Catalytic properties of rhenium(v) complexes with thiourea derivatives in cyclohexene hydrogenation

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The catalytic properties of $Re^VOL_2Cl_3$ complexes, where L are thiourea derivatives, were studied. The rhenium(v) complex with di-*o*-tolylthiourea is most active in cyclohexene hydrogenation.

Key words: Re^V complexes, thiourea, cyclohexene, hydrogenation.

Catalytic systems based on rhenium and its compounds are less active, as a rule, in cyclohexene hydrogenation than catalysts containing Platinum Group metals.[1] However, catalysts based on ReO_3,[2] $(\eta^5\text{-}C_5H_5)_2ReH$,[3] and $Re_2(CO)_{10}$[4] possess a high activity in this reaction.

In this work, we studied the catalytic properties of the rhenium(v) complexes with thiourea derivatives $Re^VOL_2Cl_3$ in cyclohexene hydrogenation. We assumed that the strong Re=O bond in the Re^V complexes provides a lability of the ligands and favors the catalytic activity.

Experimental

Compounds with the general formula $Re^VOL_2Cl_3$ were synthesized by the following reaction:

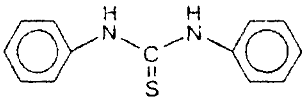
$$H_2(ReOCl_5) + 2\ L \longrightarrow Re^VOL_2Cl_3 + 2\ HCl.$$

We prepared four samples of complexes (**1—4**). Diphenyl- (**1′**), di-*o*-tolyl- (**2′**), *N*-phenyl-*N′*-2-pyridyl- (**3′**), and di-2-naphthylthiourea (**4′**) were used as ligands.

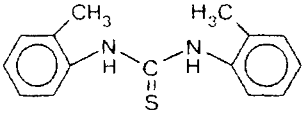
Synthesis of complexes. A solution of the ligand in acetone or ethanol with the molar ratio Re : L = 1 : 2 was added to a 0.1 *M* solution (10 mL) of $H_2(ReOCl_5)$ prepared by a known procedure[5] in concentrated HCl. The precipitated crystals were filtered off, washed with HCl and *n*-propanol, and dried above $CaCl_2$. Complexes **1—4** were analyzed for the content of rhenium,[6] sulfur,[7] and chloride ions.[8] The elements were determined after the decomposition of samples with H_2O_2 in a poorly alkaline medium and removal of its excess by heating. The content of C, N, and H was determined by organic microanalysis.

Complex 1. Found (%): C, 39.8; H, 2.8; Cl, 14.7; N, 7.11; Re, 24.60; S, 10.0. $C_{26}H_{24}Cl_3N_4OReS_2$ (molecular weight (*M*) 765.18). Calculated (%): C, 40.80; H, 3.16; Cl, 13.9; N, 7.36; Re, 24.30; S, 8.38.

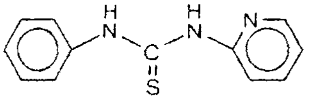
Complex 2. Found (%): C, 44.53; H, 4.22; Cl, 11.51; N, 5.95; Re, 22.90; S, 8.10. $C_{30}H_{32}Cl_3N_4OReS_2$ (*M* 821.29). Calculated (%): C, 43.87; H, 3.92; Cl, 12.45; N, 6.82; Re, 22.68; S, 7.80.



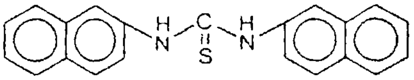
1′



2′



3′



4′

Complex 3. Found (%): C, 36.90; H, 2.41; Cl, 12.50; N, 10.87; Re, 23.40; S, 8.00. $C_{24}H_{22}Cl_3N_6OReS_2$ (*M* 767.16). Calculated (%): C, 37.57; H, 2.89; Cl, 13.86; N, 10.95; Re, 23.67; S, 8.35.

