Complexes of palladium(II) and platinum(II) with the $PW_{11}O_{39}^{7-}$ heteropolyanion as catalytically active species in benzene oxidation

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Abstract

Aqueous solutions prepared from $Pd(H_2O)_4^{2+}$ and $PtCl_4^{2-}$ with heteropolytungstate $PW_{11}O_{39}^{7-}$ at the Pd(II) or Pt(II) to PW_{11} ratio from 1 to 8 and pH 2 and 4 have been characterized by means of UV–VIS and IR spectroscopy and ^{31}P and ^{195}Pt NMR. Three types of complexes have been detected in Pd(II) containing solutions. Two of them, $[PW_{11}O_{39}Pd]$ (1) and $[PW_{11}O_{39}Pd-O-PdO_{39}W_{11}P]$ (2) had sharp peaks at δ_1 −13.2 and δ_2 −12.8 ppm in ^{31}P NMR spectra. Possessing a broad signal at about −13 ppm, complex (3) represented a water-soluble oligomeric Pd(II) hydroxide stabilized by the heteropolytungstate. The complex of type (1) $(PW_{11}O_{39}Pt)$ was predominant in solutions of Pt(II). The Pd(II) complexes proved capable to catalyze the oxidation of benzene into phenol with a mixture of O_2 and H_2 gases in a two-phase water–benzene system at the temperature of 10 to 40°C. The yield of phenol for 1 h depended on the Pd(II) to PW_{11} ratio and on pH and reached a maximum at an O_2/H_2 ratio equal to 2. The catalytic action was attributed mainly to complexes (1) and (2). Under the reaction conditions, these complexes have been found to be reduced into Pd(0) species which readily activate dioxygen and are stabilized in solution by heteropolytungstate. Pt(II) containing systems were one order of magnitude less active than Pd(II) containing ones.

Keywords: Heteropolytungstate; Palladium complexes; Platinum complexes; Benzene oxidation; Oxygen; Hydrogen

1. Introduction

Complexes with heteropolymetalates (HPM), which behave as polydentate ligands to transition metal ions, are currently under intensive study. In particular, growing attention is paid to complexes with heteropolytungstates (HPT). In comparison with complexes of other metals, few data have been collected, however, for complexes of Pd(II) and Pt(II). This is obviously due to the molecular structure of HPT; while octahedral coordination of the metal ion is most suitable for incorporating into HPT, such a structure is not typical for Pd(II) and Pt(II). Several derivatives have been synthesized and characterized by spectral methods: $[Pd_3(A, \alpha-W_9PO_{34})_2]^{12-}$ [1], $[PW_{11}O_{39}PdL]^{m-}$ (L = H_2O, OH^-, Cl) [2], $[(WZnPd_2^{II})(ZnW_9O_{34})_2]^{12-}$ and $[(WZnPt_2^{II})(ZnW_9O_{34})_2]^{12-}$ [3,4]; the crystal structure of $K_2Na_6[Pd_2W_{10}O_{36}]\cdot 22H_2O$ has been found to include two four-coordinated Pd(II) ions surrounded by two polytungstate ligands [5].

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Transition metal complexes with HPM or a combination of transition metal compounds and HPM provide great possibility for designing homogeneous redox catalytic systems. They can function in three paths.

(1) HPM can be involved into the redox cycle. Some of these compounds are usable for re-oxidation of transition metal ions with dioxygen. For this purpose, P–Mo–V heteropolyacids were introduced into a Pd(II)-based catalytic system for alkene oxidation to aldehydes [6–8]. Several other catalytic systems containing Pd(II), Pt(II) or related ions and HPM are listed in recent reviews [9,10].

(2) When metal ion forms a complex with the HPM anion, the combined action of both parts may provide specific catalytic properties for the complex. This proposal has been formulated by Neumann [4] for the catalytic effect of complexes $[(WZnPd_2^{II})(ZnW_9O_{34})_2]^{12-}$ and $[(WZnPt_2^{II})(ZnW_9O_{34})_2]^{12-}$ in oxidation of alkene with hydrogen peroxide.

