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Abstract

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RADIATION CHEMISTRY OF AQUEOUS SOLUTIONS OF DIVALENT PALLADIUM SALTS

Earlier we described ([1,2]) a radiation method for obtaining platinum and palladium catalysts, consisting in the irradiation of aqueous solutions of complex salts of these elements with a beam of high-energy electrons. In the present work the radiolytic reduction of divalent palladium in aqueous solutions has been studied in greater detail. As the source of ionizing radiation, a direct-acceleration electron tube was used. The electron energy was 0.7—0.9 MeV. The dose rate was determined by the ferrous sulfate method and was monitored with an ionization chamber–monitor or by means of a platinum electrode introduced into the solution*. The solutions were irradiated in membrane cells made of Pyrex glass. During the experiments the cells were thermostated.

The starting substances used for preparing the solutions were palladium chloride (a commercial reagent of "pure" grade), potassium tetrachloropalladate(II), palladium nitrate, and palladium sulfate. Potassium tetrachloropalladate(II) was synthesized by evaporating a mixture of solutions of theoretical amounts of potassium chloride and palladium chloride ([3]). Palladium nitrate was prepared by dissolving finely divided metallic palladium in concentrated nitric acid with boiling ([4]). Palladium sulfate was obtained by fusing palladium with potassium pyrosulfate, and also by dissolving the metal in a mixture of concentrated nitric and sulfuric acids, followed by evaporation of the solution until crystals separated ([5]). The solutions were prepared with twice-distilled water. In all cases, solutions saturated with air were subjected to radiolysis.

In the case of aqueous solutions of palladium chloride (concentration 0.1—0.001 M), potassium tetrachloropalladate(II) (concentration 0.01—0.001 M), and palladium sulfate (concentration 0.03 M), the action of a beam of fast electrons produces a black precipitate. Chemical and X-ray structural analyses proved that this precipitate is palladium black. If the absorbed dose is sufficiently high, the reduction of the salt to the metal proceeds completely. However, irradiation of aqueous solutions of palladium nitrate (concentration 0.01—0.001 M) leads to the formation of the hydroxide. The radiolysis of aqueous solutions of palladium chloride was studied in the greatest detail.

The radiation-chemical yields of palladium were determined by measuring the optical density of the solutions (at a wavelength of 415 mμ) as a function of irradiation time and by parallel weighing of the metal precipitating out. In Fig. 1, as an example, the change in the optical density of a 0.01 M solution of $PdCl_2$ at different absorbed-dose rates is shown. For solutions of other concentrations these curves have an analogous character. On the basis of these curves the radiation-chemical yield of reduction of divalent palladium, $G(-\mathrm{Pd}^{2+})$, was determined (see Table 1).

* It had previously been shown that the platinum electrode had no effect on the radiolysis process.

Figure 2 shows the dependence of the amount of metal deposited on the absorbed energy at various dose rates for a 0.1 M solution of PdCl_2 (the curves for other concentrations are similar). From the slopes of these curves the radiation-chemical yield of palladium black, $G(\mathrm{Pd})$, was calculated (see Table 1).

Table 1

Solution concentration, M	$0.9 \cdot 10^{17}$ eV/ml · sec	$0.9 \cdot 10^{18}$ eV/ml · sec	$0.9 \cdot 10^{19}$ eV/ml · sec			
	$G(-\mathrm{Pd}^{2+})$	$G(\mathrm{Pd})$	$G(-\mathrm{Pd}^{2+})$	$G(\mathrm{Pd})$	$G(-\mathrm{Pd}^{2+})$	$G(\mathrm{Pd})$
0.1	–	–	0.29	0.26	0.21	0.20
0.01	1.04	0.96	0.50	0.42	0.20	0.16
0.001	0.38	–	0.18	0.14	0.14	0.12

As is evident from the data in this table, $G(\mathrm{Pd})$ and $G(-\mathrm{Pd}^{2+})$ for all investigated concentrations of PdCl_2 increase as the absorbed-dose rate decreases. The yields also depend on the concentration of the irradiated solution. However, no definite regularity is observed in this case.

The formation of metallic palladium apparently occurs through reactions of Pd^{2+} with atomic and molecular hydrogen and hydrogen peroxide, which arise during the radiolysis of water. Some evidence for this assumption is provided by the results of experiments on the radiolysis of dilute PdCl_2 solutions with the prior addition of finely dispersed palladium black, which, as is known, actively sorbs atomic and molecular hydrogen and catalyzes the decomposition of hydrogen peroxide*. Figure 3 shows the change in optical density (at 415 mμ) of a 0.001 M solution of palladium chloride as a function of irradiation time, both without addition of palladium black and in the presence of Pd (0.0018 g of metal per 8 ml of solution).

Fig. 1. Change in optical density (at 415 mμ) of a 0.01 M solution of palladium chloride as a function of irradiation time (D_0 is the optical density of the initial solution, D is the optical density of the irradiated solution). Dose rate (eV/ml · sec): 1 $-8.6 \cdot 10^{16}$; 2 $-9 \cdot 10^{17}$; 3 $-9 \cdot 10^{18}$.

