SELECTIVITY IN THE HYDROGENATION OF AROMATIC NITRO-COMPOUNDS IN THE PRESENCE OF A PLATINUM—POLYETHYLENEIMINE COMPLEX

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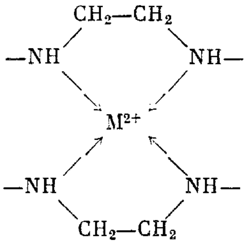
It has been shown [1-4] that complex catalysts based on platinum are highly selective in the hydrogenation of aromatic nitro-compounds to the corresponding N-arylhydroxylamines in aprotic solvents containing aliphatic amines. In the present study we have investigated the catalytic properties of a water-soluble complex of platinum with polyethyleneimine (Pt—PEI).

Carrying out the catalytic process in aqueous solution makes it possible to convert the single-phase catalytic system into a two-phase system, in which the catalyst is present in solution, while the reaction product is only slightly soluble in water. It may be noted that complexes of Group VIII metals with polymers containing amino groups catalyze the hydrogenation of monoolefins, dienes and aromatic compounds [5-7] and the disproportionation of olefins [8, 9].

RESULTS AND DISCUSSION

1. Synthesis and Investigation of the Pt—PEI Complex. The complex Pt(IV)—PEI can be obtained by the reaction of H_2PtCl_6 with PEI, and the complex Pt(II)—PEI by the reaction of K_2PtCl_4 with PEI. In both cases complexes of constant composition are obtained, independent of the proportions of the reactants; the complex Pt(IV)—PEI contains 37% Pt and the complex Pt(II)—PEI 16% Pt. A Rh(III)—PEI complex, containing 16% Rh, is also known [10].

The structure of the complexes synthesized is presumably analogous to that described for the complexes of Cu and Co [11, 12], in which the metal is coordinated to four nitrogen atoms



The platinum complexes are not reduced by H_2 at atmospheric pressure, or by hydrazine hydrate, formalin or formic acid. The reduced form of the complexes is obtained by the action of $NaBH_4$.

The electronic absorption spectrum of Pt(II)—PEI contains a band with λ_{max} = 255 nm. The same band is observed for its reduced form, persisting in air for a long time, which is evidence for a reversible oxidation-reduction conversion.

A PMR study of Pt(II)—PEI showed that complex formation considerably perturbs the spectrum of the polymeric ligand: signals at 0.8 ppm for PEI and at 0.35, 1.02 and 1.13 ppm for the complex. The parameters of the signal with δ = 0.35 ppm change markedly on increasing the temperature, which permits its assignment to the protons of the NH groups of PEI, apparently participating in various types of hydrogen bond. The remaining signals are naturally assigned to the protons of the CH_2 groups of the polymer chain. The nonequivalence of these protons in the PMR spectrum may be due to branching in the polymer chain or to conformational transitions in the ethyleneimine portion [13]. The addition of $NaBH_4$ hardly

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TABLE 1. Binding Energy (eV) and Integrated Intensity* of the XPE and Auger Peaks for the Complex Pt(IV)–PEI

Spectral line	E_b(A)	E_b(B)	I (A)	I (B)
Pt4f	72,8 **	–	6.4	0
C1s	285,0	285,0	61,0	72.0
Cl2p	197	198,9	4,7	3,9
B1s	–	192,1	–	3,3
Na1s	–	1071,3	–	26,8
N1s	399,0	399,6	14,2	7,0
Na($KL_{2,3}L_{2,3}$)	–	264,4	–	30,1

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*The intensities are given on the same scale for the initial and the reduced samples, A and B

**Value for the peak Pt4$f_{7/2}$.

changes the PMR spectrum, except for the appearance of a new signal with δ = 2.62 ppm and a change in the shift of the signal from the NH groups of the polymer.