(3) Formation of complex with HPM may stabilize transition metal ion in the oxidation state most suitable for catalysis. The Finke's complex $[(n-C_4H_9)_4N]_5Na_3[(1,5-COD)M \cdot P_2W_{15}Nb_3O_{62}]$ (M = Ir, Rh) represents a good example [11,12]. In this case, heteropolyanion acts as a kind of support, which 'surface' fixes metal ions both in oxidized and reduced state, so that the catalytic oxidations with O_2 or O_2/H_2 mixture proved possible, as well as the hydrogenation with H_2.

In the present work, we tried the inactive with respect to oxygen HPT $[PW_{11}O_{39}]^{7-}$ as a ligand in Pd(II) and Pt(II) complexes and investigated catalytic properties of the systems in benzene oxidation with an O_2/H_2 gaseous mixture. Metallic Pt, Pd, Ir, Rh are known as catalysts of alkene and aromatic oxidations under similar conditions (see [13,14] and references cited therein). Here, we have shown that benzene oxidation with a O_2/H_2 mixture is catalyzed by Pd(II) complexes with HPT, as well. Due to the stabilizing effect of HPT, the complexes prove rather stable under the reaction conditions, although some reduction into metallic phase occurs.

2. Experimental

The aqueous solution of the $Pd(H_2O)_4^{2+}$ complex was obtained upon dissolving palladium hydroxide in 5.8 M H_2SO_4. The hydroxide was precipitated with Na_2CO_3 from a solution of H_2PdCl_4 followed by a thorough washing from Cl^- ions.

Solutions of Pd(II) complexes with HPT were prepared at ambient temperature by mixing a 0.01 M solution of $Na_7PW_{11}O_{39}$ (pH 4) and a 0.5 M solution of $Pd(H_2O)_4^{2+}$, with a molar ratio of $n = Pd(II)/PW_{11}$ being varied from 1 to 8. Pt(II) complexes with HPT were prepared by dissolving K_2PtCl_4 in a 0.01 M solution of $Na_7PW_{11}O_{39}$ at 90°C. In all cases a concentrated solution of Na_2CO_3 was used to adjust the pH to the required value (pH 4 for Pt(II) and pH 2 or 4 for Pd(II)). A stable pH value was installed in 12 h. Solutions of complexes have been consumed within a week; for this time, no changes in their composition have been detected by spectral means.

To deposit the complexes from the solutions, $[(C_4H_9)_4N]NO_3$ (TBA NO_3) at a molar ratio of TBA to HPT equal to 10 has been used. The separated TBA-salts were dried at 60°C and recrystallized from acetonitrile.

IR spectra of TBA-salts were registered in KBr on a Specord IR-75, UV–VIS spectra of solutions were recorded on a Specord M-40 (30000–11000 cm^{-1}), and NMR spectra on a Bruker MSL-400 spectrometer (all at room temperature). The resonance frequency of 161.98 MHz and accumulation frequency of 0.05 Hz were used for ^{31}P NMR, chemical shifts (δ) were measured with respect to an external aqueous solution of 85% H_3PO_4. A 0.1 M solution of $Na_7PW_{11}O_{39}$ has been used to estimate the concentration of HPT. ^{195}Pt NMR spectra were recorded at a resonance frequency of 86.0 MHz

and an accumulation frequency of 3 Hz; δ were counted from $\Xi = 21.4$ MHz.

For catalytic experiments, an aqueous solution of Pd(II) or Pt(II) complexes and benzene (3/10 v/v) was poured into a thermostatic flask equipped with a reflux condenser. The liquid phases were subjected to intensive stirring, while the reactor was continuously blown through with O_2/H_2 mixture. Products collected in an organic phase were analyzed on a Tsvet-500 chromatograph supplied with FID and a column of 0.4% nitroanilineanthraquinone on a carbon black.

3. Results

3.1. Characteristics of a system containing Pd(II) or Pt(II) and HPT

At the molar ratio of Pd/PW_{11} from 1 to 8 and pH 2 or 4, $Pd(H_2O)_4^{2+}$ and $PtCl_4^{2-}$ formed water soluble complexes with HPT $PW_{11}O_{39}^{7-}$. In the absence of HPT, the aqua-ion $Pd(H_2O)_4^{2+}$ underwent hydrolysis at pH > 1 with final production of solid palladium hydroxide [15].

