COMPLEXES OF RHENIUM(V) WITH CYCLIC SULFIDES: CATALYSTS OF HYDROGENATION AND ISOMERIZATION OF OLEFINS

L. I. Gvinter, N. V. Borunova, R. G. Akhmadieva,
N. V. Antseva, N. A. Yusupova, I. U. Numanov,
and V. Z. Sharf

UDC 541.49:546.719:541.128:
542.941.7:542.952.1:547.313

The possibilities of using rhenium complexes as catalysts of hydrogenation have been studied very little [1-3].

New complexes of rhenium with cyclic sulfides: thiophane and 2-propylthiophane, were synthesized and their catalytic properties were investigated in reactions of hydrogenation of olefins and dienes in the present study.

EXPERIMENTAL

Complexes of rhenium with cyclic sulfides (Table 1) were prepared by the reaction of oxopentachloro(oxopentabromo)rhenic acid (V) (0.1 M solution in 6 N HCl) with thiophanes in the ratio of 1:2 (molar). The structure of the complexes was confirmed by the IR spectroscopic data. An intense absorption band (a.b.) in the 980 cm^{-1} region, assigned to stretching vibrations of the Re=O bond [4], and an a.b. at 230 cm^{-1}, characteristic of the Re—S bond [5], were found in the IR spectra of all of the complexes. Three intense a.b. corresponding to the Re—Cl bond at 270-280, 320, and 340-360 cm^{-1} for the chloride complexes, and at 225 cm^{-1} characteristic of the Re—Br bond for the bromide complexes were observed. The a.b. in the 710-740 cm^{-1} region are due to the vibrations of the emthylene groups in the rings.

The IR spectra in the 3600-400 cm^{-1} region were obtained on a UR-20 spectrometer (KBr pellets), and the spectra in the 400-200 cm^{-1} region were recorded on a Hitachi Fis-3 spectrophotometer (CsI pellets).

The catalytic properties of the complexes in hydrogenation reactions were studied in a static system in a glass reactor or a rotating autoclave.

The concentration of substrate and catalyst was 0.2 and 0.05 mole/liter respectively. The reaction time was 4 h. The composition of the products of the reaction was determined by GLC in a 3 mm × 5 m column with 15% β,β'-oxydipropionitrile on Celite-545 for 1-pentene, 1-hexene, 1,3-pentadiene, and a 3 mm × 3 m column with 15% Triton X-305 on Celite-545 for allyl benzene.

RESULTS AND DISCUSSION

Complexes (I)-(IV) do not exhibit catalytic activity in hydrogenation of α-olefins at ~20°C and H_2 atmospheric pressure. At 100°C and a pressure of 10 MPa, (I) catalyzes hydrogenation of 1-hexene. Isomerization with the formation of cis-2-hexene simultaneously takes place (Table 2). However, the activity of the catalyst is low: the total degree of conversion of 1-hexene is 19%. When Br^- is substituted by Cl^-, the activity of the catalyst increases slightly. Introduction of an alkyl substituent in thiophane has little effect on the catalytic activity of the complex and the direction of the reaction. The rate of hydrogenation of 1-pentene is higher than for 1-hexene.

The complexes studied exhibit significantly higher activity in reactions of the transformation of allyl benzene, and total conversion of the substrate is attained in the same conditions (Table 3). A comparison of the degree of conversion of allyl benzene in softer conditions with incomplete conversion of the substrate showed that the catalytic activity of the complexes decreases in the order: (IV) $\geq$ (III) > (I).

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. V. I. Nikitin Institute of Chemistry, Academy of Sciences of the Tadzhik SSR, Dushanbe. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 755-759, April, 1988. Original article submitted November 11, 1986.

TABLE 1. Characteristics of the Rhenium Complexes

Complex	Found / Calculated, %				T decomp., °C	Yield, %
	Re	Br, Cl	C	H		
(I)	30,3 / 30,1	38,4 / 38,8	15.54 / 15,5	2,84 / 2,59	–	95,5
(II)	38,22 / 38,36	21.69 / 21,47	19,58 / 19,80	3,49 / 3,30	123	91,2
(III)	26.3 / 26,5	24,16 / 23,9	15,2 / 15.18	4,3 / 3,99	–	76,7
(IV)	32.2 / 32,71	18.5 / 18,73	29,55 / 29,6	4,81 / 4,94	110	72

TABLE 2. Transformations of α-Olefins in the Presence of Re Catalysts (100°C, p_{H_2} = 10 MPa, Solvent C_2H_5OH)

Complex	α-Olefin	Product of the reaction		Degree of conversion, %	Specific activity, mole/g·atom Re·min
		hydrocarbon	%		
(I)	1-Hexene	cis-2-Hexene Hexane	17 83	19	0,8
(II)	1-Hexene	cis-2-Hexene Hexane	9 91	41	1,4
	1-Pentene	cis-2-Pentene Pentane	18 82	65	1,9
(IV)	1-Hexene	cis-2-Hexene Hexane	10 90	25	1,1

The specific activity of (I) in transformation of allyl benzene is 2.2 mole/g·atom Re·min, for 1-hexene in the same conditions, it is 0.8 mole/g·atom Re·min, and for (IV) it is 3.1 and 1.1 mole/g·atom Re·min (Tables 2 and 3).