The complexes Pt(II)–PEI, Pt(IV)–PEI and their reduced forms were investigated by x-ray photoelectron spectroscopy (XPES). The Pt4f line was absent from the XPE spectra of the reduced forms of both complexes. It was found that in air the reduced form of the complex Pt(II)–PEI is readily hydrolyzed (or becomes covered with adsorbed water molecules), so that the intensity of the other lines changes considerably with time. For this reason Table 1 gives the positions and intensities of the main peaks only for the complex Pt(IV)–PEI (A) and its reduced form (B). The absence of appreciable quantities of Pt in the analysis zone (15-30 Å), in spite of the high concentration of platinum (37%) and the high specific intensity of the Pt4f line, may be due either to the very high degree of aggregation of the Pt atoms or to complex formation with the polymer. In the case of complex formation the activity of the complex as a catalyst will be determined by the diffusion through the polymer of molecules (or portions of molecules) of the reactant.

The line Cl2p has a fairly high intensity both for complex A and for complex B. However, if the chlorine is bound mainly to platinum ions in complex A, in complex B it is bound mainly to sodium ions, as shown by the change in the value of E_b Cl2p.

In the analysis zone of complex B there is also a decrease in the number of N atoms, while the energy of the N1s level increases somewhat, which may be interpreted as a certain decrease in the negative charge on N. In particular, the decrease in the intensity of the N1s level may indicate that the groups containing nitrogen interact to some extent with the boron atoms, and/or are enclosed by them.

The binding energy B1s on the surface of the complex B is greater than E_bB1s in $NaBH_4$ (187.4 eV), but less than in B_2O_3 (193.2 eV). The boron is probably present as Na_3BO_3. This is also supported by the Wagner Auger parameter for Na, 2060.5 eV, appreciably less than the value for NaCl (2062.0 eV).

Following Nefedov [14], let us convert the ratio of the integrated intensities of the XPE lines into atomic ratios. In Pt(IV)–PEI the ratio $[Cl/N]_{at}$ = 0.24, which indicates that the content of chlorine is less in the analysis zone than in the bulk ($[Cl/N]_{at} \approx 1.5$), and accounts for the value of E_bPt4$f_{7/2}$ (see Table 1). Actually, the measured values of E_bPt4$f_{7/2}$ for the complexes K_2PtCl_6, K_2PtCl_4 and $Pt(PPh_3)_4$ are respectively 75.8, 73.2 and 71.7 eV, so that on the surface of the complex Pt(IV)–PEI the platinum is present in a state of oxidation less than +4. This may be due to the diffusion of chlorine within the polymer globule.

On the surface of the B complexes the ratio $[Cl/N]_{at}$ increases to 0.42 for Pt(IV)–PEI and 0.82 for Pt(II)–PEI.

2. Catalytic Properties of the Complex Pt(II)–PEI. This complex is the most interesting as a catalyst on account of its ready solubility in water.

The complex Pt(II)–PEI, reduced with $NaBH_4$, catalyzes the hydrogenation of aromatic nitro-compounds with H_2 at atmospheric pressure and temperatures of 10-70°C. At higher temperatures the activity of the catalyst falls and the deposition of grains of platinum

TABLE 2. Hydrogenation of Aromatic Nitro-compounds in the Presence of the Reduced Complex Pt(II)—PEI (20 cm^3 water, $5 \cdot 10^{-2}$ $mole \cdot dm^{-3}$ nitro-compound, 10^{-5} mole Pt dm^{-3})

Number of experiment*	T, °C	Specific activity, moles H_2 per mole Pt per min	[PEI],** wt. %	Reaction products (%)
1	20	2,2	–	Aniline (100)
2	30	3,9	–	Aniline, traces of azo- and hydrazobenzene
3	30	18,0	35,5	»
4	30	22,1	65,5	»
5	30	33,5	78,5	Phenylhydroxylamine (89.5)
6	30	37,1	91,4	» (93,0)
7	30	39,2	95,4	» (93,0)
8	30	11,0	99,5	» (93,0)
9	10	19,6	95,5	» (93,5)
10	20	25,6	95,5	» (93,5)
11	40	43,0	95,5	» (92,0)
12	50	58,0	95,5	» (92,0)
13	60	75,0	95,5	» (92,0)
14	30	34,6	87,0	p-Toluidine (98,0)

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*In experiments 1-13 the substrate was nitrobenzene, and in 14 p-nitrotoluene.

