Ligand Exchange in Pd(II)–NaCl–H₂O and Pd(II)–HCl–H₂O Systems: Quantum-Chemical Consideration

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Abstract—The behavior of potassium tetrachloropalladate(II) in media simulating biological liquids is studied. The rate of aquation in aqueous NaCl solutions is shown to be higher than the rate at which the Cl⁻ ligand enters the inner coordination sphere of the Pd atom. In HCl solutions, the formation of the Pd chloro complexes predominates due to protonation of water molecules in the composition of aqua complexes. The reactions of replacement of the ligands (H₂O molecules and H₂O⁺ ion) in the planar Pd(II) complexes by the chloride ion are studied by the ZINDO/1 method. All the complexes containing H₂O and H₂O⁺ ligands, except for [Pd(H₂O)₄]²⁺, contain intramolecular hydrogen bonds. The ZINDO/1 and RHF/STO-6G(d) calculations revealed “nonclassic” symmetrical O···H···O hydrogen bond in the [[Pd(H₂O)₄(H₂O)⁺]²⁺ and trans-[Pd(H₂O)₂(H₂O)Cl]²⁺ complexes. The replacement of the H₂O⁺ ion by the Cl⁻ ion at the first three steps is thermodynamically more advantageous than the displacement of water molecules from the metal coordination sphere. The logarithms of stepwise stability constants of Pd(II) chloro complexes are found to correlate linearly with the enthalpies (ZINDO/1, PM3) of reactions of H₂O replacement by Cl⁻.

The Pd-containing compounds exhibit the biological activity. The variety of the biological properties of the Pd ions and of another platinum-group metals is determined by the chemical and stereochemical properties of coordination compounds of these metals with the biologically active ligands (DNA, amino acids, peptides, etc.) and, in particular, by the structure of the metal–ligand coordination site (fragment or functional group of a biological system) [1]. The Pd(II) complexes with organic ligands are considered to be promising in the production of medicines [2].

While studying reactions of the Pd²⁺ ion with bioligands, one should take into consideration its interaction with inorganic compounds contained in liquid media of a living organism. It is not improbable that inorganic ligands (H₂O, Cl⁻, etc.) can compete with the biologically active ligands for the metal ion and thus reduce toxicity of the latter ion. On the other hand, binding of the metal cation with inorganic ligands can decrease the efficiency of medicines prepared from compounds of this metal. The Pd(II) complexes are known to be bonded by the DNA molecules and to violate ordinary course of the replication process (transcription and translation) [1].

The Pd(II)–NaCl–H₂O and Pd(II)–HCl–H₂O systems can be used to model the behavior of the Pd(II) compounds in biological liquids. For instance, a 0.86% (0.147 M) solution of NaCl can be used as a model of blood plasma, while a 0.1 M solution of HCl, as that of a gastric juice [3].

The aim of this work was to study the reactions of exchange of the H₂O and H₂O⁺ ligands for Cl⁻ in the chloride and hydrogen chloride solutions of Pd(II).

EXPERIMENTAL

Potassium tetrachloropalladate(II) was synthesized as described in [4] from metallic Pd and PdCl₂. The K₂[PdCl₄] (0.03067 M) and NaCl (0.1 M) solutions were prepared from the precisely weighed samples; a 0.1 M solution of HCl was prepared from a reagent with fixed concentration.

The kinetic studies were carried out using spectrophotometric method. The electronic absorption spectra of the reaction mixtures were recorded on a UV VIS SPECORD spectrophotometer. The working solution of K₂[PdCl₄] with a concentration of 8.496 × 10⁻⁵ mol/l was prepared by dilution. The initial solution of K₂[PdCl₄] (3.610 ml) and the solution of 0.1 M NaCl or HCl (20 µl) were poured into a cell (1 cm) with the aid of a dispenser.

The quantum-chemical calculations were performed by ZINDO/1 [5], PM3 [6], and RHF/STO-6G(d) [7] methods with the HyperChem¹ program package and full optimization using the Polak–Ribiere algorithm [8]. The gradient rate did not exceed 0.02 kcal/(mol Å).

¹HyperChem (TM), Hypercube, Inc, 1115 NW 4th Street, Gainesville, Florida 32601, USA.
Table 1. The plots of $\ln A = a + bt$ and the correlation coefficient $r$ for the Pd(II)–NaCl–$\text{H}_2\text{O}$ and Pd(II)–HCl–$\text{H}_2\text{O}$ reaction systems

<table>
<thead>
<tr>
<th>System</th>
<th>$a$</th>
<th>$b$, min$^{-1}$</th>
<th>$r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(II)–NaCl–$\text{H}_2\text{O}$</td>
<td>$-0.6280 \pm 0.0351$</td>
<td>$-0.001817 \pm 0.000282$</td>
<td>$-0.9596$</td>
</tr>
<tr>
<td>Pd(II)–HCl–$\text{H}_2\text{O}$</td>
<td>$-0.1304 \pm 0.0079$</td>
<td>$0.0008128 \pm 0.0001725$</td>
<td>$0.9525$</td>
</tr>
</tbody>
</table>

The regression analysis was performed for the confidence level 0.95 with allowance for the Student coefficient.

