PHYSICAL CHEMISTRY

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Abstract

Full Text

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KINETICS AND MECHANISM OF THE REDUCTION OF K_2PdBr_4 BY CARBON MONOXIDE IN AQUEOUS SOLUTIONS

Coordination compounds of Pd(II) are active homogeneous catalysts involving carbon monoxide and olefins ([1]-[5]). The complex anion $[PdBr_4]^{2-}$ has the greatest catalytic activity ([6]). It is known that CO forms carbonyl compounds with Pd(II) salts, which are very labile in aqueous solutions ([7]-[10]). To establish their composition it is necessary to study the interaction of CO with the catalyst in the absence of an oxidant, proceeding according to the overall equation

$$[PdBr_4]^{2-} + CO + H_2O \rightarrow Pd + CO_2 + 2H^+ + 4Br^-. \quad (1)$$

K_2PdBr_4 was prepared by the method of ([11]). A weighed portion of the complex, calculated to absorb 25 ml of CO at NTP ($3.37 \cdot 10^{-2}$ mol/l), was placed in an intensively shaken reaction vessel connected to a measuring gas burette. The reduction of the complex was studied by recording the rates of CO absorption and CO_2 evolution during the reaction ([12]).

Fig. 1. Reduction of K_2PdBr_4 by carbon monoxide in a 25% KBr solution at 5°

Figure 1 shows the results of two parallel experiments: curve 1—absorption of CO by a solution of K_2PdBr_4 and of CO_2 at the moment of liberation by a 25% KOH solution (V_{CO}); 2—absorption of CO_2 by a solution of K_2PdBr_4 without absorption of CO_2 ($V_{CO} - V_{CO_2}$). Separate measurement of the rates of CO absorption with absorption and without absorption of CO_2 makes it possible to calculate the rate of hydrolysis of the carbonyl complex of Pd(II) being formed (curve 3).

CO_2 appears in the gas phase long before the precipitation of metallic Pd. Consequently, upon hydrolysis of carbonyl bromide Pd(II), a complex is formed in which the charge of the central atom is equal to 0, since oxidation state 1 is unknown for palladium. This complex gradually decomposes with the liberation of metallic Pd. A number of cases of identification of Pd(0) complexes with coordination number 2, stabilized by electrophilic ligands, have been described in the literature ([9], [13–16]).

Table 1

Reduction of K_2PdBr_4 by carbon monoxide in aqueous solutions

t°	Conc. KBr, %	V_{CO}/V_{CO_2}	$V_{CO_2}^{end}$, ml	V_{CO}^{end}, ml	n	τ, min	t°	Conc. KBr, %	V_{CO}/V_{CO_2}	$V_{CO_2}^{end}$, ml	V_{CO}^{end}, ml	n	τ, min
5	0	3.9	10.2	35.0	0.0	2.5	25	0	2.7	21.3	38.5		0.5
5	5	4.1	8.5	37.0	−1.2	3.0	25	10	3.0	21.5	40.0	0.0	1.0
5	10	3.8	9.7	38.5	−1.0	4.0	25	30	2.9	22.5	39.5	0.0	1.5
5	15	4.4	20.0	38.0	−1.0	3.5	30	0	2.8	18.3	28.0		1.0
5	20	4.3	18.7	37.5	−1.0	4.5	30	10	2.8	21.6	38.0	0.0	1.5
5	25	4.5	14.5	38.0	−1.0	5.0	30	30	2.9	19.2	39.0	0.0	1.5
5	30	4.2	17.6	38.5	−1.0	10.0	40	0	2.9	21.8	25.0		0.5
15	0	4.2	10.4	35.5	0.0	1.0	40	10	2.6	22.3	36.0	0.0	1.0
15	10	4.9	18.5	36.0	−1.0	1.0	40	30	2.9	23.4	36.0	0.0	1.0
15	30	4.1	19.0	37.0		3.0	50	0	2.8	20.0	20.0		0.5
20	0	3.5	19.8	37.0	0.0	0.5	50	10	3.1	22.7	31.0	0.0	0.5
20	10	3.4	21.2	37.5	0.0	0.5	50	30	2.9	24.6	35.0	0.0	0.5
20	30	3.1	22.4	39.0		2.0							

Note. V_{CO}/V_{CO_2} is the ratio of the volume of CO absorbed to the volume of CO_2 evolved in 0.25-0.5 min before the appearance of metallic Pd; $V_{CO_2}^{end}$ is the volume of CO_2 evolved by the end of the reaction; V_{CO}^{end} is the volume of CO absorbed by the end of the reaction; n is the reaction order with respect to Br^-; τ is the time of appearance of metallic Pd.

Experimental data on the reduction of K_2PdBr_4 by carbon monoxide are given in Table 1.

It follows from the data in Table 1 that at temperatures above 20°, $V_{CO}/V_{CO_2} \approx 3$. This means that one volume of CO is used for the reduction of Pd(II) to Pd(0), while the other two coordinate with Pd(0), forming the complexes $Pd(CO)_2$ or $K_2[Pd(CO)_2Br_2]$. The reduction process, in the general case, may be considered as consecutive reactions:

Fig. 2. Effect of temperature on the value of K_B (1—without KBr, 2—10% KBr, 3—30% KBr)

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Figure 2: Fig. 2. Effect of temperature on the value of K_B (1—without KBr, 2 —10% KBr, 3—30% KBr)

Fig. 3. Effect of temperature on the value of K_g (1—without KBr, 2—10% KBr, 3—30% KBr)

Figure 3: Fig. 3. Effect of temperature on the value of K_g (1—without KBr, 2 —10% KBr, 3—30% KBr)

