STRUCTURE AND CATALYTIC ACTIVITY OF METAL COMPLEXES ON CARRIERS.

3. RHODIUM COMPLEXES ON MODIFIED POLYMERS AND THEIR CATALYTIC PROPERTIES IN THE REDUCTION OF NITROBENZENE BY CHEMICALLY BOUND HYDROGEN

V. F. Dovganyuk, V. Z. Sharf, V. K. Belyaeva,
I. N. Marov, Zh. L. Dykh, L. I. Lafer,
and V. I. Yakerson

UDC 541.128.34:541.49:546.97:541.64:542.941.7:547.546

Heterogenized catalysts based on rhodium complexes attached to polymers modified by the groups 3(5)-methylpyrazole, imidazole and benzimidazole have been synthesized. The process of their formation has been investigated by IR, UV, and EPR spectroscopy. Results have been obtained for the catalytic activity of the complexes in the hydrogenation of nitrobenzene by hydrogen transfer from propan-2-ol and $NaBH_4$.

It has been shown [1, 2] that rhodium complexes on modified silica gels catalyze hydrogenation reactions. Transition metal complexes immobilized on polymer matrices are known to be extremely effective in hydrogenation reactions of unsaturated compounds [3].

In this study we have synthesized rhodium complexes attached to polymers containing the groups 3(5)-methylpyrazole, imidazole, and benzimidazole. The process of metal complex formation was investigated by IR, UV, and EPR spectroscopy. The catalytic properties of these complexes was studied in the hydrogenation of nitrobenzene by hydrogen transfer from propan-2-ol and $NaBH_4$.

EXPERIMENTAL

Data on the composition and activity of the synthesized catalysts is presented in Table 1. Polymers containing heterocyclic amine groups were used as carriers. The polymeric carriers of type Polyorgs IV and Polyorgs XVI were obtained by amination of the chloromethylated copolymers of styrene with divinylbenzene, 3(5)-methylpyrazole or imidazole. Polyorgs XI was synthesized by copolymerization of N-vinylbenzylimidazole and divinylbenzene [4]. Catalysts A-C were obtained by treating the polymeric carriers with an alcoholic $RhCl_3$ solution. The carrier (2 g) was put into a three-necked flask and 40 ml 0.01 M solution of $RhCl_3$ in MeOH was added. The reaction was carried out in boiling solvent in an atmosphere of Ar with continuous mixing for 1-3 h. The rhodium content of the polymer was calculated from the decrease in complex concentration in solution determined spectrophotometrically. Homogeneous analogs of these complexes were synthesized by reacting $RhCl_3$ and the corresponding heterocyclic amine in MeOH solution. The molar ratio Rh:amine was 1:10. The complex precipitated out during the course of the reaction and was recovered by filtration, washed with alcohol and ether and dried in air.

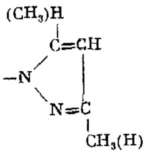
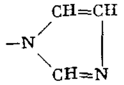
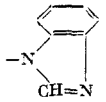
EPR spectra of initial and hydrogenated (by $NaBH_4$) heterogeneous rhodium complexes were recorded on a Radiopan SE/X2544 spectrometer at 77 and 298 K. A JTM-247 magnetometer was used to calibrate the magnetic field. EPR spectra were recorded in air for the initial immobilized complexes and in vacuo for the reduced samples. The reductions were carried out as follows. The calculated quantities of catalyst and $NaBH_4$ were mixed in a test tube with a quartz ampul sealed on to it. Propan-2-ol heated to its boiling point (82°C) was poured into the test tube and allowed to stand for 15 min. The system was then cooled, the solvent was removed, and the catalyst was dried (30-40°C). All the operations were carried out under

---

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, pp. 268-273, February, 1990. Original article submitted July 11, 1988.

