Structure and catalytic activity of metallocomplexes immobilized on carriers

6.* Hydrodehalogenation of *p*-bromotoluene in the presence of silica-deposited Ru complexes

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Mono-, bi-, and trinuclear Ru complexes with various ligands immobilized on the surface of silica gels modified with γ-aminopropyl, formamide, sulfide, cyano, or mercapto groups, catalyze hydrodehalogenation of *p*-bromotoluene by the transfer of hydrogen from $NaBH_4$ in 2-propanol both in an Ar atmosphere and in air. The structures of the heterogenized metallocomplex catalysts prepared (the nature of the ligand environment, the oxidation number of the central atom) were studied by IR and XP spectroscopy. The immobilized binuclear $Ru^{II,III}$ tetraacetate, which retains the structure of the original complex, exhibits higher catalytic activity in the hydrogenolysis of *p*-bromotoluene than heterogenized mononuclear systems.

Key words: *p*-bromotoluene, dehalogenation; ruthenium, immobilized complexes; modified silica gel.

It has been shown previously[1] that the nature of the ligand environment of immobilized binuclear Rh^{II} complexes determines the structure and properties of the catalytic system being formed; in the case of acetate ligands, the binuclear structure with a M—M bond is retained. Deposited binuclear Rh^{II} complexes differ from mononuclear complexes by higher activities in the reduction of ketones, the reduction of halogen derivatives of benzene, and the reduction of substituted phenylcyclopropanes.[1,2] To continue the investigations along this line, in the present work we studied the effect of the structure of Ru complexes deposited on modified silica gels on the activity of the resulting catalyst in the reductive hydrodehalogenation of *p*-bromotoluene (*p*-BT) occurring *via* the transfer of hydrogen from $NaBH_4$ in 2-propanol.

Experimental

The following Ru compounds were chosen for immobilization on the surface of modified silica gels: mononuclear $RuCl_3$, binuclear ruthenium(II,III) tetraacetate and tetrasulfate containing M—M bonds, and trinuclear hexaacetate in which the Ru atoms are only linked through bridging ligands. For comparison, immobilized dirhodiumtetraacetate was prepared by the known procedure.[3] $[Ru_2(\mu\text{-}O_2CMe)_4]$,[4] $[Ru_2(\mu\text{-}SO_4)_4(H_2O)_2]$,[5] and $[Ru_3(\mu^3\text{-}O)(\mu\text{-}O_2CMe)_6]$[6] were prepared according to the reported procedures. Ru black and Ru/SiO_2 were synthesized by treating a methanolic solution of $RuCl_3$ or Ru chloride preliminarily deposited on SiO_2 by impregnation,[7] respectively, with sodium tetrahydroborate. Silochrom silica gels (S_{sp} = 120 m^2 g^{-1}) modified with γ-aminopropyl (γ-AMPS), formamide, sulfide, cyano, and mercapto groups were used as carriers (the concentration of a modifier amounted to $7 \cdot 10^{-4}$ mol g^{-1}).

Heterogenization of complexes was carried out from aqueous and methanolic solutions in an Ar atmosphere.[2] *p*-BT of 98 % purity and "pure" grade 2-propanol were used. The experiments were carried out in a reactor equipped with a magnetic stirrer, a water jacket, a reflux condenser, and a facility for sampling.[1] A catalyst (0.05—0.1 g, $4.95 \cdot 10^{-6}$ g-at. of Ru) and $NaBH_4$ (0.025 g) were placed in the reactor, the system was filled with Ar (or air), and 2-propanol (5 mL) was added. The reaction mixture was stirred at 82.5 °C to activate the catalyst, and then *p*-BT ($9.9 \cdot 10^{-5}$—$4.95 \cdot 10^{-4}$ mol) was added. According to the data of atomic absorption spectrometric analysis, the immobilized complexes are not washed out during hydrodehalogenation.

The composition of the catalysate was determined by GLC using a Biokhrom-21 chromatograph with a flame ionization

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* For Part 5, see Ref. 1.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 70—74, January, 1995.

detector at 100—170 °C (with N_2 as the carrier gas, and a 3 m×3 mm stainless-steel column filled with Triton on X-545 Celite).

The activity of the catalysts was characterized by the initial specific rate of the formation of toluene determined graphically, w_0/mol (g-at. of Ru)$^{-1}$ min^{-1}.

The IR spectra of the immobilized metal complexes were recorded on a Specord M-80 instrument.