**Relative to the weight of the catalyst.

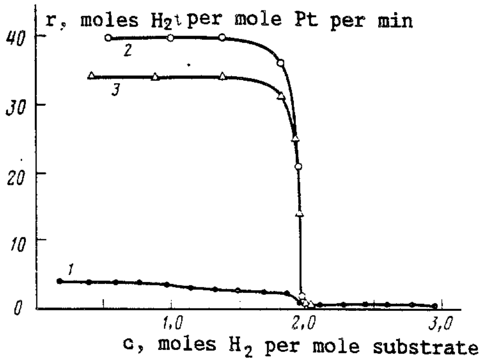

Fig. 1. Hydrogenation of aromatic nitro-compounds at 30°C. Concentration of nitro-compound 0.2 $mole \cdot dm^{-3}$ and of catalyst $2 \cdot 10^{-4}$ moles $Pt \cdot dm^{-3}$. 1) nitrobenzene, 2) nitrobenzene in the presence of a 95.5% excess of PEI, 3) p-nitrotoluene in the presence of an 87% excess of PEI.

is observed. The stability of the complex also depends on the pH of the solution; it is decomposed at pH < 6.96.

Up to two moles of H_2 per mole of substrate the rate of absorption of H_2 is practically constant, but then falls sharply, and the third mole of H_2 is absorbed 20-25 times more slowly. The typical shape of the curves is shown in Fig. 1.

The high stability of the catalyst should be mentioned; the hydrogenation of several successive samples of substrate takes place at the same rate. At concentrations of the nitro-compound >0.3 $mole \cdot dm^{-3}$ the catalyst is salted out as a dark brown oil, which after separating from the mother liquor and dissolving in water has the same catalytic activity as initially.

In the hydrogenation of nitrobenzene or p-nitrotoluene in water or in aqueous alcoholic solutions the main reaction product after the absorption of 2 moles of H_2 is the corresponding N-arylhydroxylamine, which can be separated by filtration with yields of up to 70%, the remainder being a mixture of the amine with the corresponding azo-, azoxy- and hydrazo-compounds. Nitrosobenzenes were not detected, but the presence of a number of products suggests that the reaction proceeds through nitroso-compounds.

The addition of aliphatic amines increases the yield of N-arylhydroxylamines [1-4], and therefore the hydrogenation of nitrobenzene and p-nitrotoluene was investigated in the presence of added PEI with the object of increasing the selectivity. When PEI is added the rate of absorption of the first 2 moles of H_2 increases by orders of magnitude (see Fig. 1), while the rate of hydrogenation of the N-arylhydroxylamines formed depends on the amount of PEI added. Thus the addition to the reaction mixture of up to 78% of PEI (relative to the mass of the complex) reduces the rate of reaction by a factor of 60-100, on adding 78-95.5% this factor is 200-300, while the addition of more than 95.5% PEI reduces the overall activity of the catalyst (Table 2). Under the optimum conditions the yield of N-phenylhydroxylamine reached 93.5%, and that of p-tolylhydroxylamine 98%.

The increase in the reaction rate for the absorption of the first two molecules of H_2 in the presence of added PEI may be attributed to the formation of molecular complexes of PEI with the aromatic nitrocompounds [15], thus reducing E_{act} for the rate-limiting stage, electron transfer to the aromatic nitro-compound.

On the other hand, PEI (being a stronger base) will displace N-arylhydroxylamines from the coordination sphere of the complex, thus sharply decreasing their rate of hydrogenation.

EXPERIMENTAL

The reagents and solvents have been described previously [16]. Hydrogenation was carried out as in [4]. At the end of the reaction the products were filtered off and the catalyst solution used repeatedly. The complexes were prepared from $H_2PtCl_6 \cdot 6H_2O$, K_2PtCl_4 and branched PEI with a molecular weight of 10,000.

Synthesis of Pt(IV)—PEI. A solution of PEI in acetone was added to a solution of 0.518 g $H_2PtCl_6 \cdot 6H_2O$ (10^{-3} moles) in 20 cm^3 acetone until the complex had been completely precipitated. The yellow precipitate was filtered off and washed with acetone. The complex is practically insoluble in water, acetone and alcohols.