0568-5230/90/3902-0217$12.50

TABLE 1. Catalytic Activity of Fixed Rhodium ($RhCl_3$) Complexes in the Reduction of Nitrobenzene by Propan-2-ol (a) and Sodium Borohydride (b) ($8.7 \cdot 10^{-6}$ g-atom Rh, $17.4 \cdot 10^{-5}$ mole substrate, 10 ml propan-2-ol, 82°C; for a [KOH] = $8.7 \cdot 10^{-1}$ mole/liter, for b [$NaBH_4$] = $34.8 \cdot 10^{-5}$ mole/liter)

Catalyst	Carrier		$[Rh] \cdot 10^5$, mole/g	Hydrogen donor	$W_0 \cdot 10$ mole/g-atom Rh·min
	polymer	functional group			
A	Polyorgs IV		17,5	Propan-2-ol $NaBH_4$	0,6 7,4 7,2 * 4,0 †
B	Polyorgs XVI		19,4	Propan-2-ol $NaBH_4$	1,1 0,3
C	Polyorgs XI		19,4	Propan-2-ol $NaBH_4$	0,2 1,9

---

*In H_2.
†In presence of O_2.

Ar. The system was evacuated and the sample transferred to the quartz ampul which was then sealed up under vacuum.

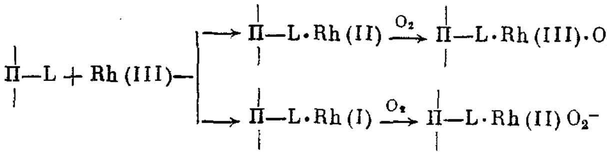
IR spectra in the region 3600-700 cm^{-1} were recorded on UR-20 and Specord M-80 spectrometers. Samples of the modified polymeric carriers, the heterogenized complexes, and their homogeneous models, imidazole and benzimidazole, were prepared by compressing them with KBr. IR spectra in the region 700-200 cm^{-1} were recorded on a Perkin-Elmer spectrophotometer. Samples of the solid substances were prepared in the form of vaseline oil suspensions inserted between CsI plates. UV spectra were recorded in the visible region on a Specord M-40 spectrometer by the diffusion reflection method (SDR) with the aid of an integrater.

The catalytic experiments were carried out by the method described in [5].

RESULTS AND DISCUSSION

Physicochemical Investigations on the Synthesized Metal Complexes

In the EPR spectrum of sample A (Fig. 1a) a signal for rhombic symmetry X with parameters $g_1 = 2.088$, $g_2 = 2.046$, and $g_3 = 1.987$ is observed which can be attributed [6, 7] to the formation of paramagnetic $Rh(II) \cdot O_2^-$ and $Rh(III) \cdot O_2^-$. It is evident that during the preparation of the fixed complexes in hot alcoholic solutions the $RhCl_3$ is partially reduced to form unsaturated coordination complexes of Rh(II) and Rh(I). The samples obtained were stored in air. On contact with the air acidic adducts are formed according to the scheme:



This scheme is in accordance with the presence of lines in the spectrum of sample A with g values of 2.835, 2.255, and 1.896 which are components of g-tensor rhombic symmetry caused by Rh(II) stabilized by nitrogen-containing groups of the carrier in addition to the lines for the acidic adducts of Rh (signal X). The existence of partially reduced Rh(III) during the process of complex formation is confirmed by UV spectroscopic data on the homogeneous analogs. In the UV spectra of $RhCl_3$ complexes with heterocyclic amines, absorption bands

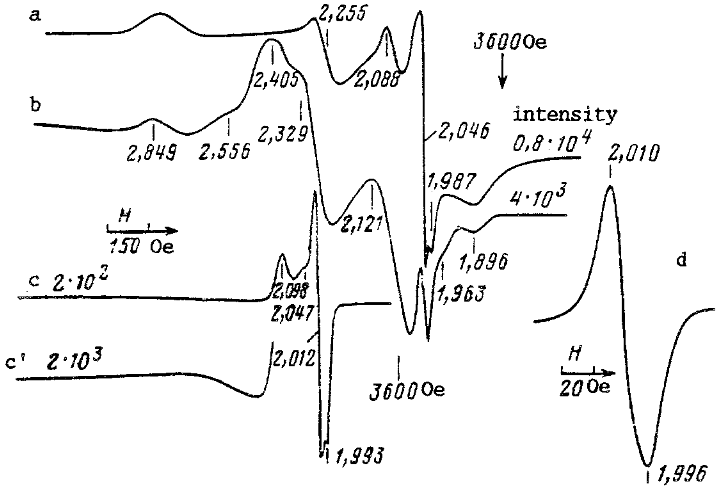


Fig. 1. EPR spectra of sample A (77 K): a) initial; b) activated with $NaBH_4$; c) sample B after contact with air; d) spectrum of sample B at 298 K.

