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Abstract

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EQUILIBRIUM OF COMPLEX FORMATION BETWEEN PALLADIUM CHLORIDE AND ETHYLENE IN AQUEOUS SOLUTIONS

In studying the kinetics of the oxidation of ethylene by palladium chloride in aqueous solution it was found (1) that the rate of this reaction decreases sharply with increasing concentration of hydrogen and chlorine ions, as well as of neutral salts whose anions are incapable of complex formation with palladium. Our experiments showed that under conditions in which the oxidation of ethylene is inhibited (at chlorine and hydrogen ion concentrations greater than 1 mol/l, palladium chloride below 0.2 mol/l, and at temperatures below 40°), palladium chloride solutions rapidly absorb ethylene in amounts exceeding the solubility of ethylene in the absence of the palladium salt. The absorption of ethylene in this case is not accompanied by the precipitation of metallic palladium or the formation of acetaldehyde. It is evident that the increase in the solubility of ethylene due to the presence of the palladium salt under these conditions is caused by a complex-formation reaction, and from the change in solubility one can judge the concentration of π-complexes in solution.

The solubility of ethylene was studied at constant pressure in a thermostated apparatus (see Fig. 1), equipped with a high-speed magnetic stirrer. The solution under investigation (previously deaerated in vacuum at 25°) was drawn, from ampoule 1, where it was under the pressure of its own vapors, into pipette 2 with the vacuum pump operating. After the remaining part of the apparatus had been filled with ethylene, the solution was forced from the pipette into flask 5 and stirred with the magnetic stirrer. The pipette was calibrated with mercury by the gravimetric method. The volume of the filled part of the pipette is 19.87 cm^3. The non-thermostated part of the apparatus consists of capillary tubes with an internal diameter of 1 mm; the volume of the non-thermostated part is 0.2 cm^3, which has practically no effect on the results of the experiments. The gas volume was measured with a thermostated gas burette 6 of 10 cm^3 capacity, with graduations of 0.02 cm^3, to an accuracy of 0.01 cm^3.

Fig. 1. Diagram of the apparatus for determining the solubility of ethylene in

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Fig. 1. Diagram of the apparatus for determining the solubility of ethylene in aqueous palladium chloride solutions

Figure 1: Fig. 1. Diagram of the apparatus for determining the solubility of ethylene in aqueous palladium chloride solutions

Fig. 2

Figure 2: Fig. 2

aqueous palladium chloride solutions

Figure 2 presents the results of experiments on measuring the solubility of ethylene in aqueous solutions containing 1 mol/l lithium chloride and 3.46 mol/l hydrochloric acid, at 13.4°, in the presence of palladium chloride (curves 2 and 3) and in the absence of the palladium salt (curve 1). The main amount of gas is absorbed within 5–10 min after contact between the liquid and

gas, and equilibrium is reliably established within 25–30 min. The rectilinear portion of the curve is almost strictly horizontal and corresponds to the solubility of ethylene in the given solution. Absorption of ethylene by aqueous solutions of palladium chloride proceeds completely reversibly. Special experiments showed that, after removal of ethylene from the solution by evacuation (for 40–50 min at 20°, with trapping of the evaporating liquid), on repeating the experiment the solution absorbs the same amount of ethylene. At higher temperatures and lower concentrations of hydrogen or chloride ions, after rapid absorption of the main amount of ethylene (2.5–9.0 cm^3 in 10 min), slow absorption of small amounts of ethylene is observed at a constant rate (0.03–0.05 cm^3 in 10 min), associated with the oxidation reaction of ethylene to acetaldehyde, which is appreciable under these conditions. In these cases, when calculating the volume of dissolved gas, a correction was introduced by graphical linear extrapolation to the time required for establishment of equilibrium in the absence of palladium salt (10 min).

Fig. 2. Absorption of ethylene by aqueous solutions:
1 –1 N LiCl, 3.46 N $HClO_4$;
2 –1 N LiCl, 3.46 N $HClO_4$, 0.0759 mol/l $PdCl_2$;
3 –1 N LiCl, 3.46 N $HClO_4$, 0.1236 mol/l $PdCl_2$. Temperature 13.4°

The difference between the solubilities of ethylene in solutions containing and not containing palladium salt corresponds to the amount of ethylene bound in π-complexes.