The X-ray photoelectron spectroscopic (XPES) studies were carried out on a ES-200V instrument. The 1s (E_b = 285 eV) line corresponding to the layer of hydrocarbons adsorbed on the surface (the diffusion oil) was used as the reference line. Deconvolution of unresolved lines was carried out using the program for the synthesis of peaks on a PDP 11/03L microcomputer. The Ru/Si atomic ratios were determined from the corresponding integral intensities taking into account the corrections for the cross-section of photoionization and the depth of free leakage of the transmission coefficient of the analyzer for electrons with various kinetic energies.[7]

Results and Discussion

The metallocomplex systems studied exhibited activity in the hydrodehalogenation of *p*-BT occurring *via* the transfer of hydrogen from $NaBH_4$ in 2-propanol. Systems based on Ru tetrasulfate deposited on silica gels modified with γ-aminopropyl, formamide, sulfide, cyano, and mercapto groups catalyze the hydrogenolysis of *p*-BT; the rates of the reactions (w_0) are similar and are 0.27—0.31 mol (g-at. of Ru)$^{-1}$ min^{-1} (Table 1). The activity of these metallocomplex catalysts obviously does not depend on the nature of the group grafted to silica gel.

The structure of the immobilized complex is of much greater significance (Table 2). In the presence of the mononuclear compound $RuCl_3$ deposited onto γ-AMPS, hydrogenolysis of the C—Br bond occurs at a lower rate than that in the presence of heterogenized binuclear Ru sulfate. Immobilized binuclear Ru tetraacetate exhibits the highest activity of the catalytic systems studied. The heterogenized trinuclear Ru hexaacetate containing no M—M bond exhibits low activity equal to that of deposited $RuCl_3$. Thus, the catalytic properties of an immobilized system depend both on the nature of the ligand environment and on the structure of the original complex.

Table 1. Hydrodehalogenation of *p*-bromotoluene in the presence of $[Ru_2(\mu\text{-}SO_4)_4(H_2O)_2]$ immobilized on modified silica gels ($2.5 \cdot 10^{-6}$ g-at. of Ru, $4.45 \cdot 10^{-5}$ mol of *p*-BT, 10 mL of 2-propanol, $7.7 \cdot 10^{-4}$ mol of $NaBH_4$, $3.8 \cdot 10^{-4}$ mol of CaO, 82 °C)

The modifying group	$w_0/\dfrac{\text{mol}}{\text{(g-at. of Ru) min}}$
$-(CH_2)_3-NH_2$	0.28
$-CH_2-S-(CH_2)_2-CN$	0.27
$-(CH_2)_2-SH$	0.29
$-(CH_2)_3-NHCOH$	0.31

Table 2. Hydrodehalogenation of *p*-bromotoluene in the presence of Ru (Rh) complexes deposited on silica gel modified with γ-AMP ($4.9 \cdot 10^{-6}$ g-at. of Ru (or $2.4 \cdot 10^{-6}$ g-at. of Rh), $9.9 \cdot 10^{-5}$ (or $4.45 \cdot 10^{-5}$) mol of *p*-BT, 10 mL of 2-propanol, $7.7 \cdot 10^{-4}$ (or $3.35 \cdot 10^{-4}$) mol of $NaBH_4$, $3.8 \cdot 10^{-4}$ mol of CaO, 82 °C)

The compound being immobilized	$w_0/\dfrac{\text{mol}}{\text{(g-at. of Ru (or Rh)) min}}$		
	Ar	Air	
		static conditions	bubbling
$RuCl_3$	0.17	0.15	0.08
$[Ru_2(\mu\text{-}SO_4)_4(H_2O)_2]$	0.54	0.16	—
$[Ru_2(\mu\text{-}O_2CMe)_4]$	1.37	1.17	1.31
$[Ru_3(\mu^3\text{-}O)(\mu\text{-}O_2CMe)_6]$	0.17	0.15	—
$[Rh_2(O_2CMe)_4]$	6.98	0.51	—

The conditions of the preliminary treatment of a catalyst with sodium tetrahydroborate have a substantial effect on the catalytic activity (Fig. 1). The interaction of sodium tetrahydroborate with alcohol affords hydride ions[8] that activate the metal complex and recombine to give molecular hydrogen, which is inactive in the reaction under study. The higher specific rate at the initial period is probably due to the presence of a great number