RESULTS AND DISCUSSION

The electronic absorption spectra of the reaction systems obtained by mixing of aqueous solutions of $K_2\text{PdCl}_4$ and NaCl (HCl) show that the tetrachloropalladate ion undergoes aquation in these aqueous solutions and gives complexes of different composition ($\text{Pd(H}_2\text{O)}_4\text{Cl}_2$), [$\text{Pd(H}_2\text{O)}_2\text{Cl}_3$], [$\text{Pd(H}_2\text{O)}\text{Cl}_3$] as a result of replacement of $\text{H}_2\text{O}$ in the inner coordination sphere of the hydrated Pd atom by the Cl ion. According to the data in [9, 10], the aqua chloride complexes ($[[\text{Pd(H}_2\text{O)}_2\text{Cl}_3]$, [$\text{Pd(H}_2\text{O)}_2\text{Cl}_3$], [$\text{Pd(H}_2\text{O)}\text{Cl}_3$] and the chloride complex [$\text{PdCl}_4^{2-}$ have close spectroscopic characteristics. Therefore, it would be natural to consider the optical density at wavelengths corresponding to the maxima of absorption bands of the reaction mixtures (222, 235.5, 279 nm) as a value characterizing the total absorption of the Pd(II) chloro complexes and almost proportional to the total concentration of species with the Pd–Cl bonds.

We found that the optical density of the reaction mixture $K_2\text{PdCl}_4$–NaCl–$\text{H}_2\text{O}$ at $\lambda = 222$ nm decreases with time. On the contrary, the optical density of the $K_2\text{PdCl}_4$–HCl–$\text{H}_2\text{O}$ system grows with time. Hence, in aqueous solutions of NaCl, the aquation rate is higher than the rate of Cl$^-$ entering the inner coordination sphere of the Pd atom, whereas in HCl solutions, the total absorption of the Pd(II) chloro complexes and formation of chloro complexes (each proceeding in two ions Na$^+$ and H$^+$). Therefore, only one reasonable explanation of different kinetic behavior of these systems can be suggested, namely, the protonation of the $\text{H}_2\text{O}$ ligand in the presence of HCl. This suggestion agrees with the quantum-chemical data.

We performed the quantum-chemical study of the replacement of the ligands (H$_2$O molecules and H$_3$O$^+$ ion) in the planar Pd(II) complexes by the chloride ion using the ZINDO/I method. We also assumed that in an acid medium, one aqua ligand in the composition of each of these two complexes is protonated. A single protonation of either of the studied aqua complexes (except for $[\text{Pd(H}_2\text{O)}\text{Cl}_3]$), whose one water molecule can be protonated in principle), results in the formation of positively charged complex ions, while the addition of one more proton to these complexes is doubtful (particularly to a triple-charged $[\text{Pd(H}_2\text{O)}_3(\text{H}_2\text{O})]^3^+$ and double-charged cis- and trans-$[\text{Pd(H}_2\text{O)}_2(\text{H}_2\text{O})\text{Cl}]^{2+}$ cations).

Given below are the quantum-chemical data on the point group of symmetry we obtained for the complexes: $C_1$ for [$\text{Pd(H}_2\text{O)}_3]^{2+}$, $C_2$ for [$\text{Pd(H}_2\text{O)}_2(\text{H}_2\text{O})]^3^+$, $C_1$ for [$\text{Pd(H}_2\text{O)}_3\text{Cl}]^{2+}$, $C_1$ for cis-$[\text{Pd(H}_2\text{O)}_2(\text{H}_2\text{O})\text{Cl}]^{2+}$,

The plots $\ln A$–$t$ (A is the optical density, $t$ is time) are almost linear (Table 1; Figs. 1, 2), which is typical for the first-order reactions. Since in both chloride and hydrogen chloride solutions the reactions of aquation and formation of chloro complexes (each proceeding in many stages) occur simultaneously, these plots cannot be perfectly linear. Even if the conclusion on the first-order reaction is too categorical, it is important that the order reaction is too categorical, it is important that the sign of a slope of the $\ln A$–$t$ plots is common for the reactions of aquation and replacement of the aqua ligand by the chloride ion and the comparison of two reaction systems Pd(II)–NaCl–H$_2$O and Pd(II)–HCl–H$_2$O we performed is correct. These systems only differ in two ions Na$^+$ and H$_2$O$^+$. Therefore, only one reasonable explanation of different kinetic behavior of these systems can be suggested, namely, the protonation of the H$_2$O ligand in the presence of HCl. This suggestion agrees with the quantum-chemical data.

![Fig. 1. The plot of $A$ vs. $t$ for the Pd(II)–NaCl–$\text{H}_2\text{O}$ system.](image1)

![Fig. 2. The plot of $A$ vs. $t$ for the Pd(II)–HCl–$\text{H}_2\text{O}$ system.](image2)