UV–VIS spectra of the solutions containing Pd(II) or Pt(II) and PW_{11} were characterized by intensive absorption in the region of ν 30000–24000 cm^{-1} (Fig. 1a). The presence of HPT increased the absorption from $Pd(H_2O)_4^{2+}$ and $PtCl_4^{2-}$ by approximately 5 and 10 times, respectively, at $M(II)/PW_{11} = 1$. When the absorption of Pd(II)-containing solutions was plotted against the molar ratio $n = Pd(II)/PW_{11}$, the curves showed bending around $n = 1$ (Fig. 1b, curves 1, 2), which indicated on formation of, at least, two complexes. First of them, which formed at $n \approx 1$, exhibited relatively low absorption comparing with the second complex, which formed at $n > 1$ and displayed strong absorption at ν around 24000 cm^{-1} (Fig. 1a, spectra 1–6).

In contrast, the shape of corresponding curve for the Pt(II)-containing solution (Fig. 1b, curve 3) witnesses for a single complex to be formed upon interaction of $PtCl_4^{2-}$ with PW_{11}. The solu-
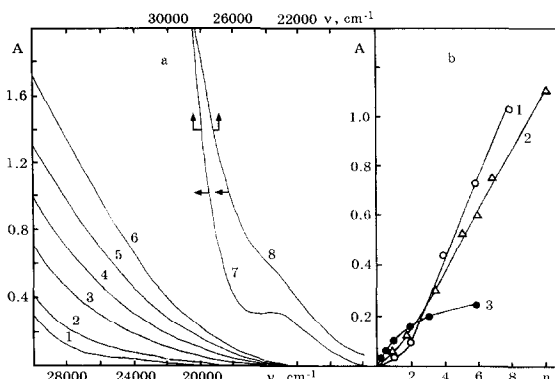

Fig. 1. (a) UV–VIS spectra of solutions prepared from $PW_{11}O_{39}^{7-}$ (0.01 M) and $Pd(H_2O)_4^{2+}$ at different $Pd(II)/PW_{11}$ ratio: 0.9 (1), 1.7 (2), 3.5 (3), 5.2 (4), 7.0 (5), 10.4 (6); pH 4, l 0.006 cm; 1.0 (7); pH 2, l 0.1 cm; 0.9 (8); pH 4, l 0.1 cm. (b) Intensity of absorption (ν 24000 cm^{-1}) of solutions prepared from $Pd(H_2O)_4^{2+}$ (1–2) and $PtCl_4^{2-}$ (3) with PW_{11} versus $n = M(II)/PW_{11}$: (1) pH 2, l 0.01 cm; (2) pH 4, l 0.01 cm, (3) pH 2, l 0.02 cm.

tion is characterized by the relatively low absorption in the visible region, and the Pt(II) complex with a strong absorption did not form in considerable concentration.