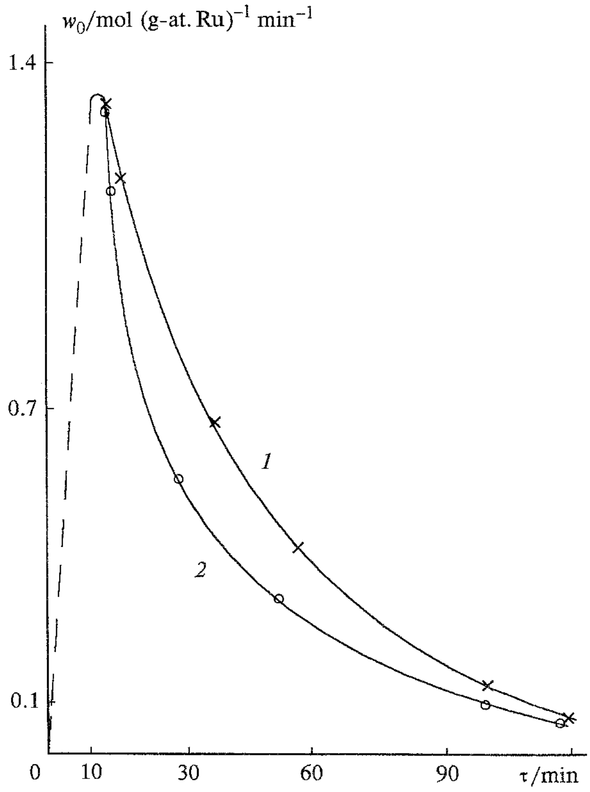

Fig. 1. The effect of the duration of the preliminary treatment with $NaBH_4$ on the rate of hydrodehalogenation of *p*-BT in the presence of $[Ru_2(\mu\text{-}O_2CMe)_4]$/γ-AMPS in an Ar atmosphere (*1*) and in air (*2*).

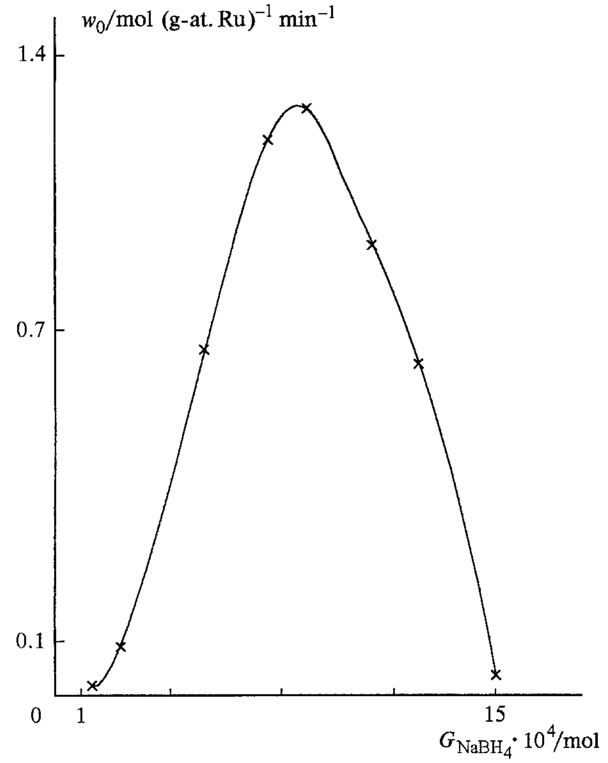

Fig. 2. The effect of the amount of $NaBH_4$ (G) on the rate of hydrodehalogenation of *p*-BT in the presence of $[Ru_2(\mu\text{-}O_2CMe)_4]/\gamma$-AMPS.

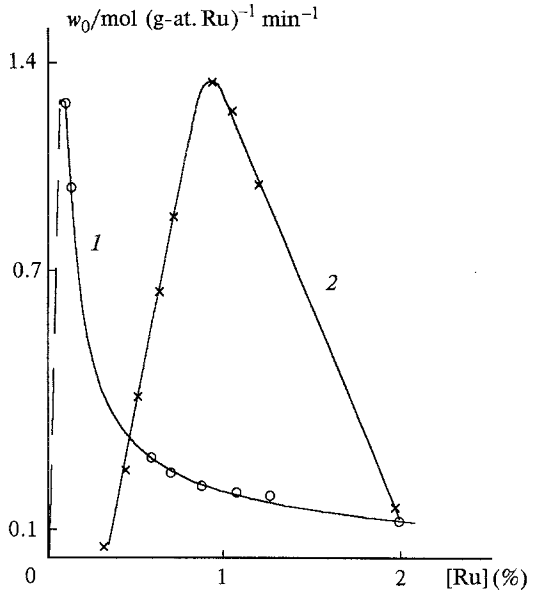

Fig. 3. The effect of the content of Ru in the catalyst on the rate of hydrodehalogenation of *p*-BT in the presence of $[Ru_2(\mu\text{-}SO_4)_4(H_2O)_2]/\gamma$-AMPS (*1*) and $[Ru_2(\mu\text{-}O_2CMe)_4]/\gamma$-AMPS (*2*).