As is evident from this figure, in the presence of Pd the reduction of Pd^{2+} does not proceed to completion. The reduction of Pd^{2+} to metallic palladium in solutions of palladium chloride and sulfate probably includes the following reactions:

$$Pd^{2+} + 2H \rightarrow Pd + 2H^{+}, \tag{1}$$

$$H + O_2 \rightarrow HO_2, \tag{2}$$

$$Pd^{2+} + 2HO_2 \rightarrow Pd + 2H^{+} + 2O_2, \tag{3}$$

and also

$$Pd^{2+} + H_2O_2 \rightarrow Pd + 2H^{+} + O_2, \tag{4}$$

$$Pd^{2+} + H_2 \rightarrow Pd + 2H^{+}. \tag{5}$$

As follows from the equations, the process of reduction of Pd^{2+} should be accompanied by an increase in the acidity of the solutions. Indeed, precipitation of metallic palladium always leads to a decrease in the pH of the solution.

OH radicals apparently oxidize the palladium that has formed:

$$Pd + 2OH \rightarrow Pd^{2+} + 2OH^{-} \tag{6}$$

* V. I. Duzhenkov took part in carrying out these experiments.

or interact with chloride ions (in the case of palladium chloride and potassium tetrachloropalladate):

$$Cl^{-} + OH \rightarrow Cl + OH^{-}. \tag{7}$$

The atomic chlorine formed as a result of the reaction oxidizes metallic palladium:

$$Pd + 2Cl \rightarrow Pd^{2+} + 2Cl^{-} \tag{8}$$

or

$$Pd + 2Cl + 2Cl^{-} \rightarrow [PdCl_4]^{2-}. \tag{9}$$

The possibility of reactions (8) and (9) is confirmed by the fact that, upon standing for some time, solutions with completely precipitated palladium show partial oxidation of the metal. In addition, in a 0.1 *M* solution of $PdCl_2$ complete reduction of Pd^{2+} to the metal does not occur (probably owing to establishment of the equilibrium $Pd^{2+} \rightleftarrows Pd - 2\bar{e}$). In the case of 0.01 and 0.001 M solutions, at a sufficiently high absorbed dose, Pd^{2+} is completely reduced to Pd.

As follows from equations (1)–(9),

$$G(\mathrm{Pd}) = G_{\mathrm{H_2O_2}} + G_{\mathrm{H_2}} + \tfrac{1}{2}\left[G_{\mathrm{H}} - G_{\mathrm{OH}}\right]. \quad (10)$$

(Figure: Figure 2)

Fig. 2. Dependence of the amount of metallic palladium precipitated on the irradiation time of a 0.1 M solution of palladium chloride (solution volume 8 ml). Dose rate (9) (eV/ml • sec):
1 $-8.6 \cdot 10^{17}$; 2 $-8.6 \cdot 10^{18}$

However, the experimental values of G(Pd) at all investigated solution concentrations and absorbed-dose rates are lower than those calculated on the basis of equation (10). This is probably explained by partial sorption of atomic and molecular hydrogen by the palladium black formed during radiolysis, and also by decomposition of some fraction of the hydrogen peroxide under the influence of palladium.

For the curves of the change in optical density of $PdCl_2$ solutions as a function of irradiation time, as is seen from Fig. 1, the presence of a maximum is characteristic. Its appearance may be explained either by the formation of some intermediate compound (for example, a complex compound with a coordination sphere different from that of the initial substance), or by the formation of metallic palladium in the colloidal state. There is still insufficient experimental material for a final solution of this question.

(Figure: Figure 3)

Fig. 3. Change in optical density (at 415 mμ) of a 10^{-3} M palladium chloride solution as a function of irradiation time (absorbed-dose rate $0.9 \cdot 10^{16}$ eV/ml • sec): 1 –$PdCl_2$ solution without addition of palladium black; 2 –the same solution with addition of palladium black (0.0018 g Pd per 8 ml of solution)

In the case of aqueous solutions of palladium nitrate, possible radiation-chemical reactions involving NO_3^- ions should be taken into account. The absence of metallic palladium among the radiolysis products of these solutions indicates that the ratio of the rate constants for the reactions of atomic hydrogen with NO_3^- and Pd^{2+} ions considerably exceeds unity. An aqueous solution of palladium nitrate has a comparatively low pH value. Therefore the hydrogen peroxide formed during the radiolysis of water reacts with nitrite ions formed as a result of the reaction of H atoms with NO_3^- ions.* This thereby excludes the possibility of formation of metallic–

* $G(NO_2^-)$ in the radiolysis of aqueous solutions of palladium nitrate is very small.

···of palladium due to the reaction of Pd^{2+} ions with hydrogen peroxide. The formation of palladium hydrooxide $PdO \cdot xH_2O$ is due to an increase in the pH of the solution as a result of irradiation.

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