The composition of the solutions was investigated more in detail by NMR. ^{31}P NMR spectra of Pd(II) with PW_{11} had two characteristic peaks at δ_1 – 13.2 ppm and δ_2 – 12.8 ppm and a broad signal centered around – 13 ppm. The ratio between the integral intensities of the δ_1 and δ_2 peaks was 0.9 at $n = Pd(II)/PW_{11} = 1$ and pH 2 (Fig. 2, spectrum 1), 0.3 at $n = 1$ and pH 4 (spectrum 5), and decreased upon increasing n (compare spectra 1 and 3). Simultaneously, the broad signal around – 13 ppm appeared at $n > 1$ (Fig. 2, spectrum 3) and increased in intensity upon rising n. At n equal to 1 and pH 4, a peak of free $PW_{11}O_{39}^{7-}$ was observed at δ – 10.9 ppm which was replaced at pH 2 by a peak at δ – 12.4 ppm, probably belonging to $P_2W_{20}O_{70}^{10-}$ [16]. Free $PW_{11}O_{39}^{7-}$ contributed not more than 30% to total amount of HPT at pH 4 and $n = 1$ and was absent at $n = 3$. The sum of integral intensities of ^{31}P NMR signals corresponded to a total HPT concentration in the solution, thus evidencing that all HPT-containing species have been detected.
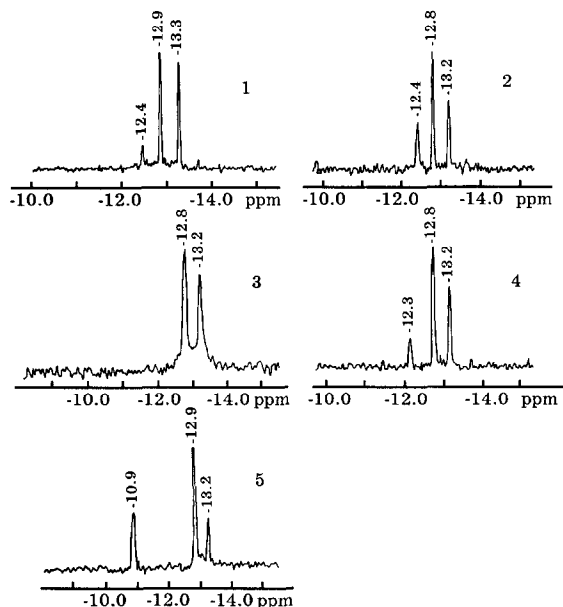
Fig. 2. ^{31}P NMR spectra of solutions of $PW_{11}O_{39}^{7-}$ (0.01 M) with $Pd(H_2O)_4^{2+}$: (1) 0.01 M Pd(II), pH 2; (2) solution (1) 1 h after beginning reaction with benzene; (3) 0.03 M Pd(II), pH 2; (4) solution (3) 1 h after beginning reaction with benzene; (5): 0.01 M Pd(II), pH 4.

Table 1
Results of elemental analysis of TBA-salts precipitated from $Pd(H_2O)_4^{2+} + PW_{11}O_{39}^{7-}$ solutions: pH 2 for Nos. 1–3, pH 4 for Nos. 4–6

No.	Pd/PW$_{11}$ ratio in solution	Weight content (%)			Atomic ratio P:W:Pd
		P	W	Pd	
1	1	0.64	42.9	2.45	1:11.3:1.1
2	2	0.72	45.4	4.72	1:10.6:1.9
3	6	0.56	35.2	12.2	1:10.6:6.4
4	1	0.72	45.6	2.57	1:10.7:1.0
5	6	0.59	40.7	11.9	1:11.6:5.9
6	8	0.55	36.1	15.3	1:11.0:8.1

(Fig. 3, spectrum 1) belonging to vibrational frequencies of the central PO_4 tetrahedron but differing from those for TBA-salt of $PW_{11}O_{39}^{7-}$ anion (ν 1105 and 1048 cm^{-1}, Fig. 3, spectrum 3) and for metal-substituted anions [17]. The spectrum of Pd(II) complexes (2 in Fig. 3)

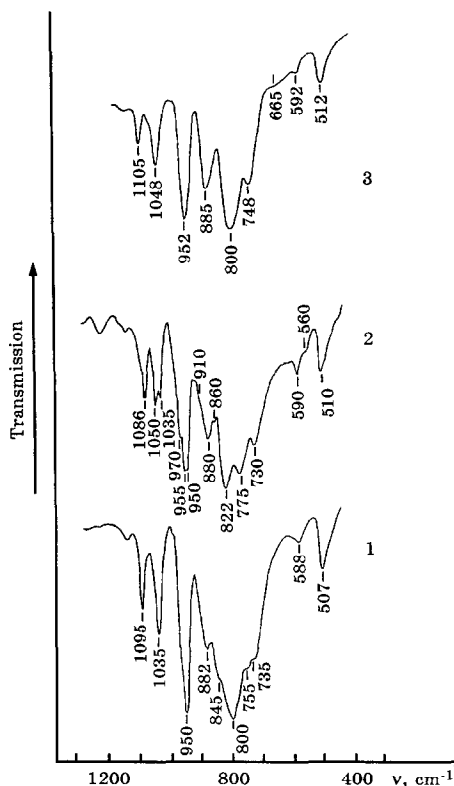In ^{31}P NMR spectra of a Pt(II) solution, a peak of a single complex at δ_1 − 13.2 ppm and a peak of free HPT have been observed, with the latter comprising to 80% of the total amount of HPT. The ^{195}Pt NMR spectrum had peaks of both the Pt(II) complex with HPT at δ 3347 ppm and the starting compound $PtCl_4^{2-}$ at δ 2909 ppm.