Complex 4. Found (%): C, 50.50; H, 1.98; Cl, 10.85; N, 5.00; Re, 19.90; S, 5.82. $C_{42}H_{32}Cl_3N_4OReS_2$ (*M* 965.42). Calculated (%): C, 52.25; H, 2.50; Cl, 11.02; N, 5.80; Re, 19.30; S, 6.64.

The IR spectra of **1—4** were recorded on IKS-22 B, IKS-22 V, and IKS-14 A spectrometers in the 200—2000 cm^{-1} region as suspensions in Nujol and hexachlorobutadiene.

Cyclohexene was hydrogenated at T = 230 °C, p_{H_2} = 100—120 Torr, and Re content 0.35% of the cyclohexene weight in a static installation (reaction time 3 h). Complex **1—4** and cyclohexene (reagent grade) (4 g) were placed in a 0.15-L

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Table 1. Hydrogenation of cyclohexene over rhenium catalysts

Compound	Catalyst	Re (%)	Reaction conditions			Yield of cyclohexane (wt.%)
			T/°C	*p*/Torr	τ/h	
1	$C_{26}H_{24}Cl_3N_4OReS_2$	0.35	230	100	3.0	16.3
2	$C_{30}H_{32}Cl_3N_4OReS_2$	0.35	230	118	3.0	65.7
3	$C_{24}H_{22}Cl_3N_6OReS_2$	0.35	230	115	3.0	3.0
4	$C_{42}H_{32}Cl_3N_4OReS_2$	0.35	230	100	3.0	4.0
5	ReO_3 (*in situ*)[3]	1.3	240	205	4.0	100.0
6	$(\eta^5\text{-}C_5H_5)ReH$ [4]	0.6	100	100	1.0	10.4
		0.4	180	100	0.5	100.0
7	$Re_2(CO)_{10}$ [5]	1.0	180	100	1.0	16.4
		1.0	200	100	1.0	32.9
		0.5	230	100	1.0	100.0

autoclave with a glass insert. Compounds **1—4** at ~20 °C and on heating are undissolved in cyclohexene. Nitrogen and hydrogen were successively passed through the autoclave, the H_2 pressure was fixed, and the autoclave was heated to the experimental temperature. The reaction products were analyzed by GLC on an LKhM-8MD chromatograph (h.c.d., He as the carrier gas, 15% polyethylene glycol adipinate on Chromosorb P as the liquid phase) and by refractometry (Table 1).

Results and Discussion

Cyclohexene hydrogenation with complexes **1—4** was studied under conditions close to those found previously[3,4] for the active catalysts rheniecene hydride and rhenium pentacarbonyl (T = 230 °C, p = 100—118 Torr, τ = 3 h).

The data in Table 1 show that complex **2** possesses a high catalytic activity in cyclohexene hydrogenation. The yield of cyclohexane with complex **2** is 65.7%, that with **1** is 16.3%, and samples **3** and **4** are virtually inactive: the yield of cyclohexane is 3—4%. For sample **2** bearing the ligand with two Me groups, the hydrogenating activity increases as compared to that of sample **1**, and the yield of cyclohexane increases from 16.3 to 65.7%. The replacement in ligand **1′** of one benzene ring by pyridine (**3′**) or two naphthene cycles (**4′**) gives inactive samples **3** and **4**.

The IR spectra of complexes **1—4** are very complicated because of many vibrations of the aryl derivatives of thiourea. Therefore, the IR spectra were not interpreted in the region containing the absorption bands corresponding to the Re—Cl and Re—S bonds. However, the intense bands in the region of 930—970 cm^{-1} in the spectra of the complexes can be attributed to stretching vibrations of the Re=O bond (by analogy to the data obtained previously for the rhenium(v) complexes with thiourea[9,10] and its several derivatives[11,12]).

