

## PROPERTIES OF HOMOGENEOUS AND HETEROGENEOUS RHENIUM CATALYSTS IN THE HYDROGENATION OF NITRO COMPOUNDS

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(Received August 27, 1989; accepted December 23, 1989)

### Summary

The behaviour of soluble rhenium(V) oxohalide complexes with coordinatively bound thiourea, triphenylphosphine and their derivatives has been studied in the hydrogenation of C<sub>6</sub>–C<sub>10</sub> olefins, nitrobenzene and *p*-nitrotoluene. Under homogeneous conditions rhenium complexes containing a Re—S bond were found to catalyze the reduction of the nitro group selectively, whereas those involving a Re—P bond catalyze the reduction of olefins.

Activated rhenium thiourea complexes have been isolated in the solid state from the reaction medium. Their analogs, thio complexes, displaying similar physicochemical properties and catalytic activity, and which work without an induction period under atmospheric pressure have been synthesized.

In the hydrogenation of 15 substituted nitrobenzenes, soluble rhenium complexes and solid rhenium heptasulfide were found to possess similar catalytic activities due to having the same catalytic center. The hydrogenation of the nitro group is accelerated by electron-acceptor functional groups and is inhibited by electron-donor ones.

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### Introduction

Heterogeneous rhenium compounds act as highly efficient and selective catalysts in hydrogenation reactions [1], and are resistant to catalytic poisons. There is little information on homogeneous hydrogenation on rhenium complexes [2]. To elucidate the relationship between homogeneous and heterogeneous catalysis, the behaviour of homogeneous and heterogeneous rhenium catalysts should be examined and compared.

The present paper considers a specific role of organo-sulfur or organo-phosphorus ligands capable of forming a homogeneous rhenium catalytic center displaying different selectivities in the hydrogenation of olefins and nitro compounds.

To elucidate the nature of the catalytic action of the active center under homogeneous and heterogeneous conditions, it is necessary:

- (1) to determine which soluble rhenium complexes are the most active and selective in the hydrogenation of the nitro group of substituted nitrobenzenes;
- (2) to isolate solid active rhenium complexes;
- (3) to examine the composition and structure of the complexes isolated;
- (4) to select their analogs among heterogeneous catalysts;
- (5) to compare the catalytic behaviour of the soluble and solid rhenium catalysts in the hydrogenation reactions.

## Experimental

The following rhenium oxohalide complexes with organo-phosphorus ligands have been used as catalysts:

- $\text{ReOHal}_3\text{L}_2$  (where  $\text{Hal} = \text{Cl}, \text{Br}$ ;  $\text{L} =$  thiourea (Tu), 2-mercaptobenzothiazole (2-MBT), 2-mercaptobenzoimidazole (2-MBI), 1-methyl-2-mercaptoimidazole (2-MI), triphenylphosphine ( $\text{PPh}_3$ ), 1,2-bis(diphenylphosphino)ethane (P—P), 1,2-bis(diphenylphosphino)ethene (P=P) synthesized by the procedures reported in [3, 4]),
- rhenium thiocomplex  $\text{Re}_2\text{S}_6\text{Tu}_3\text{Cl}_2$  (elemental analysis:  $[\text{Re}] = 42\text{--}43\%$ ;  $[\text{S}] = 32.5\text{--}33.5\%$ ;  $[\text{N}] = 8.8\text{--}9.5\%$ ;  $[\text{Cl}] = 8.2\text{--}9.5\%$ ) synthesized from alkali metal perrhenates in 6 M HCl solution with an 8-fold excess of thiourea in argon atmosphere at 368 K, sedimentation time 2 h [5],
- rhenium heptasulfide  $\text{Re}_2\text{S}_7$ , obtained from the interaction of lithium perrhenate in hydrochloric acid solution with hydrogen sulfide.

Linear  $\text{C}_6\text{--C}_{10}$  olefins with a terminal double bond, aromatic nitro compounds of the  $(\text{NO}_2)\text{C}_6\text{H}_4\text{L}$  type (where  $\text{L} = \text{—H}, \text{—NH}_2, \text{—COOH}, \text{—CHO}, \text{—OH}, \text{—CH=CHCOOH}, \text{—NO}_2$ ), as well as 3,5-dinitrobenzoic acid have been examined as substrates.

Hydrogenation tests were conducted at a hydrogen pressure ranging from 0.1 to 4.0 MPa and at temperatures varying from 343 to 368 K. Dimethylformamide has been chosen as a solvent.

The content of the reaction products, alkanes and aromatic amines, was determined chromatographically. In addition, the accumulation of amines was verified by diazotization.