Allyl benzene undergoes transformations in two directions: it is hydrogenized and isomerized with migration of the C═C bond to the α-position. The rate of transformation in methanol is significantly higher than in toluene. An unusual finding should be noted: the high concentration of the cis-isomer in the products of isomerization, and the ratio of trans- and cis-propenylbenzenes is significantly lower in toluene than in methanol.

The reaction of isomerization of allyl benzene also takes place in an inert atmosphere: at 100°C in Ar, the degree of isomerization was 25% after 4 h. Only one product of the reaction, cis-propenylbenzene, was found in the catalyzate. The nature of the solvent in this case does not affect the rate and direction of the reaction.

The effect of the temperature and H_2 pressure on the activity of the complex in transformations of allyl benzene was studied on the example of (IV). Table 4 shows that in the 25-70°C range, the degree of conversion of allyl benzene in toluene and methanol does not exceed 15-25%. At 70°C, the reaction rate begins to increase significantly. Isomerization of allyl benzene primarily takes place in methanol up to 70°C, and hydrogenation takes place to a small degree; in toluene, hydrogenation does not take place in general. At 100°C, hydrogenation with the formation of propylbenzene takes place together with isomerization.

As Fig. 1 shows, the reaction rate in methanol in the 0-2.5 MPa range increases directly proportionally to p_{H_2} and is almost independent of the pressure at 2.5-10 MPa. The dependence of the reaction rate on the pressure is extreme in toluene solutions.

Based on the available spectral data, the proposed structure of the complexes is a nonsymmetrically flattened octahedron, where the halogen atoms are positioned in the equatorial plane around Re, and the organic sulfides are located in the cis position relative to each other

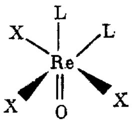

TABLE 3. Transformations of Allyl Benzene in the Presence of Re Catalysts (100°C)

Complex	Solvent	p_{H_2}, MPa	Specific activity, mole/g• atom Re•min	Composition of catalyzate, %				Hydrogenation/ Isomerization	Propenylbenzene: trans/ cis
				allyl benzene	cis-propenylbenzene	trans-propenylbenzene	propylbenzene		
(I)	Methanol	2,5	2,2	37	4	15	44	2,3	4,0
	»	5,0	3,5	Traces	4	18	78	3,6	4,3
	»	10,0	3.5	–	2	19	79	3,7	9,7
	Toluene	2,5	–	100	–	–	Traces	0	0
(III)	Methanol	2,5	3,0	7	10	29	54	1,4	2,8
	»	5,0	3,2	–	9	18	73	2,7	2,0
	»	10,0	3,2	–	13	8	79	3,8	0,6
	Toluene	2,5	0,6	80	17	Traces	3	0,14	0
(IV)	Methanol	2,5	3,1	7	25	14	54	1,4	0.60
	»	5,0	3,3	–	25	11	63	1,7	0,46
	»	10,0	3,3	–	25	7	68	2,1	0,26
	Toluene	2,5	1,5	55	20	1	24	1,1	0,06
	Methanol*	10,0		73	27	0	0	0	0
	Toluene *	10,0		74	26	0	0	0	0

*The reaction was conducted in Ar.

TABLE 4. Effect of the Temperature on the Rate and Direction of Transformation of Allyl Benzene in the Presence of (IV) (p_{H_2} = 5 MPa)

Solvent	T, °C	Composition of catalyzate, %				Hydrogenation/ Isomerization	Propylbenzene: trans/cis
		allyl benzene	cis-propenylbenzene	trans-propenylbenzene	propylbenzene		
Methanol	25	86	14	–	–	0	0
	50	81	17	–	2	0.1	–
	70	77	16	–	7	0.4	–
	100	–	25	12	63	1.7	0.5
Toluene	25	76	24	–	–	–	–
	50	83	17	–	–	–	–
	70	85	15	–	–	–	–
	100	21	28	12	39	1.0	0,4

where X = Cl, Br; L = thiophane, propylthiophane. The significant change in the activity of the complex as a function of the nature of the solvent indicates entry of the solvent in the coordination sphere of the complex.