The results of elemental analysis of the synthesized complexes **1—4**, the IR spectral data, and ion-exchange chromatography confirmed the formation of complexes with the composition $Re^VOL_2Cl_3$. The interaction of $[ReOCl_5]^{2-}$ with L can be presented as the successive substitution of the Cl atoms in the equatorial plane of the $[ReOCl_5]^{2-}$ ion by the L molecules. This process is accompanied by the distortion of the octahedral shape of the rhenium(v) oxochloride complex,[13] in which the O atom is arranged along the axis perpendicular to the equatorial plane of the octahedron. The labilizing effect of the Re=O group is manifested by the $ReOCl_5^{2-}$ ions forming very unstable compounds with other ligands and then readily eliminating these ligands.[14]

The distinction in the catalytic activities of four synthesized rhenium complexes with thiourea derivatives can be attributed to the properties of the substituents in the thiourea molecule and the character of the L—Re bond.

The published data[10,13,14] (IR spectra, X-ray structural analysis) show that thiourea and its derivatives are coordinated to the metal through the S atom to form the donor-acceptor bond by the $3p_\pi$-AO of the S atom.

In addition, coordination of the ligands (phenylthiosemicarbazide and thiosemicarbazone-methyl 2-pyridyl ketone — thiourea derivatives) with the metal at the S and N atoms to form chelate cycles has been reported.[12] The substituents involved in the conjugation chain also affect the properties of thiourea. For example, the introduction of electron-donating substituents increases the coordination ability of the ligands, whereas acceptors exert the opposite effect.[14] The number and nature of substituents in the thiourea substantially affect the strength of the Re=O bond in the complexes.[10,15]

It can be assumed that the strength of the Re=O bond plays an important role determining the catalytic activity of the complexes. The repulsion between the bulky ligands prevents the shortening of the O=Re—S angles in the octahedron. This results in a considerable repulsion between unpaired pairs of electrons of the S atom and π-electrons of the Re=O bond and, as a consequence, in a weakening of this bond. An increase in the frequency $\nu_{Re=O}$ in the Re^V complexes with two thiourea molecules (unlike the Re^V complexes with four thiourea molecules) confirms this assumption.[15] Indeed, a decrease in the number of ligands decreases their interelectron repulsion in the equatorial plane of the molecule, which creates the conditions for an increase in the O=Re—S angle (extrusion of the Re atom from the equatorial plane) and enhances the Re=O bond.[15] Therefore, the low catalytic activity of the Re^V complex with *N*-phenyl-*N'*-pyridylthiourea can be explained by the formation of stable chelate centers due to the bond of the Re atom with the S and N atoms. The low catalytic activity of the rhenium(v) complex with dinaphthylthiourea can be explained, most likely, by the strong screening of the central rhenium(v) atom with the bulky ligand.

Taking into account the aforesaid, we may assume that the Me groups in di-*o*-tolylthiourea play an important role in the enhancement of the catalytic activity of complex **2** as compared to that of complex **1**, weakening the Re—S coordination bond. Perhaps, the catalytic activity of **1** and **2** in cyclohexene hydrogenation appears due to the bonding of rhenium with oxygen.

According to previously published data,[2] cyclohexene hydrogenation on ReO_3 catalyst (prepared *in situ*) occurs in 100% yield at a hydrogen pressure of 200 Torr, rhenium amount of 1.3% of the substrate weight, and reaction time of 4 h. In our experiments, the hydrogen pressure was 100 Torr, the amount of rhenium was 0.35%, the reaction time was 3 h, and the yield of cyclohexane was ~66%. Comparison of these results confirms indirectly the assumption that rhenium oxide can be the active site of the rhenium(v) complex with di-*o*-tolylthiourea (**2**) in cyclohexene hydrogenation.

Thus, the presence of different aryl derivatives of thiourea in the complex with pentavalent rhenium exerts a substantial effect on the catalytic activity in the structure-insensitive reaction of cyclohexene hydrogenation. Perhaps, the rhenium complexes with thiourea that are inactive in the hydrogenation of the C=C bond in cyclohexene can manifest catalytic activity in the hydrogenation of the C=C bond in organic compounds containing nitrogen and sulfur.

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