of metallocomplex species containing active hydride forms of Ru.[9] The decrease in the activity is apparently caused by the decrease in the amount of undecomposed $NaBH_4$. The dependence of w_0 on the content of $NaBH_4$ presented in Fig. 2 has an extremal character. This results from the dual role of $NaBH_4$ (a donor of hydrogen and an activator of the metallocomplex). The increase in the activity may be explained by the increase in the number of active complex Ru-containing species, while the decrease in the activity corresponds to the "over-reduction" of Ru to give Ru(0), which is inactive in the reaction. In fact, both Ru black and Ru metal deposited onto silica gel exhibit no activity in the hydrodehalogenation of *p*-BT. A similar phenomenon (an extremal dependence of w_0 on the amount of $NaBH_4$) has been observed previously[1] in the hydrogenolysis of *p*-BT in the presence of dirhodiumtetraacetate immobilized on the same carrier.

Further investigation showed that the activity of the catalytic systems under consideration depends on the amount of the complex being deposited. Figure 3 indicates that the activity is characterized by a maximum, the position of which can be substantially different depending on the composition of the complex. The optimal concentration of Ru in the catalyst is 1 % for the acetate cluster and 0.14 % for the sulfate cluster. These dependences are quite typical of immobilized metallocomplexes.[10] The dramatic increase in the initial specific rate of the reaction at low concentrations of ruthenium may be due to an increase in the number of active sites. The decrease in the activity is probably associated with the fact that not all of the catalytic sites are accessible to the substrate when the amount of the complex deposited exceeds a certain limiting value.

From the results of the XPS study (Table 3), it follows that the Ru/Si ratio for the γ-AMPS-supported sulfate complex with 0.5 % (w/w) Ru on the carrier is half that for the specimen with 1 % (w/w) Ru. However, for the specimens with 1 and 2 % (w/w) Ru, these ratios are identical, which may result from the penetration of the Ru complexes into deep pores inaccessible to X-ray photoelectron measurements. This is in agreement with the catalytic results: in the presence of the catalyst containing 2 % (w/w) Ru the initial specific rate of the reaction is half that for the specimen with 1 % (w/w) Ru. It is likely that some of the metallocomplexes located in the deep pores do not participate in the catalysis.

Table 3. The state of Ru in γ-AMPS-supported complexes

The complex being immobilized	[Ru] (%, w/w)	E_b $(3d_{5/2})$/eV* Ru^{II}	Ru^{III}	Ru/Si
$[Ru_2(\mu\text{-}SO_4)_4(H_2O)_2]$	—**	281.8 (40)	283.2 (60)	—
$[Ru_2(\mu\text{-}SO_4)_4(H_2O)_2]$	0.5	282.0 (18)	283.4 (82)	0.010
$[Ru_2(\mu\text{-}SO_4)_4(H_2O)_2]$	1.0	282.0 (25)	283.0 (75)	0.021
$[Ru_2(\mu\text{-}SO_4)_4(H_2O)_2]$	2.0	281.7 (48)	283.1 (52)	0.018
$[Ru_2(\mu\text{-}O_2CMe)_4]$	1.0	282.0 (49)	283.2 (51)	0.015

* The contents (%) of Ru^{II} and Ru^{III} in the complex, respectively, are given in parentheses. ** Unsupported complex.

Many metallocomplex systems are known[11] to be readily deactivated by oxygen. The activity of the catalytic systems under consideration in air depends on the nature of the ligand environment in the immobilized complex (see Table 2). The immobilized Ru tetraacetate was found to be the most oxygen-resistant: the rate of the reaction in the presence of this complex did not change even when air was bubbled through the reaction mixture. The previously studied immobilized dirhodiumtetraacetate is more sensitive to exposure to air: the initial specific rate of hydrodebromination in the presence of this catalyst decreased by a factor of ~15 in an air atmosphere. Thus, the Ru catalysts under study possess high resistance to atmospheric oxygen under the conditions of hydrodehalogenation. This is an important advantage of these catalysts over Rh-based (especially Rh^{I}-based) catalytic systems.

