yield of diamines is as high as 10 mol. In hydrogenation of the other substrates, after about 30% conversion, the rate of hydrogen consumption remains practically unchanged. The main end product of the hydrogenation of all

nitro compounds examined proved to be the amine; its yield after 8 h reaction is as high as 40-80 mol % and the selectivity amounts to 70-100 %.

According to the initial rates of hydrogen consumption, nitro compounds can be arranged in the sequence:  $m\text{-dNBA} > o\text{-NBd} > o\text{-NT} > m\text{-dNB} = p\text{-NT} > p\text{-NBA} > \text{NB} > m\text{-NCA} = o\text{-NBA} > p\text{-NBd} = m\text{-NBA} > m\text{-NA} > p\text{-BPh} > o\text{-NA} > p\text{-NA}$ . It is evident that various substituents differently affect the reactivity of nitro groups in aromatic hydrocarbons. According to the general electronic concepts of organic chemistry, catalytic hydrogenation of substituted nitrobenzenes to amines, which are reaction products exhibiting a direct resonance effect, are more satisfactorily described by the Hammett equation using the substituent constants  $\sigma^*$  [6]. The literature lacks a numerical value of  $\sigma^*$  for the  $-\text{CH}=\text{CH}-\text{COOH}$  substituent. Hence we used  $\sigma = 0.141$ .

A logarithmic dependence of the consumption rate for hydrogen on the substituent constants is shown in Fig. 2. Application of the reaction rate rather than its constant to obtain such a correlation, is valid, since under our experimental conditions, the reaction proved to be first order with respect to substrate.

Analysis of experimental data shows that the electron-acceptor groups enhance and the electron-donor ones hinder the nitro group hydrogenation. An activating effect of the electron-acceptor groups on the reduction of substrates can be illustrated by comparison of the rates of hydrogen consumption by NB and  $m\text{-dNB}$ ,  $m\text{-NBA}$  and  $m\text{-dNBA}$ . Upon introducing the electron-acceptor  $\text{NO}_2$  group into the ring of NB and  $m\text{-NBA}$ , the hydrogenation rate increases by a factor of 1.3 and 2.5, respectively. But if an electron-donor group, e.g.  $\text{NH}_2$ , is introduced, the reaction rate decreases by a factor of 1.3 (Table 1). Hence, the nitro group reduction is promoted by the lowered electron density at the reaction center (nitrogen atom). This is also confirmed by the fact that the reaction constant calculated as the slope of the straight line,  $\lg W = f(\sigma^*)$ , has a positive sign ( $\rho = 0.24$ ).

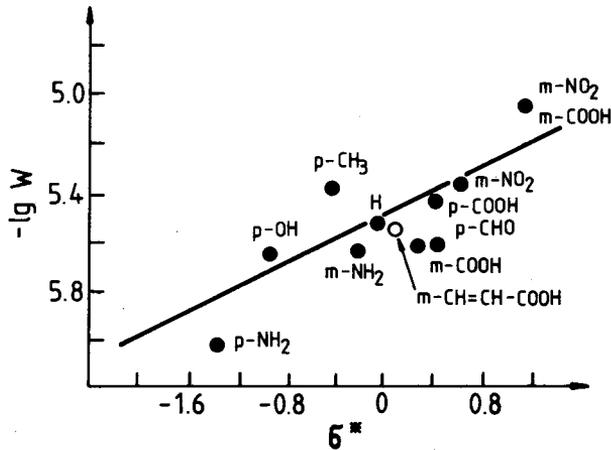


Fig. 2. Correlation between  $\lg W$  and  $\sigma^*$  for catalytic hydrogenation of aromatic nitro compounds on  $\text{Re}_2\text{S}_6\text{Thio}_3\text{Cl}_2$  in dimethylformamide solutions at  $P_{\text{H}_2} = 0.10$  MPa and  $T = 343$  K

Thus the results indicate that a complex of the composition  $\text{Re}_2\text{S}_6\text{Thio}_3\text{Cl}_2$  is a specific homogeneous catalyst for the hydrogenation of nitro groups in all aromatic hydrocarbons examined. Homogeneous catalysts can be applied for the hydrogenation of nitrobenzoic acids. Reactivity of nitro group is dependent on the nature and position of substituents in the aromatic ring. It is expressed in the form of the Hammett correlation with a satisfactory agreement between the experimental and calculated values using the equation  $\lg W = \rho\sigma^*$  data.

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