On the basis of the known properties of platinum π-complexes with olefins, it may be expected that, in solutions of palladium chloride in the presence of an excess of chloride ions, the interaction of the acidocomplex $PdCl_4^{2-}$ with ethylene should lead to the formation of π-complexes: $C_2H_4PdCl_3^-$, $C_2H_4PdCl_2OH_2$, and $C_2H_4PdCl_2OH^-$. Thus, for example, Zeise' s salt in aqueous solutions is

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Fig. 3

Figure 3: Fig. 3

hydrolyzed with formation of the aquo form of the π-complex $C_2H_4PtCl_2OH_2$, the equilibrium constant of this process (^{2,3}) at 25° being $3 \cdot 10^{-3}$ mol/l. The aquo complex $C_2H_4PtCl_2OH_2$ is a weak acid (dissociation constant $\sim 10^{-5}$) and, at low concentrations of hydrogen ions in solution, dissociates with formation of $C_2H_4PtCl_2OH^-$.

Fig. 3. Dependence of the quantity K on the concentration of chloride ions

Measurements of the solubility of ethylene in aqueous solutions containing different concentrations of hydrochloric acid at constant ionic strength (the $HClO_4$-$LiClO_4$ system) and constant concentrations of LiCl and $PdCl_2$, at 13.4°, showed that the concentration of ethylene bound in π-complexes does not depend on the concentration of hydrogen ions in the range 0.9–3.46 mol/l. This permits one to suppose that, under the conditions of our experiments, dissociation of the aquo complex does not occur and, consequently, the concentration of the hydroxo complex may be neglected.

Table 1 presents the results of experiments on determining the solubility of ethylene at 13.4° in aqueous $PdCl_2$ solutions containing lithium chloride, HCl, and $HClO_4$, at constant ionic strength and acidity of the solutions.

From the data given in Table 1 it follows that, with increasing concentr-

of palladium chloride, the concentration of bound ethylene (ΔV) increases; moreover, between the equilibrium concentrations of free ($[C_2H_4]$) and bound (ΔV) ethylene and the equilibrium concentration of $PdCl_4^{2-}$ ions, for small changes in the concentration of chloride ions (experiments Nos. 2–6, 7–10, 13–14), there exists the relation:

$$\frac{\Delta V[Cl^-]}{[PdCl_4^{2-}][C_2H_4]} = K. \quad (1)$$

When the concentration of chloride ions is varied over a wide range, changes in the values of K become appreciable, and K decreases linearly with increasing $1/[Cl^-]$ (see Fig. 3). This fact indicates the formation, in commensurate amounts, of the π-complexes $C_2H_4PdCl_3^-$ and $C_2H_4PdCl_2OH_2$.

Table 1

No.	$[PdCl_4^{2-}]_0 \cdot 10^2$	$[PdCl_4^{2-}]^a \cdot 10^2$	$[Cl^-]_0$	$[Cl^-]^b$	$\Sigma[C_2H_4] \cdot 10^{3c}$	$\Delta V \cdot 10^{3d}$	K
1	0	0	1.000	1.000	4.50	0	–
2	1.572	1.405	1.000	0.970	6.03	1.53	23.6
3	2.71	2.44	1.000	0.948	7.18	2.68	23.2

No.	$[PdCl_4^{2-}]_0\cdot 10^2$	$[PdCl_4^{2-}]^a\cdot 10^2$	$[Cl^-]_0$	$[Cl^-]^b$	$\Sigma[C_2H_4]\cdot 10^{3c}$	$\Delta V\cdot 10^{3d}$	K
4	7.59	6.78	1.000	0.856	12.59	8.06	22.7
5	9.80	8.69	1.000	0.815	15.60	11.10	20.5
6	10.79	9.51	1.000	0.795	17.25	12.75	23.7
7	4.91	4.70	2.108	2.013	6.62	2.07	19.5
8	10.84	10.48	2.108	1.896	9.55	5.00	19.9
9	10.95	10.46	2.108	1.894	9.45	4.90	19.5
10	24.52	23.33	2.108	1.624	16.45	11.90	18.2
11	15.49	14.98	2.730	2.425	9.68	5.11	18.1
12	17.15	16.67	3.360	3.022	9.43	4.83	19.0
13	13.55	13.28	4.460	4.197	7.35	2.70	18.3
14	21.35	20.93	4.460	4.036	8.83	4.18	17.3
15	24.70	24.21	4.460	3.970	9.58	4.93	17.4

[a] Equilibrium concentration of acidocomplexes $PdCl_4^{2-}$, equal to the difference between the initial concentration of the palladium salt and the concentration of π-complexes (ΔV) (mol/l).

[b] Equilibrium concentration of chloride ions, determined as the difference between the initial concentration of Cl^- ions and the concentration of chloride ions bound in complexes with palladium ($2 \times [PdCl_4^{2-}]$) (mol/l).

[c] Solubility of ethylene in the given solution (mol/l).

[d] Equilibrium concentration of ethylene bound to palladium, equal to the difference between the solubilities of ethylene in the presence and in the absence of the palladium salt (mol/l).