The metallocomplex systems synthesized were studied by IR and XP spectroscopy. When the acetate complex is deposited onto γ-AMPS, some variations occur in the region of the stretching vibrations of the grafted groups in the IR spectrum: along with the two absorption bands (AB) typical of primary amines recorded in the spectrum of the starting γ-AMPS, two additional AB were recorded at 3260 and 3180 cm^{-1}, which may be assigned to the amino groups coordinated by Ru atoms, since a short-wavelength displacement of the N—H stretching frequencies is characteristic of coordinate-bonded amines.[12] The absorption band at 3280 cm^{-1} cannot be observed in the spectrum, since the band at 3260 cm^{-1} is superimposed on it. Thus, one may conclude that Ru is coordinated to NH_2 groups and that some of the amino groups remain free. Bands typical of COO vibrations (ν_{as} 1585 cm^{-1} and ν_s 1420 cm^{-1}) are present in the region of carboxyl group vibrations. These AB are also observed in the spectrum of the original complex (1585 and 1425 cm^{-1}). The high intensity of these bands and also the fact that the COO vibration frequencies are not displaced indicate that the four acetate bridges are retained in the complexes immobilized on the carrier surface.

A different picture is observed when the trinuclear Ru hexaacetate complex containing no M—M bond is deposited. The IR spectrum of this complex exhibits no AB typical of vibrations of carboxyl groups. In the region of the stretching vibrations of the grafted groups, changes similar to those described above for the immobilized binuclear Ru tetraacetate are observed. Thus, it may be suggested that heterogenization of the trinuclear acetate complex containing no Ru—Ru bond, unlike that of binuclear complexes containing M—M bonds, is accompanied by the destruction of the original complex to give a mononuclear complex in which the acetate groups have been replaced by the amino groups of the carrier.

In the case of the γ-AMPS-supported sulfate complex, the Ru atoms are coordinated by the amino groups of the carrier, as shown by IR spectroscopy. However, the IR spectra do not allow one to judge whether the original ligand environment is retained, since the AB of the carrier are superimposed on the AB of the sulfate groups. Using XP spectroscopy we managed to show that the 2p line associated with sulfur is missing, which probably implies that the sulfate groups have been replaced by the amino groups of the carrier.

The XP spectrum of the Ru acetate complex immobilized on γ-AMPS has a $3d_{5/2}$ line with E_b = 283.0 eV and the $3d_{5/2}$ line with E_b = 281.0 eV corresponding to Ru^{III} and Ru^{II}, respectively. The Ru^{III} : Ru^{II} ratio is 1 : 1. Together with the data of IR spectroscopy, this may indicate that the binuclear structure of the Ru^{II}—Ru^{III} tetraacetate complex is retained after its immobilization on the surface. An analogous phenomenon has been observed previously for the immobilization of dirhodiumtetraacetate on γ-AMPS where the presence of bridging acetate ligands favored the retention of the binuclear structure.[2]

From the data of Table 3, one can see that when the heterogenized sulfate complexes are used, the specimen containing 2 % (w/w) Ru is the closest to the original complex: the ratio between the intensities of the lines associated with Ru^{II} and Ru^{III} is 1 : 1. As the content of the complex on the carrier decreases, some variations are observed in the X-ray photoelectron spectrum (compared with the spectrum of the unsupported compound), namely, the intensity of the line corresponding to Ru^{II} decreases; the content of the Ru^{III} species correspondingly increases and is as high as 85 % for the specimen containing 0.5 % (w/w) Ru. It is likely that the binuclear $Ru^{II,III}$ sulfate complex is partially destroyed during deposition to give a mononucler Ru^{III}-containing complex.

The results obtained make it possible to consider the problem of the relationship between the structure of metallocomplexes and their catalytic properties. As was noted above, the heterogenized acetate Ru complex exhibits the highest activity. According to the data of IR and XP spectroscopy, the binuclear structure of the complex is most likely retained after immobilization. In the case of the sulfate complex, which is less active than the acetate complex, one may assume that both mono- and binuclear structures are present on the carrier. Immobilized trinuclear Ru hexaacetate, in which the metal atoms (nuclei) are linked through bridging acetate groups and the central O atom, is an order of magnitude less active than the catalyst based on binuclear Ru tetraacetate containing an M—M bond; its activity is equal to that of the heterogenized mononuclear $RuCl_3$. Based on the spectral data, one may assume that the trinuclear complex decomposes at the carrier surface to give a mononuclear complex.

Thus, it was concluded that an immobilized Ru complex that retains the binuclear structure of the original compound possesses higher catalytic activity in the hydrogenolysis of *p*-bromotoluene than heterogenized mononuclear systems.

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Received February 8, 1994;
in revised form June 9, 1994