Pd(II) and Pt(II) complexes with HPT were separated as TBA-salts. Pd(II) was completely precipitated from the solution in the form of complexes with HPT. According to elemental analysis data, the composition of the separated complexes corresponded to the relative amounts of Pd(II) and PW_{11} in solution in the whole range of n studied (Table 1). Providing that HPT was completely bonded with Pt(II) at $n = 6$, 30% of Pt(II) were precipitated as complexes with an averaged composition of $Pt/PW_{11} = 2/1$.

The IR spectrum of the solid Pt(II) complex contained two bands at ν 1095 and 1035 cm^{-1}

Fig. 3. IR spectra of TBA-salts separated from $PtCl_4^{2-}$ and $PW_{11}O_{39}^{7-}$ (Pt(II)/PW$_{11}$ = 6, pH 4) (1); $Pd(H_2O)_4^{2+}$ and $PW_{11}O_{39}^{7-}$ (Pd(II)/PW$_{11}$ = 1, pH 2) (2), $PW_{11}O_{39}^{7-}$, pH 4 (3).

contained three bands in this region: ν 1086, 1050 and 1035 cm^{-1}. The two latter bands may be referred to different Pd(II) complexes with HPT. Formation of Pd(II) complexes changed the spectrum of $PW_{11}O_{39}^{7-}$ anion in the region of bridged W–O–W bonds, but the spectrum was not affected upon varying n from 1 to 8.

3.2. Catalytic properties

Pd(II) and Pt(II) containing systems showed catalytic activity in benzene oxidation with an O_2/H_2 gaseous mixture in the two-phase liquid system. During the reaction, phenol was formed with a selectivity of 98%, along with other detectable products comprising cyclohexanol and quinone (by 1% each). Negligible conversion of benzene was observed in the absence of hydrogen.

In Table 2, the data are given on the yield of phenol for 1 h in the systems based on Pd(II) and Pt(II) complexes. The presence of an equimolar amount of $PW_{11}O_{39}^{7-}$ produced no effect on activity of K_2PtCl_4 but increased activity of $Pd(H_2O)_4^{2+}$. When the $Pd(II)/PW_{11} = n$ ratio was increased to 2, the amount of phenol was increased by a factor of 1.5–2. However, further increase of the n ratio had only a slight effect on activity of Pd-containing system.
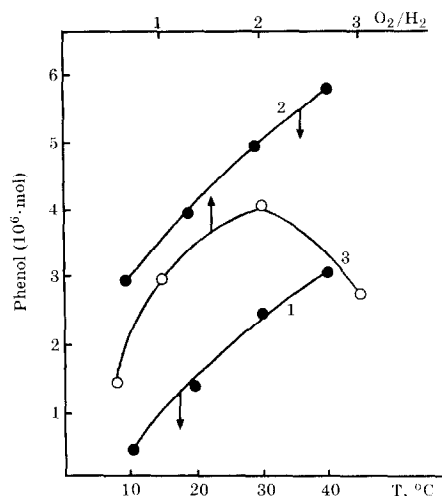

Fig. 4. Dependence of the yield of phenol for 1 h on the temperature (1, 2) and O_2/H_2 ratio (3). Conditions: $3 \cdot 10^{-6}$ mol Pd(II), $3 \cdot 10^{-6}$ mol PW_{11}; (1) $O_2/H_2 = 2$, pH 4; (2) $O_2/H_2 = 2$, pH 2; (3) pH 2, T 20°C.

Upon increasing pH from 2 to 4, the formation of phenol was retarded. Such a tendency has been observed at any n (within 1 to 8) and is probably caused by changes in the composition of the complexes in solution, rather than by a direct effect of acidity on the reaction rate. Alkalization of the solution from pH 2 to pH 4 just before the reaction did not result in appreciable influence on the yield of phenol. In this case, the composition of the complexes in the solution was not changed yet, as confirmed with ^{31}P NMR.