Thus, the total concentration of palladium in solution [Pd] is:

$$[Pd] = [PdCl_4^{2-}] + [C_2H_4PdCl_3^-] + [C_2H_4PdCl_2OH_2].$$

The complexing degree of palladium Φ (the ratio of the total concentration of palladium to the equilibrium concentration of $PdCl_4^{2-}$ ions) is related to the concentrations of palladium complexes by the relation:

$$\Phi = \frac{[Pd]}{[PdCl_4^{2-}]} = 1 + \frac{[C_2H_4PdCl_3^-]}{[PdCl_4^{2-}]} + \frac{[C_2H_4PdCl_2OH_2]}{[PdCl_4^{2-}]}.$$

Using the expressions for the equilibrium constants of formation of $C_2H_4PdCl_3$

$$\left(K_1 = \frac{[C_2H_4PdCl_3^-][Cl^-]}{[PdCl_4^{2-}][C_2H_4]}\right)$$

and $C_2H_4PdCl_2OH_2$

$$\left(K_2 = \frac{[C_2H_4PdCl_2OH_2][Cl^-]^2}{[PdCl_4^{2-}][C_2H_4]}\right),$$

we obtain

$$\frac{(\Phi - 1)[Cl^-]^2}{[C_2H_4]} = K_1[Cl^-] + K_2.* \tag{2}$$

* In calculating the equilibrium concentration of chloride ions entering into equations (1) and (2), the change in the concentration of $[Cl^-]$ caused by substitution of Cl^- ions by water during the formation of $C_2H_4PdCl_2OH_2$ from $C_2H_4PdCl_3^-$ was not taken into account. Since the total concentration of π-complexes and, consequently, the concentration of $C_2H_4PdCl_2OH_2$ in all the cases investigated is considerably less than the concentration of chloride ions, this approximation does not introduce any appreciable error.

Fulfillment of the dependence expressed by equation (2) is illustrated by the graph in Fig. 4. The slope of the straight line is $K_1 = 16.3$, and the intercept on the ordinate axis is $K_2 = 6.5$ mol/l at 13.4°.

Preliminary experiments showed that the degree of complexation of palladium increases with increasing ionic strength of the solution and changes only slightly with increasing temperature. The thermal effect of formation of the π-complex $C_2H_4PdCl_3^-$ from ethylene and $PdCl_4^{2-}$ is close to zero. Thus, the energy of the bond of palladium with the ethylene molecule in the complex $C_2H_4 \cdot PdCl_3^-$ is greater than the energy of the bond of palladium with the chloride ion in $PdCl_4^{2-}$ by the amount $\Delta Q = Q_{PdCl_4^{2-}} + Q_{C_2H_4} - Q_{Cl^-} - Q_{C_2H_4PdCl_3^-}$, where Q_i are the corresponding heats of solvation. On the basis of thermochemical data on the heats of solvation of singly and doubly charged anions in aqueous solutions (4), one may expect that $\Delta Q > 0$.

It is interesting to note that the equilibrium constant for the reaction of replacement of a chloride ion in the complex $C_2H_4PdCl_3^-$ by water at 13.4° is $K_2' = \frac{K_2}{K_1} = 0.4$ mol/l. For the reaction of replacement of a chloride ion by water in the complex $H_2OPdCl_3^-$ at 25°, the equilibrium constant (5,6) is $10^{-2.6}$.

Fig. 4. Dependence of the palladium complexation function $\frac{(\Phi - 1)[Cl^-]^2}{[C_2H_4]}$ on the concentration of chloride ions

The increase in the equilibrium constant upon replacement of the water molecule by ethylene should apparently be attributed to the trans influence of the ethylene molecule. It may therefore be assumed that the aquo complex $C_2H_4PdCl_2 \cdot OH_2$

has a trans configuration. Similar changes in equilibrium constants are observed in the case of the corresponding platinum complexes (^{2}).

It should be noted that the equilibrium of the complex-formation reactions studied is established very rapidly. With an increase in the intensity of stirring (shaking in a thermostated duck-shaped vessel on a shaker), the time for establishment of equilibrium is reduced to 3–5 min, while the main amount of gas, even under these conditions of diffusion inhibition, is absorbed in ~ 1 min. Leden and Chatt (^{2}) noted that the equilibrium of hydrolysis of the anion $C_2H_4PtCl_3^-$ with formation of trans-$C_2H_4PtCl_2OH_2$ is established in less than 2 min. Apparently, the hydrolysis of the palladium analogue of Zeise' s salt is also a rapid reaction, since substitution reactions in palladium complexes proceed faster than in platinum complexes (^{7}).

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