The rate of hydrogen absorption by the reaction solutions corresponds to the rate of hydrogenation of nitro compounds. The rate of olefin hydrogenation was determined from the rate of alkane accumulation using chromatography.

## Results

It has been established that, under given conditions of catalysis, only the nitro group reduces, while the benzene ring and other functional groups are not affected. In olefins, the double bond exclusively is hydrogenated; isomers are not formed.

Figure 1 shows the change in the conversion of nitro compounds (nitrobenzene, NB, and *p*-nitrotoluene, *p*-NT) and C<sub>6</sub>-C<sub>10</sub> olefins in the presence of rhenium-coordinated oxobromide complexes involving 2-MI and PPh<sub>3</sub> and that of the same complexes with 2-MI and PPh<sub>3</sub> taken in excess [6]. It is seen that on ReOBr<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> NB and *p*-NT are reduced one thousandth as fast as olefins and the rate of olefin reduction is not affected by the hydrocarbon chain length. ReOBr<sub>3</sub>(2-MI)<sub>2</sub> proved to be inactive in the hydrogenation of olefins.

In the absence of complex-forming additives (2-MI or PPh<sub>3</sub>) the hydrogenation of nitro compounds on the rhenium triphenyl-phosphine complex proceeds with an induction period. For NB and *p*-NT, this period is 2 and 1 h, respectively. The reduction rate of NB is less than that for *p*-NT. With an 8-fold excess of 2-MI or PPh<sub>3</sub> relative to the rhenium complex, no induction period was detected. The hydrogenation of nitrobenzene on ReOBr<sub>3</sub>(2-MI)<sub>2</sub> occurs without an induction period and its rate is 40 times faster than on ReOBr<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>.

The effect of the nature of the ligand environment in the rhenium complexes on the catalytic activity and selectivity of the nitro group and olefin bond hydrogenation is illustrated in Table 1, which lists the specific rates of nitrobenzene and hexene-1 reductions [7].

Sulfur-containing rhenium oxohalide complexes become active at atmospheric pressure either after their preliminary treatment at a hydrogen

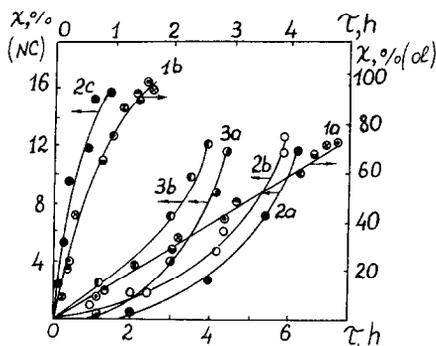


Fig. 1. Change in the conversion of C<sub>6</sub>-C<sub>10</sub> olefins, nitrobenzene and *p*-nitrotoluene on the soluble rhenium(V) oxohalide complexes. 1 = C<sub>6</sub>-C<sub>10</sub> olefins (C<sub>6</sub>-○-○-○, C<sub>7</sub>-⊗-⊗-⊗, C<sub>8</sub>-⊙-⊙-⊙, C<sub>9</sub>-●-●-●, C<sub>10</sub>-⊖-⊖-⊖); 2 = nitrobenzene; 3 = *p*-nitrotoluene; a = ReOBr<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>; 1b = ReOBr<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> with 8-fold excess of triphenylphosphine; 2b, 3b = ReOBr<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> with either 8-fold excess of triphenylphosphine or 1-methyl-2-mercaptoimidazole; c = ReOBr<sub>3</sub>(2-MI)<sub>2</sub>.

TABLE 1

Effect of the ligand composition in complexes of the  $\text{ReOHal}_3\text{L}_{1-2}$  type on ratio of productivity (A) to concentration of rhenium in nitrobenzene and hexene-1 hydrogenation

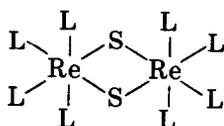
Complex		$A/[\text{Re}] \times 10^4$ ( $\text{s}^{-1}$ )	
Hal	L	Nitrobenzene	Hexene-1
Cl	2-mercaptobenzothiozole	3.1	0.0
	2-mercaptobenzoimidazole	1.1	0.0
	1-methyl-2-mercaptoimidazole	0.44	0.0
Br	2-mercaptobenzothiozole	13.5	0.0
	2-mercaptobenzoimidazole	3.3	0.0
	1-methyl-2-mercaptoimidazole	1.7	0.0
Cl	triphenylphosphine	0.05	54.4
	1,2-bis(diphenylphosphino)ethane	—	0.38
Br	triphenylphosphine	—	144.0
	1,2-bis(diphenylphosphino)ethylene	—	128.0

$P_{\text{H}_2} = 4 \text{ MPa}$ ,  $T = 368 \text{ K}$ , substrate concentration  $0.2 \text{ M}$ .

pressure of 4 MPa and 368 K or after admittance of the optimal amount of the complex-forming organic additives involved in the outer coordination sphere of the complexes.