The reaction was conducted in the temperature range of 10–40°C and showed a positive temperature dependence of the phenol yield for 1 h (Fig. 4, curves 1 and 2). The highest amount of phenol was obtained at the O_2/H_2 ratio equal to 2 (Fig. 4, curve 3).

As seen from the curves in Fig. 5, there is a progressive increasing of the reaction rate for approximately 1 h, but a decrease becomes appreciable after 5–6 h. Several minutes from starting the reaction, a slight deposition of metal was observed on the walls of the glass reactor. However, a part of palladium still remained in

Table 2
Yield of phenol in the reaction catalyzed by Pd(II) and Pt(II) complexes. Conditions: $H_2O/C_6H_6 = 3/10$, $O_2/H_2 = 2/1$. 20°C, reaction time 1 h

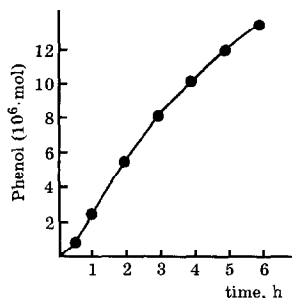| Composition of aqueous solution	PW_{11} (10^6 mol)	Pd(II) or Pt(II) (10^6 mol)	Phenol (10^6 mol)
Pd(II) + PW$_{11}$, pH 2	3	3	4.0
	3	6	6.2
	3	18	6.9
Pd(II) + PW$_{11}$, pH 4	3	3	1.0
	3	6	2.5
	3	18	3.1
Pd(H$_2$O)$_4^{2+}$, pH 2	0	3	1.0
Pt(II) + PW$_{11}$, pH 4	3	3	0.1
PtCl$_4^{2-}$, pH 3	0	3	0.1

Fig. 5. The yield of phenol versus time. Conditions: $3 \cdot 10^{-6}$ mol PW_{11}, $3 \cdot 10^{-6}$ mol Pd(II), $H_2O/C_6H_6 = 3/10$, $O_2/H_2 = 2$, pH 4, T 30°C.

solution even 6 h after the beginning of the reaction (approximately 50% in the experiment depicted in Fig. 5). When the solution of $Pd(H_2O)_4^{2+}$ without HPT was taken for the reaction (immediately after pH 2 had been adjusted), complete reduction and deposition of metal proceeded in 5 min. In the presence of HPT, the metal deposition became pronounced only upon contacting the solution with net hydrogen at an increased temperature (e.g., nearly all palladium was deposited from the solution for 30 min under the action of hydrogen at 60°C). The pre-reduced solution of the Pd(II) complex with HPT at pH 2 showed a 4 times lower activity in the formation of phenol as compared with the initial one.

We investigated the reduction of the complexes of Pd(II) with HPT under the standard conditions of our experiments more in detail, as well as the influence of the metal deposition on the catalytic performance of the system. The effect proved to be substantially different for the three cases.

(1) Fig. 2 presents ^{31}P NMR spectra of a solution containing Pd(II) and PW_{11} in equimolar ratio at pH 2: the initial one (1) and that 1 h after the beginning of the reaction (2). The peak at δ_1 -13.2 ppm decreased during the reaction, which resulted in the increase of the peak from free HPT at δ -12.4 ppm. After separation of metallic Pd, the solution still contained 70% of initial palladium. This solution was repeatedly

tested in benzene oxidation and showed only half of its initial activity.

(2) When the Pd(II) to PW_{11} ratio n was 3 at pH 2, the broad band around δ -13 ppm disappeared 1 h after starting the reaction and a peak of free HPT was developed. Other peaks at δ_1 and δ_2 stayed nearly unchanged (Fig. 2, spectra 3 and 4). The palladium content in the solution comprised 56% of the initial value; nevertheless, the activity proved to be the same as the initial one.

(3) At pH 4 and $n = 1$, the change in intensity for peaks at δ_1 -13.2 and δ_2 -12.8 ppm was negligible, so that the spectrum of the solution after reaction was identical to the initial one. The solution contained 80% of initial palladium but exhibited even a somewhat higher activity in benzene oxidation.

