COMPLEX OF PALLADIUM WITH p-BENZOQUINONE

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In the study of the catalytic oxidation of ethylene to acetaldehyde in solutions containing aqua ions of Pd(II) and quinones, it has been proposed that palladium (o)-quinone complexes are formed as intermediate products, and their redox conversion to Pd(II) and hydroquinone determines the rate of the reaction [1]. In this work conditions were found in which a complex of palladium with quinone is isolated from the reaction solution.

EXPERIMENTAL METHOD

Production of the Complex. A 150 ml portion of a solution containing \(6 \cdot 10^{-3} \) M PdSO\(_4\), \(1.2 \cdot 10^{-2} \) M \(p-C_6H_4O_2\), \(0.15 \) M H\(_2\)SO\(_4\), and \(50\%\) (by volume) C\(_2\)H\(_4\)OH was shaken for 30 min at \(0^\circ\) in an atmosphere of N\(_2\) containing 5% ethylene or propylene. The red precipitate formed after the absorption of 120 ml of olefin was washed with 50% alcohol, then with pure alcohols, with ether, and dried at \(\sim 20^\circ\); yield of the complex 1.37 g (97%).

Analysis of the Complex. A weighed sample of the complex was dissolved in a mixture of conc. HNO\(_3\) and HClO\(_4\), 1:1, with heating or in diluted (1:1) hydrochloric acid at \(\sim 20^\circ\). Samples were collected from the solution obtained for the determination of Pd (precipitation with dimethylglyoxime [2]) and SO\(_4^{2-}\) (precipitation with Ba\(^{2+}\) [3]) by a gravimetric method. The content of C and H was determined by the standard method of combustion. The amount of p-benzoquinone in the complex was determined according to the amount of hydroquinone formed in the redox decomposition of the complex in HCl, by potentiometric titration with K\(_2\)Cr\(_2\)O\(_7\) [4]. For this purpose a weighed sample of the complex was dissolved in the minimum amount of HCl (for example, 0.25 g in 3 ml of conc. HCl). The solution obtained was diluted and acidified with H\(_2\)SO\(_4\). Control titration of a solution of p-C\(_6\)H\(_4\)O\(_2\) of known concentration was conducted under analogous conditions. Found: Pd 44.9, C 13.4; H 2.0; C\(_6\)H\(_4\)O\(_2\) 23.2; SO\(_4^{2-}\) 21.8; H\(_2\)O (by difference) 10.1\%; C\(_6\)H\(_6\)O\(_9\)SPd\(_2\). Calculated: Pd 45.2; C 15.3; H 2.1; C\(_6\)H\(_4\)O\(_2\) 22.9; SO\(_4^{2-}\) 20.4; H\(_2\)O 11.5%.

The IR spectra of p-benzoquinone and its complex, tableted with KBr, were obtained on a UR-10 spectrometer. The spectra of these substances, suspended in liquid petrolatum, were identical with the former.

The derivatogram of the complex was obtained on the derivatograph of the system of F. Paulik - I. Paulik - L. Erdey, sample weight 200 mg, rate of heating 5 deg/min.

The x-ray L\(_{III}\) absorption spectra of palladium in the investigated complex and in PdSO\(_4\) were obtained on a DRS-2 spectrometer in the first order of reflection from the system of planes of quartz 10 T1 with resolving power 10,000. The density of the absorbent was 3 mg/cm\(^3\) Pd. The sample is not decomposed in the case of irradiation.

DISCUSSION OF RESULTS

The interaction of ethylene or propylene, diluted with nitrogen, with aqueous alcohol solutions of PdSO\(_4\) and p-benzoquinone leads to the formation of a fine crystalline red diamagnetic substance with the composition (p-C\(_6\)H\(_4\)O\(_2\))Pd\(_2\)SO\(_4\)·3H\(_2\)O.
Fig. 1. IR spectra of p-benzoquinone (1) and the investigated complex (2).

The IR spectra of substituted p-benzoquinone were discussed in detail in [5]. On the basis of these studies, let us consider the changes in the frequencies of the nonplanar $\delta_{C-H}$ (895, 945 cm$^{-1}$) and valence vibrations $\nu_{C=O}$ (region of 1655-1672 cm$^{-1}$), occurring during complex formation (Fig. 1). The frequency 1595 cm$^{-1}$ evidently belongs to $\nu_{C=C}$ of the ring. As is well known [5, 6], as a result of Fermi resonance, in the spectra of p-benzoquinones, instead of one frequency $\nu_{C=O}$, two appear, while in the case of formation of a complex with coordination through the ring [7], one remains, shifted by $\sim$100 cm$^{-1}$ into the long-wave region. A comparison of the spectra in Fig. 1 permits us to consider that in the complex that we obtained, palladium is also coordinated with the quinone ring, and not through the oxygen. In the first place, one band remains in the spectrum, shifted to 1620 cm$^{-1}$ ($\Delta = \sim$43 cm$^{-1}$), overlapping with $\nu_{C=C}$, which is shifted in the short-wave direction, which agrees with the $\pi$-acceptor properties of p-benzoquinone. In the case of coordination with one of the oxygens, two frequencies $\nu_{C=O}$ should appear in the spectrum. Moreover, in the case of such coordination $\delta_{C-H}$ should change little, as, for example, $\delta_{C-H}$ changes little in triphenylphosphines when the phosphorus atom is coordinated with metal. From Fig. 1 it is evident that in the region of $\delta_{C-H}$, the frequencies correspond to the frequencies observed in the spectra of monosubstituted quinones [5] (865, 900 cm$^{-1}$), and their intensity is sharply lowered. Thus, the change in the spectrum in the region of $\delta_{C-H}$ can be explained only by coordination of Pd with the quinone ring.

We should note that neither the shape of the IR spectrum nor the chemical composition of the complex depends on the nature of the organic solvent (alcohol, acetone, dioxane) and olefin (ethylene, propylene) used for its production. In all cases there are no bands in the spectra belonging to the vibrations of the coordinated olefin and the molecules of the organic solvent. These results agree with the conclusion that olefins and the organic solvent do not enter into the complex.

On the basis of the data of [8], let us assign the broad band with maximum 3450 cm$^{-1}$ to the valence vibrations of the coordinated water, in which the protons participate in the formation of hydrogen bonds. The deformational vibrations of water (usually 1640 cm$^{-1}$) are overlapped by the intense $\nu_{C=O}$.

The vibrations of the coordinated $SO_4^{2-}$ ion distinctly appear in the spectrum. On the basis of the well-known assignment of the frequencies in the spectrum of solid CaSO$_4$ [9], let us consider that the vibrations in the region of 1120, 1145, and 1170 cm$^{-1}$ belong to the type of $\nu_3$, 1000 cm$^{-1}$ to $\nu_1$, and 625, 640 cm$^{-1}$ to $\nu_4$. The frequency in the region of 430 cm$^{-1}$ is assigned to $\nu_2$. However, this assignment is conditional, since a superposition of the vibrations of the quinone is possible here.

The composition cited above is confirmed by the thermogram and derivatogram of decomposition of the complex (Fig. 2). AT 140$^\circ$ the complex loses 11% of its mass with evolution of heat, which corresponds to the removal of three molecules of water (11.5% theoretically). At 150$^\circ$ (up to 220$^\circ$), 22.5% of the mass is lost, which corresponds to the elimination of a molecule of p-benzoquinone (22.9% theoretically). Above