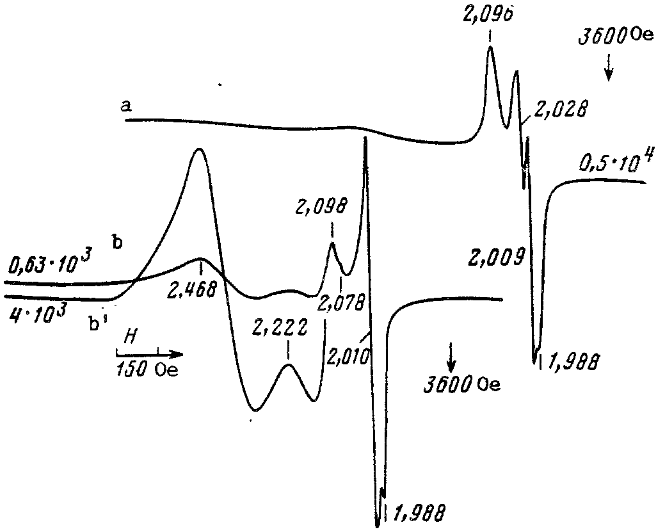


Fig. 2. EPR spectrum of sample C (77 K): a) initial, b) activated by $NaBH_4$.

(a.b.) are observed at 19,000 and 24,500 cm^{-1} characteristic of divalent rhodium complexes [8].

In the EPR spectrum of sample C (Fig. 2a) there is a signal similar to X (g_1 = 2.096, g_2 = 2.009, and g_3 = 1.987) attributable to the acidic adducts of Rh and a signal of weak intensity with g = 2.47 probably due to Rh(II). A very small residual concentration of Rh(II) benzimidazole complexes on the surface of sample B was due to their high reaction capacity relative to the acid.

IR spectra of rhodium complexes fixed on modified polymers contained inadequate information due to poor transmission of the samples. So we investigated model homogeneous analogs of the fixed complexes.

IR spectra of the samples of 3(5)-methylpyrazole, imidazole, and benzimidazole used agreed with spectra of these compounds given in the literature [9, 10]. In the IR spectra of all the heterocyclic amines a very weak a.b. in the region 3450-3520 cm^{-1} is observed corresponding to vibration of N—H bond. During complex formation with $RhCl_3$ and N—H bond vibrations shift to a region of lower frequency: intense a.b. at 3260 cm^{-1} (imidazole and benzimidazole) and 3290 cm^{-1} [3(5)-methylpyrazole] appear in the spectra indicating formation of H bonds between the N—H groups and the chloride anions [11, 12]. Absorption bands for the C—H group bond vibrations undergo insignificant changes.

In the region 1700-600 cm^{-1} where the bond vibrations of five-membered rings and deformation vibrations of the groups =C–H and –C–H are found a shift of 5-15 cm^{-1} is observed for a series of a.b. together with a change in the absorption intensity characteristic of complexes of transition metals with heterocyclic amines [13, 14]. During formation of the imidazole complex there is a sudden change in absorption in the region of deformation vibrations of the heterocyclic ring and for benzimidazole in the bond vibrations of the benzene ring.

In the region 700-200 cm^{-1} where a.b. for Rh–N bond vibrations should occur, in the process of $RhCl_3$ complex formation with imidazole an a.b. appears at 348 cm^{-1} with shoulders at 325, 292, and 278 cm^{-1}, with benzimidazole at 350 and 315 cm^{-1}, medium intensity at 250 cm^{-1}, and for 3(5)-methylpyrazole at 335 cm^{-1} with a shoulder at 342 cm^{-1} and 298 cm^{-1} with a shoulder at 305 cm^{-1}. Although there is no well defined reference a.b. for Rh–N and Rh–Hal bond vibrations in the literature, a.b. in the region 300-350 cm^{-1} are usually attributed to M–Hal bond vibrations [13, 14] and a.b. in the region 250-300 cm^{-1} to M–N bond vibrations.