Experiments have also been performed with some transition metal containing HPT instead of $PW_{11}O_{39}^{7-}$. $[PW_{11}O_{39}Cu(H_2O)]^{5-}$, $[PW_{11}VO_{40}]^{4-}$, $[PW_{11}TiO_{40}]^{5-}$ have been tried. They were mixed with Pd(II) at pH 2 and a Pd(II)/HPT ratio of 1. Formation of insoluble Pd(II) hydroxide did not take place in these cases either.

The presence of the second metal ion in the HPT moiety influenced the activity of the Pd(II) + HPT systems. Pd(II) together with Ti-containing HPT appeared practically inactive whereas Pd(II) combined with Cu-containing HPT was twice as active as Pd(II) with $PW_{11}O_{39}^{7-}$. Pd(II) together with V-containing HPT catalyzed the oxidation with about the same activity as Pd(II) with $PW_{11}O_{39}^{7-}$.

4. Discussion

Spectral data allow a tentative conclusion to be made on the structure of the three types of complexes of Pd(II) and Pt(II) with HPT.

The metal ions in the $[PW_{11}O_{39}M]$ (1) and $[PW_{11}O_{39}M-O-MO_{39}W_{11}P]$ (2) complexes (M is Pd or Pt) are connected with several (1 to 4) oxygen atoms situated near the vacancy in the

structure of HPT. Asymmetrical interaction in complex (1) results in significant deformation of the HPT central fragment, thus shifting one of the PO_4 IR bands to ν 1035 cm^{-1}. The corresponding band at ν 1050 cm^{-1} for complex (2) lies closer to that for free $PW_{11}O_{39}^{7-}$. In the ^{31}P NMR spectrum, peaks at δ_1 − 13.2 ppm and δ_2 − 12.8 ppm correspond to complexes (1) and (2). The identical position of the ^{31}P signals for Pd(II) and Pt(II) complexes can be explained by the lack of the fifth coordination bond between the metal ions and the HPT moiety. Such a bond would affect phosphorus considerably but is not formed because of the square planar location of ligands typical for Pd(II) and Pt(II). The intensity of the visible absorption of complexes (1) and (2) is several times higher than that of the starting $Pd(H_2O)_4^{2+}$ and $PtCl_4^{2-}$ complexes.

Complex (3) consists of oligomeric Pd(II) hydroxide species [18] which are stabilized in solution due to bonding with HPT. The oligomeric complex is characterized by a very intensive absorption in the region of 30000–24000 cm^{-1}. Including a great and variable number of metal ions (up to 8, on an average), complex (3) does not give individual discrete IR bands distinct from (1) and (2) in the region characteristic for the $PW_{11}O_{39}^{7-}$ anion. In the ^{31}P NMR spectrum, the complex displays a broad band around − 13 ppm, which is widened due to H$^+$ exchange between the hydroxide fragment and water.

There are three types of complexes in a solution of $Pd(H_2O)_4^{2+}$ with $PW_{11}O_{39}^{7-}$. An increased concentration of Pd(II) and pH (from 2 to 4) is in favor of dimeric and oligomeric Pd(II) species to be formed. It results in a preferable formation of complexes (2) and (3) which comprised the bi- and polynuclear Pd fragments. The negligible amount of such complexes with platinum is obviously due to a too slow formation of oligomeric species in this case. Therefore, a complex of type (1) predominates in solutions of $PtCl_4^{2-}$ with $PW_{11}O_{39}^{7-}$.

Because of the kinetic inertness of Pd(II) and

Pt(II) complexes with HPT, relative amount of complexes (1), (2), and (3) is controlled by the rate of their formation and does not correspond to equilibrium concentrations.