The IR spectra for the activated solutions of rhenium complexes do not contain the band at  $960\text{--}1000 \text{ cm}^{-1}$  corresponding to the  $\text{Re}=\text{O}$  group.

We have managed to isolate the solid compounds from these solutions and examine their composition and structures [5]. Elemental analysis, IR spectra, measurements of molecular mass (850–900) and conductivity indicate that the compounds isolated are a mixture of thio complexes with excess coordinate sulfur, in which binuclear clusters predominate:



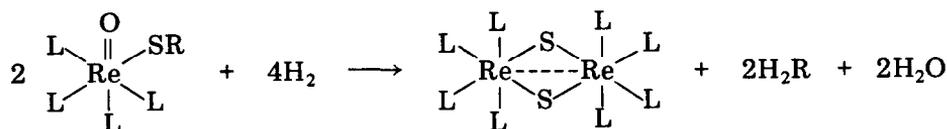
where  $L = \text{Tu}, \text{Cl}, \text{H}_2\text{O}$ .

A decrease in the frequency of  $\text{C}=\text{S}$  bond stretching vibrations from  $730$  to  $700 \text{ cm}^{-1}$  and no change in that for  $\delta \text{NH}_2$  vibrations at  $1612 \text{ cm}^{-1}$  in the IR spectra indicate the presence of thiourea coordinated by rhenium via a sulfur atom in the thio complex.

The thio complex formation requires excess of a sulfur-containing ligand, since it acts as both a ligand and a sulfidizing additive simultaneously.

The desulfurization of the initial rhenium complex occurs in the

presence of hydrogen:



With thiourea oxohalide complexes, hydrogen may be replaced by an inert gas, *e.g.* argon, since thermal treatment facilitates desulfurization of thiourea. Physicochemical characteristics of the thiocomplex synthesized from hydrochloric acid solutions of alkali metal perrhenates containing excess thiourea in argon at 368 K are identical to those of the compounds isolated from the reaction mixture after preliminary activation.

We think that the thiocomplex involves the fragments responsible for catalysis. The analogous structural binuclear center containing sulfur-bridge atoms may also be visualized on solid rhenium heptasulfide surface.

Table 2 lists the data on the hydrogenation of aromatic nitro compounds containing different functional groups, in the presence of both the soluble rhenium thiocomplex,  $\text{Re}_2\text{S}_6\text{Tu}_3\text{Cl}_2$ , and solid rhenium heptasulfide,  $\text{Re}_2\text{S}_7$  [8–10].

It is seen that the hydrogenation of the nitro group of aromatic hydrocarbons is highly selective (70–100%) in amine for practically all

TABLE 2

Hydrogenation of substituted nitrobenzenes on soluble rhenium thiocomplex (t.c.) and solid rhenium heptasulfide ( $\text{Re}_2\text{S}_7$ )<sup>a</sup>

Substrate	Reaction time <sup>b</sup> (h)	Amine yield (mol %)		Selectivity (%)	
		t.c.	$\text{Re}_2\text{S}_7$	t.c.	$\text{Re}_2\text{S}_7$
nitrobenzene	5	22	25	55	80
<i>p</i> -nitrotoluene	4	36	19	80	91
<i>o</i> -nitrotoluene	3	33	20	68	100
<i>p</i> -nitrophenol	7.5	36	20	88	83
<i>p</i> -nitroaniline	3	0	5	0	7
<i>o</i> -nitroaniline	3	3	0	22	0
<i>m</i> -nitroaniline	4	10	13	39	24
<i>p</i> -nitrobenzaldehyde	8	44	81	74	87
<i>o</i> -nitrobenzaldehyde	4	70	53	99	100
<i>m</i> -nitrobenzoic acid	7	16	25	37	83
<i>o</i> -nitrobenzoic acid	8	82	26	90	100
<i>p</i> -nitrobenzoic acid	7	35	34	39	72
3,5-dinitrobenzoic acid	7	34	32	74	100
<i>m</i> -dinitrobenzene	14.5	51	35	97	74
<i>m</i> -nitrocinnamic acid	7	34	27	100	100

<sup>a</sup>  $[\text{Re}] = 4.5 \cdot 10^{-3} \text{ M}$ ,  $[\text{substrate}] = 2.8 \cdot 10^{-2} \text{ M}$ ,  $T = 343 \text{ K}$ ,  $P_{\text{H}_2} = 0.1 \text{ MPa}$ , dimethylformamide as solvent.