It is possible to conclude from a series of experiments that complex formation proceeds by way of coordination of Rh with "pyridine" type N atoms and this is supported by data in [15, 16].

EPR and UV spectroscopic investigations indicate that Rh(III) is partially reduced during the process of complex formation. To a large extent reduction of Rh(III) results from reaction with a molecule of heterocyclic amine. This is confirmed by IR spectra of the complexes where changes in absorption of a.b. characteristic of bond and deformation vibrations of C=N and C–N groups are observed indicating transfer of electron density from nitrogen to rhodium. As a result of this electron density transfer there is partial reduction of Rh(III) to Rh(I) and an increase in the negative charge on Cl leading to the formation of a strong H bond with the N–H group (the shift in the a.b. characteristic of this bond vibration is 200 cm^{-1}).

The metal complexes which we synthesized only exhibited catalytic activity after their preliminary activation. The change in the condition of the heterogeneous catalytic system during the process of activation by $NaBH_4$ was followed by EPR.

After $NaBH_4$ treatment of sample A (Fig. 1b) a sharp decrease is observed in the intensity of signal X resulting from decomposition of the acidic adducts of rhodium. The lines with g equal to 2.849 and 1.896 remain; a line with significantly higher intensity appears in the spectrum. The spectrum can be regarded as a superposition of two signals from Rh(II) complexes of different composition. It can be assumed that two complexes exist with axial symmetry with g = (2.556; 2.220) and g = (2.405; 2.035) or g = (2.556; 2.035) and g = (2.405; 2.220). At the same time the possibility cannot be ruled out that this is a spectrum of two complexes which have rhombic symmetry in which the lines with g ~ 2.283 and g ~ 2.075 are single values of the average components of the g-tensor [17]. The signal with g ~ 2 ($g_{\perp}$ = 2.010 and $g_{\parallel}$ = 1.996) can be attributed to Rh(0) [18].

In the EPR spectrum for sample C (Fig. 2b) treated with $NaBH_4$, the signal with g = (2.098; 2.010, 1.988) (similar to X) is preserved, indicating the resistance of the acidic forms of the heterogeneous benzimidazole complex to the effects of reduction. In addition a line with g = 2.468, 2.222, appears which probably corresponds to Rh(II) [19].

Thus, during sodium borohydride treatment of catalysts A and C paramagnetic centers, heterogeneous in both structure and composition, are formed on the surface of both samples. After $NaBH_4$-activated samples of A and C have been exposed to air all the lines corresponding to nitrogen-containing complexes of Rh(II) bonded to the polymer matrix disappear and an intense signal with g = 2.098; 2.012; 1.993, appears. The latter is evidently caused by the formation of acidic adducts of rhodium.

Reduction of Nitrobenzene by Sodium Borohydride

Preliminary experiments showed that catalysts A-C are not active in the reduction of nitrobenzene (82°C, propan-2-ol) either in an inert medium (Ar) or in an atmosphere of H_2. They only become active in reduction reactions after treatment with $NaBH_4$ in propan-2-ol solution. We noticed that during $NaBH_4$ treatment the color of the catalysts change to dark cinnamon.

Specific experiments showed that $NaBH_4$ in propan-2-ol solution did not reduce nitrobenzene in the absence of the catalyst. The highest conversion rate for nitrobenzene was achieved with catalyst A ($W_0 = 7.4 \cdot 10^{-1}$ mole/g-atom Rh•min). Catalyst C only exhibited moderate activity ($W_0 = 1.9 \cdot 10^{-1}$ mole/g-atom Rh•min).

It can be assumed that the higher catalytic activity of sample A is due to decomposition of the acidic adducts and formation of Rh(0) complexes during interaction with $NaBH_4$.