In principal, the catalytic activity of the system might be attributed to metallic particles resulted from reduction of Pd(II) and Pt(II) ions. Such a reduction did take place in solutions of $Pd(H_2O)_4^{2+}$ and $PtCl_4^{2-}$ under the applied conditions of catalytic testing. The capability of metallic particles to catalyze benzene oxidation with O_2/H_2 under mild conditions is known [14] and the catalytic reaction is believed to proceed through interaction of an organic substrate with an in situ generated hydrogen peroxide.
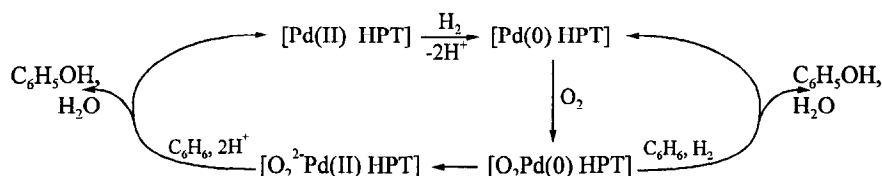
Meanwhile, the Pd(II) + HPT systems displayed a higher catalytic activity as compared with the metallic species of palladium formed in the absence of HPT. In the presence of HPT, only a part of Pd(II) complexes was transferred into the metallic phase during reaction. ^{31}P NMR spectra in Fig. 2 clearly demonstrate that Pd(II) oligomers belong to most easily reducible complexes. They converted into the metallic form before other Pd(II) complexes with HPT. For one hour, approximately half a palladium was deposited as metal from the solution including oligomeric complexes (spectrum 3, 4 in Fig. 2). Nevertheless, the activity stayed the same after removing the metal. Thus, the conclusion can be drawn that the main contribution to catalysis is made by dissolved complexes rather than metallic palladium.

This conclusion finds further confirmation when we compare activities of solutions with fixed concentration of PW_{11} and varied concentration of Pd(II). Increasing the concentration of Pd(II) above a 2-fold excess does not produce significant effect on the yield of phenol because excessive palladium is consumed to enlarge oligomeric fragment of complexes.

During reaction, the main Pd-containing species in solution are complexes (1) and (2). Partial reduction of Pd(II) complexes gives Pd(0) complexes with HPT which readily activates

dioxygen and makes possible the reaction with benzene or with benzene and hydrogen as co-re-

ducer. The concentration of Pd(0) complexes is too low to be detected by NMR.

$$
\begin{array}{c}
\text{C}_6\text{H}_5\text{OH}, \\
\text{H}_2\text{O}
\end{array}
\quad
[\text{Pd(II) HPT}] \xrightarrow[-2\text{H}^+]{\text{H}_2} [\text{Pd(0) HPT}]
\quad
[\text{O}_2^{2-}\text{Pd(II) HPT}] \xleftarrow{\quad} [\text{O}_2\text{Pd(0) HPT}]
\quad
\begin{array}{c}
\text{C}_6\text{H}_5\text{OH}, \\
\text{H}_2\text{O}
\end{array}
$$

According to ^{31}P NMR spectra before and after the reaction, complex (2) is more resistant to metal deposition during catalytic reaction than complex (1). It may be one of the reasons for the increase in activity upon increasing the Pd(II)/PW$_{11}$ ratio from 1 to 2 (Table 2). Even though at $n = 1$ and pH 2 Pd(II) is already completely involved into the complexes with HPT, an increased n ratio provides an enhanced concentration of complex (2) (Fig. 2, compare spectra 1 and 2) which keeps activity over a more extended period and, thus, produces a larger quantity of phenol than complex (1).

Pt(II)-containing systems show lower activity than Pd(II) ones both in the absence and in the presence of HPT. As in the case of a Pd-containing system, only partial deposition of Pt as metal takes place in the reaction mixture in the presence of HPT.

To get more detailed information concerning the interaction of Pd(H$_2$O)$_4^{2+}$ with metal-containing HPT like [PW$_{11}$O$_{39}$Cu(H$_2$O)]$^{5-}$, the work is to be continued. At the moment, we can establish that the second metal (Cu, V or Ti) provides an effect on catalysis by palladium. The similarity with bicomponent supported catalysts described in the literature is obvious; introduction of Cu [19] or some metal oxides [14] into the active phase of catalyst increased the catalytic activity in the oxidation of benzene with an O$_2$/H$_2$ mixture. The promotion effect was associated with the close contact of the two components on the surface of the catalyst. In the system based on HPT, a close contact of two metal ions could be realized if both metal ions

were 'absorbed' near deficiency in the structure of the PW$_{11}$O$_{39}^{7-}$ anion.

Acknowledgements

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