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may be considered as consecutive reactions:

$$[PdBr_4]^{-2} + CO \underset{K_{-B}}{\overset{K'_B}{\rightleftarrows}} [PdBr_3CO]^{-1} + Br^-, \tag{2}$$

$$[PdBr_3CO]^{-1} + H_2O \xrightarrow{K_g} Pd^0 + CO_2 + 3Br^- + 2H^+, \tag{3}$$

where: K'_B is the rate constant for the introduction of CO into the inner coordination sphere of the bromide complex of Pd(II), K_{-B} is the rate constant of the reverse reaction, and K_g is the rate constant of hydrolysis. It should be borne in mind that carbonyl bromide of Pd(II) is hydrolyzed in solutions with a small excess concentration of ligand. This is indicated by the zero order of the reaction for exchange of coordinated Br^- with Br^- ions in solution, found by Grinberg-

gen ([17]). Therefore oxidative hydrolysis may also proceed at the expense of inner-sphere water.

According to Moiseev, Vargaftik, and Syrkin ([18]), the equilibrium constant for the reaction of incorporation of C_2H_4 into the inner sphere of $[PdCl_4]^{-2}$ is $\simeq 20$, which indicates a shift of the equilibrium toward formation of the π-complex. It has been shown that, upon evacuation of the system, the process is completely reversible. In the case of the carbonyl bromide of Pd(II) this is unlikely, since CO is much more reactive than ethylene: if reverse displacement of CO from the inner sphere of the complex does occur, it does so at very low rates. Therefore it is assumed below that $K_v \gg K_{-v}$.

At lower temperatures ($\leq 15^\circ$) $V_{CO}/V_{CO_2} \simeq 4$. Under these conditions the anion $[PdBr_3CO]^{-1}$ accumulates in solution. Addition of a strong oxidizing agent (*n*-benzoquinone) causes a sharp increase in the rate of hydrolysis, and CO_2 is additionally evolved into the gas phase.

Table 2

Effect of conditions on the order of the reaction of reduction of K_2PdBr_4 by CO

P_{CO}, atm	without KBr, n 15°	without KBr, n 30°	10% KBr, n 15°	10% KBr, n 30°	30% KBr, n 15°	30% KBr, n 30°
0.2–0.4	1.1	0.9	1.2	0.8	0.5	0.5
0.4–0.6	1.1	1.0	0.9	0.8	0.4	0.7
0.6–0.8	1.0	1.1	1.1	1.1	0.4	0.8
0.8–1.0	1.1	1.0	1.1	1.0	0.5	0.9

After completion of the reduction process, a certain portion of CO remains in the bound state. For the reduction of K_2PdBr_4, instead of the calculated 25 ml of CO, from 8.5 to 24.5 ml is consumed, depending on the experimental conditions. In all probability, at low temperatures a fairly stable dimeric complex containing Pd(II) and Pd(0) is formed in solution, as in ([19]). With increasing temperature, $V_{CO_2}^{end}$ approaches the calculated value (25 ml), and the reduction of K_2PdBr_4 proceeds according to equation (1).

The influence of the partial pressure of CO in mixtures with Ar on the reaction order is shown in Table 2.

It follows from the data in Table 2 that n is close to 1, with the exception of 30% KBr solution.

On the basis of a system of equations for two consecutive reactions (2), (3), K_v and K_g were calculated. The solubility values of CO at different temperatures were taken from a handbook ([20]).

The possibility of formation of the carbonyl bromide of Pd(II) in a K_2PdBr_4 solution without excess Br^- decreases with increasing temperature, since the rate of hydrolysis of $[PdBr_3CO]^{-1}$ considerably exceeds the rate of its formation (Figs. 2, 3). In 10 and 30% KBr solutions, at first there is an increase and then a decrease in the rate of formation of the carbonyl bromide of Pd(II). Under the same conditions, K_g increases, especially sharply in 10% KBr.

Fig. 4. Effect of KBr concentration on the values of the constants K_v (1) and K_g (2). Temperature –5°

On the basis of the data obtained, the activation energy of the process of CO incorporation in the absence of, and in 10% KBr solution was calculated to be

Figure 4. Effect of KBr concentration on the values of the constants K_v (1) and K_g (2). Temperature –5°

Figure 4: Figure 4. Effect of KBr concentration on the values of the constants K_v (1) and K_g (2). Temperature –5°

10 ± 0.5 kcal/mol. When the KBr concentration in solution is increased from 0 to 10–15%, the reaction order with respect to Br^- at low temperatures changes from zero to inverse first order, while at higher temperatures it remains zero. It is known that at low KBr concentrations in solution the complex $[PdBr_4]^{-2}$ is hydrolyzed to a significant extent ([17]); therefore, upon incorporation of CO, ···

there is displacement from the inner sphere of the complex of H_2O or OH^-. This is also indicated by the fact that the ligands participating in the process are arranged in the following order according to the strength of the trans effect, and consequently also according to the stability of the complexes formed ([21]):

$$CO \gg Br^- > OH^- > H_2O.$$

The same effect explains the constancy of K_v and the decrease of K_g in the KBr concentration range 0-15% (Fig. 4). At KBr concentrations > 15%, the introduction of CO is accompanied by displacement of Br^- and a decrease in the value of K_v. Under these conditions, K_g does not depend on the KBr concentration.

The nature of the limiting stage of the overall process depends on the experimental conditions and may change even within a single experiment. In most cases, reaction (1) proceeds in the transition region, i.e., the rates of stages (2) and (3) are comparable in magnitude.

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Note: Figure translations are in progress. See original paper for figures.