By-products (10-15 wt. %) whose composition was not established were found in the catalyzates formed in conducting the reactions in methanol at 100°C and 10 MPa. The formation of products hypothetically of the same composition was determined with the GLC data on contact of methanol with the complex (without any substrate) in the same conditions. These data confirm that the oxygen-containing solvent is partially involved in the reaction in the presence of (I)-(IV).

All of the catalysts tested also accelerate the reaction of hydrogenation of 1,3-pentadiene (Table 5). As in hydrogenation of allyl benzene, the complexes containing propylthiophane ligands are more active than the complexes with thiophane ligands. In contrast to the features revealed in hydrogenation of allyl benzene and 1-hexene, the effect of the halogen ligand is significant in the case of the diene: the degree of hydrogenation in the presence of (III) is two times higher than for its chlorine-containing analog. Hydrogenation takes place nonselectively: with small degrees of conversion, formation of n-pentane is observed in addition to pentenes.

It was thus shown for the first time that the rhenium complexes studied exhibit activity in hydrogenation of the C=C bonds of olefins. According to the data in [3], only complexes with phosphine ligands are capable of catalyzing this reaction. In conditions similar to those

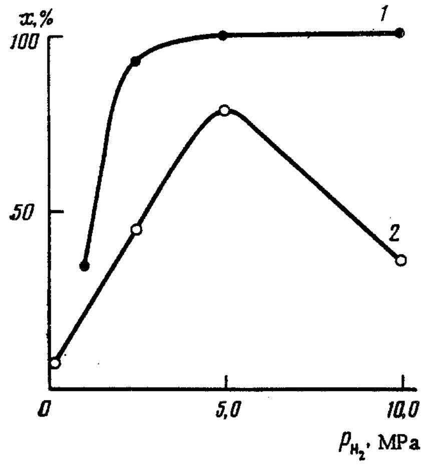

Fig. 1. Effect of the H_2 pressure on the degree of conversion of allyl benzene (x) at 100°C in the presence of (IV) in the solvent: 1) methanol, 2) toluene.

TABLE 5. Hydrogenation of 1,3-Pentadiene in the Presence of Re Catalysts (100°C, p_{H_2} = 2.5 MPa, Solvent MeOH)

Complex	Degree of conversion, %	Composition of catalyzate, %					
		cis-1,3-pentadiene	trans-1,3-pentadiene	1-pentene	cis-2-pentene	trans-2-pentene	pentane
(I)	83	11	16	18	6	34	15
(II)	14	26	60	1	2	7	4
(III)	71	11	18	13	4	36	18
(IV)	39	15	46	3	5	21	10

used in the present study, the degree of hydrogenation did not exceed ~20-30%. Re complexes with aliphatic sulfur-containing ligands (thiourea and its derivatives) exhibited significant activity in hydrogenation of the nitro group and were inert in transformation of olefins [2]. The catalysts studied in the reaction of reduction of nitro compounds were inert, but exhibited significant activity in hydrogenation and isomerization of olefins and dienes. This forms the basis for hypothesizing that the nature of the sulfur-containing ligand determines the mechanism of the catalytic effect of the complex.

CONCLUSIONS

1. Complexes of rhenium with cyclic sulfur-containing ligands (thiophane, 2-propylthiophane) catalyze hydrogenation and isomerization of olefin and diene hydrocarbons.

2. The catalytic activity of the complexes is a function of the ligand environment, the nature of the substrate, and the solvent.

3. The catalysts tested accelerate isomerization of α-olefins both in hydrogen and in an inert atmosphere with the predominant formation of cis-β-olefins.

LITERATURE CITED

1. M. A. Ryshentseva and Kh. M. Minachev, Rhenium and its Compounds in Heterogeneous Catalysis [in Russian], Nauka, Moscow (1983).
2. V. M. Belousov, G. I. Korenyako, and Yu. N. Kukushkin, Dokl. Akad. Nauk UkrSSR, Ser. B, 1011 (1979).
3. V. M. Belousov, T. A. Palchevskaya, O. M. Negomedzyanova, and K. V. Kotegov, React. Kinet. Catal. Lett., 28, 41 (1985).
4. K. I. Petrov and V. V. Kravchenko, Zh. Neorg. Khim., 14, 2890 (1969).
5. K. V. Kotegov, F. Kh. Khakimov, Yu. N. Kukushkin, and A. V. Konovalov, Zh. Obshch. Khim., 44, 2237 (1974).