<sup>b</sup> On  $\text{Re}_2\text{S}_7$  the reaction time is 2 h.

substrates in these two catalysts, except for nitroanilines, whose selectivity does not exceed 24 and 39% on the solid and soluble rhenium catalysts, respectively.

## Discussion

The synthesized soluble rhenium complexes containing Re—S and Re—P bonds display specific catalytic behaviour in the hydrogenation of olefins and nitro compounds.

Phosphorus-containing ligands facilitate the formation of rhenium complex catalysts which are selective in the hydrogenation of terminal olefin bonds, whereas sulfur-containing ones favour selective reduction of the nitro group of aromatic hydrocarbons. The rate and selectivity of the processes are mainly determined by the composition and bond nature (Re—S or Re—P) of the initial rhenium complexes.

In the hydrogenation of the NO<sub>2</sub> group of aromatic hydrocarbons, the catalytic properties of both the soluble thiocomplex and solid heptasulfide having the Re—S bond proved to be similar. (Table 2).

Quantitative evaluation of the nitro group reactivity based on the correlation of the initial reaction rates ( $W$ ) with the substituent Hammett constants,  $\sigma^+$ , may serve as additional evidence of the similar catalytic behaviour of the catalysts possessing the same reaction center. Application of the initial rates rather than reaction rate constants is valid, since all experiments were carried out under the same conditions. The reaction order with respect to substrate and catalyst was zero. The reaction sensitivity constant was found to be positive and equal to 0.24 on both catalysts (Fig. 2). Its magnitude indicates a relatively low sensitivity of the given process towards the inductive and resonance effects of the benzene ring substituents.

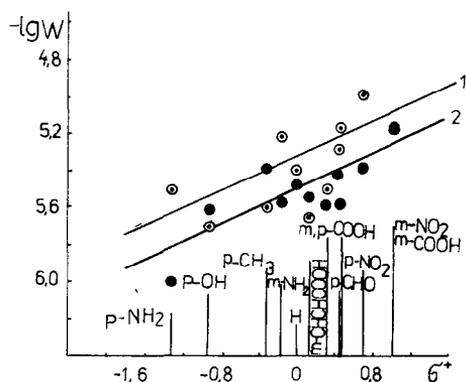


Fig. 2. Correlation between  $\log W$  and  $\sigma^+$  for catalytic hydrogenation of aromatic nitro compounds on the sulfur-containing rhenium catalysts in dimethylformamide solutions. 1 =  $\text{Re}_2\text{S}_7$ , 2 =  $\text{Re}_2\text{S}_6\text{Tu}_3\text{Cl}_2$ ;  $P_{\text{H}_2} = 0.1 \text{ MPa}$ ,  $T = 343 \text{ K}$ .

Under catalysis conditions, nitro group reduction on rhenium catalysts is promoted by lowered electron density at the reaction center, the nitrogen atom, *i.e.* the reaction is accelerated by electron-acceptor substituents and is inhibited by electron-donor ones.

Changes in the composition of the catalytic center change the shape of the Hammett correlation. It has been shown [11] that in the presence of 1% Pd/C and cerium nitrilotrimethylphosphonate, the hydrogenation rate of nitrobenzene substituents increases with increasing the electron-donor ability of the substituents, whereas on the palladium complex with poly(4-vinylpyridine) immobilized on the polyethylene surface, a bell-shaped correlation is observed [12]. According to our data [9, 10], the hydrogenation rate of nitro compounds is practically unaffected by the absolute Hammett constant when 4–5% of Pd/C was used as a catalyst.

## Conclusions

Soluble rhenium complexes containing the Re—P bond hydrogenate olefins selectively, whereas those involving the Re—S bond catalyze the reduction of the nitro group of aromatic hydrocarbons.

Homogeneous (soluble thiocomplex) and heterogeneous (solid heptasulfide) sulfur-containing rhenium catalysts were found to have the same catalytic center and catalytic properties.

The hydrogenation of nitro compounds is accelerated by electron-acceptor functional groups and is inhibited by electron-donor ones in nitro-substituted benzenes.

The catalytic activity and selectivity of metal complexes, as well as the shape of the Hammett correlation in the hydrogenation processes, are determined by the bond nature of the initial ligand in the active center.

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