Synthesis of Pt(II)—PEI. An aqueous solution of PEI (1.023 g) was added to a solution of 0.415 g (10^{-3} moles) of K_2PtCl_4 in 10 cm^3 of water and the mixture kept at room temperature for 24 h: the color then changed from red to yellow. On adding five-fold excess of ether the complex separated out as yellow droplets. The solution was decanted and the precipitate dried.

Synthesis of the Reduced Form of Pt(IV)—PEI. $4 \cdot 10^{-5}$ moles of $NaBH_4$ was added to a suspension of $4 \cdot 10^{-5}$ moles of the complex Pt(IV)—PEI in 20 cm^3 water, followed by mixing. The yellow precipitate of complex turned dark brown. The precipitate was filtered off and washed with water.

Synthesis of the Reduced Form of Pt(II)—PEI. $NaBH_4$ was added to a solution of the complex Pt(II)—PEI containing $2 \cdot 10^{-4}$ $mole \cdot dm^{-3}$ Pt to give a molar ratio Pt:$NaBH_4$ = 1:4. Reaction was complete after 2 h, when the solution had turned brown. On adding a five-fold excess of ether the reduced complex separated out on the walls of the vessel as brown oily droplets.

The catalyzate was analyzed by TLC (Silufol plates, eluent 4:1 benzene/ether, 1:4 benzene/hexane). The synthesized N-arylhydroxylamines were separated by extracting with ether; their mp agreed with published values [17].

The electronic absorption spectra were measured on Specord UV-VIS equipment. The PMR spectra were recorded (in dimethyl sulfoxide solution) on a Bruker SX F4-100 spectrometer (90 MHz). The XPE spectra were obtained on Varian IEE-15 apparatus with a magnesium anode ($h\nu$ = 1253.6 eV). The pressure at the outlet of the spectrometer chamber was $3 \cdot 10^{-4}$ Pa. The spectra were calibrated by using the C1s line (285.0 eV). The lines used in the analysis were Pt4f, B1s, C1s, Cl2p, Na1s and N1s. The values for the specific sensitivity of the lines were taken from Nefedov [14].

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CONCLUSIONS

1. Complexes of platinum with polyethyleneimine have been synthesized and characterized by spectroscopic methods.

2. It has been shown that the complex Pt(II)—PEI, reduced with sodium borohydride, is an active and selective catalyst for the hydrogenation of aromatic nitro-compounds.

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SPONTANEOUS EXPLOSIVE DECOMPOSITION OF VINYL SULFOXIDE COMPLEXES OF Fe^{3+}, Cr^{3+}, and Co^{3+} NITRATES

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With this paper, we wish to draw the attention of those involved in coordination chemistry to the need to take special safety measures in investigations of some nitrate complexes of metals containing ligands with unsaturated bonds.

While investigating the polymerization of butyl vinyl sulfoxide (BVSO) in the presence of metal salts, we observed that during the synthesis, storage, or polymerization of the vinyl sulfoxide complexes $Fe(NO_3)_3 \cdot 3BVSO$, $Cr(NO_3)_3 \cdot 3BVSO$, and $Co(NO_3)_3 \cdot 3BVSO$ their spontaneous explosive decomposition occurs with the formation of oxides of nitrogen, sulfur, metals, and coke-like products. The most unstable are iron complexes, which decompose with explosion at 20-40°C both in the pure state and in benzene, styrene, and methyl methacrylate solutions at concentrations of 40 mole % and higher. However, they are stable in alcohol, dimethyl sulfoxide (DMSO), and tributyl phosphate (TBP) solutions. We observed the decomposition of $Cr(NO_3)_3 \cdot 3BVSO$ only in the pure state at temperatures above 50°C and of $Co(NO_3)_3 \cdot 3BVSO$ only in exceptional cases (above 60°C) with the samples having been stored for a long time (more than 20 days) at ∿5°C before heating.

Such behavior of these compounds was completely unexpected because vinyl sulfoxide complexes of nitrates of bivalent metals $M(NO_3)_2 \cdot 2BVSO$, where M = Fe^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, or Mn^{2+}, and also complexes of nitrates of d and f metals in the bi- and trivalent state with saturated aliphatic and aromatic sulfoxides begin to slowly (without any explosive phenomena) decompose only with heating to 160-170°C, splitting off a sulfoxide molecule in the first

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