Note that nitrobenzene is converted selectively to aniline in the presence of sample A but for B and C an approximately equivalent amount of azoxybenzene is also formed. Carrying out the process in H_2 does not affect the reaction rate. Evidently under the given conditions the extent of H_2 participation in the formation of rhodium hydride complexes is negligible and the catalytically active centers are formed under the influence of $NaBH_4$. The introduction of O_2 leads to a reduction in the reaction rate. For example in the presence of catalyst A the reduction rate of nitrobenzene decreases ~2 times. The observed reduction in the rate can be accounted for by acidic hydride complexes of rhodium which play a key role in hydrogenation reactions of unsaturated compounds.

Reduction of Nitrobenzene by Propan-2-ol

The metal complexes A-C promoted with KOH catalyze the reaction (1)

$$PhNO_2 + 3i\text{-}C_3H_7OH \xrightarrow[Cat]{KOH} PhNH_2 + 3(CH_3)_2CO + 2H_2O \quad (1)$$

KOH (in the absence of the catalyst) does not bring about reduction of nitrobenzene (82°C, $[KOH] = 8.7 \cdot 10^{-3}$ mole/liter).

As can be seen from Table 1, when propan-2-ol is used as the hydrogen donor the reduction rate of the nitro group is much lower than in the case of $NaBH_4$; the exception is catalyst B ($W_0 = 1.1 \cdot 10^{-1}$ mole/g-atom Rh•min). Note also that in the presence of catalysts A and B reduction of nitrobenzene proceeds selectively to aniline but for catalyst C an equivalent amount of azoxybenzene is also formed.

LITERATURE CITED

1. V. F. Dovganyuk, L. I. Lafer, V. I. Isaeva, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 2660 (1987).
2. V. F. Dovganyuk, V. I. Isaeva, and V. Z. Sharf, Izv. Akad. Nauk SSSR, Ser. Khim., 1223 (1988).
3. V. Z. Sharf, V. D. Kopylova, L. P. Karapetyan, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 2746 (1977).
4. B. N. Laskorin, N. G. Zhukova, O. N. Grishina, et al., Zh. Prikl. Khim., 55, No. 3, 555 (1982).
5. V. Z. Sharf, V. F. Dovganyuk, V. I. Isaeva, and B. I. Maksimov, Izv. Akad. Nauk SSSR, Ser. Khim., 534 (1989).
6. B. Wayland, A. Newman, J. Am. Chem. Soc., 101, No. 21, 6472 (1979).
7. B. James, F. Ng, and E. Ochiai, Can. J. Chem., 50, No. 4, 590 (1972).
8. D. T. Sviridov, R. K. Sviridova, and Yu. F. Smirnov, in: Optical Spectra of Transition Metal Ions in Crystals [in Russian], Nauka, Moscow (1976), p. 4.
9. A. Zeccina, L. Cerruti, S. Coluccia, and E. Borello, J. Chem. Soc., B, No. 12, 1363 (1967).
10. A. M. Bellocq, C. Perchard, A. Novak, and M. L. Jozien, J. Chem. Phys., 1334 (1965).
11. J. Reedjik, Rec. Trav. Chim. Pays-Bas., 90, 117 (1971).
12. L. J. Bellamy and A. J. Owen, Spectrochim. Acta, 25A, 329 (1969).
13. J. Reedjik, Rec. Trav. Chim. Pays-Bas., 88, 1451 (1969).
14. J. A. Welleman, Macromol. Chem., 182, 785 (1981).
15. C. W. Reimann, A. Mighell, and F. A. Mauer, Acta Crystallogr., 23, 135 (1967).
16. A. A. Kashaev, É. A. Zel'bet, M. P. Demidov, et al., Koordinats. Khim., 4, 685 (1978).
17. D. Goldfarb and L. Kevan, J. Phys. Chem., 90, No. 22, 5787 (1986).
18. H. Caldarary, M. De Armond, K. Hanck, and V. Sahini, J. Am. Chem. Soc., 98, 4455 (1976).
19. V. E. Shubin, V. A. Shvets, and V. B. Kazanskii, Kinet. Katal., 19, 1270 (1978).