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V. A. GOLODOV, A. B. FASMAN, Academician of the Academy of Sciences of the Kazakh SSR D. V. SOKOLSKII

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Abstract

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CATALYTIC REDUCTION OF *p*-BENZOQUINONE BY CARBON MONOXIDE IN THE LIQUID PHASE

The present work is devoted to the study of the reaction of reduction of quinone by carbon monoxide on palladium catalysts in acidic aqueous-dioxane mixtures, proceeding according to the overall equation:

$$C_6H_4O_2 + CO + H_2O \xrightarrow{k} C_6H_4(OH)_2 + CO_2. \qquad (1)$$

The process was carried out either in a homogeneous system in the presence of Pd^{2+} or $[PdCl_4]^{2-}$, or in a heterogeneous one with a Pd/C catalyst (10% Pd). The method of preparing Pd/C and of carrying out the experiments has been described previously (^{1}). Like ethylene, which forms a complex salt $[PdCl_3C_2H_4]^-$ with palladium chloride (an analogue of Zeise' s salt), carbon monoxide, displacing the less firmly bound ligand Cl^- from the inner coordination sphere (^{2}), is capable of giving a palladium carbonyl chloride complex:

$$\underset{(I)}{[PdCl_4]^{2-}} + CO \rightarrow \underset{(II)}{[PdCl_3CO]^-} + Cl^-, \qquad (2)$$

which readily decomposes in aqueous solution with liberation of metallic palladium (^{3})

$$\underset{II}{[PdCl_3CO]^-} + H_2O \rightarrow Pd + CO_2 + 3Cl^- + 2H^+. \qquad (3)$$

Some authors believe that in this process formation of a complex of zerovalent Pd^0 is possible (^{4}), analogous to the previously identified cyanide complex $[Pd(CN)_2]^{2-}$ (^{5}).

Elemental palladium is oxidized by quinone with formation of the initial complex I:

$$Pd + C_6H_4O_2 + 4Cl^- + 2H^+ \rightarrow (PdCl_4)^{2-} + C_6H_4(OH)_2. \qquad (4)$$

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

In catalysis by reduced palladium, the process begins with reaction (4) ([6]). It is known that Pd dissolves in acidic media at potentials more positive than +0.35 V ([7]). Syrkin and co-workers, for dissolving the metal during oxidation of ethylene ([8]) and cyclohexene ([9]) in the presence of Pd salts in aqueous solutions, used quinone, which has a high oxidation-reduction potential.

Thus, according to the proposed mechanism of the process, the reduced and oxidized forms of palladium must participate in the reaction. Indeed, Pd introduced into the reaction vessel in the form of the ion $(\mathrm{PdCl_4})^{2-}$ has an activity several times greater than that of the metal (Fig. 1). Obviously, in the case of the Pd/C catalyst a dynamic equilibrium is established between elemental Pd and its ion in solution; moreover, only some fraction of the metal participates in the process. In our experiments, after reduction of quinone on the Pd/C catalyst, liberation of metallic Pd in the bulk, separately from the support particles, was observed.

The kinetics of the reaction of quinone reduction on a Pd/C catalyst is strongly affected by the toxicity of carbon monoxide. It is known that CO is a poison for many catalytic processes (10–13), although brief exposure to CO sometimes even increases the activity of a catalyst (14). To determine the nature of the action of CO and H_2 on the catalytic properties of Pd/C, a weighed portion of quinone was introduced into the reaction vessel immediately before the experiment or after shaking the catalyst in an atmosphere of one of these gases for a definite period of time.

Fig. 1. Effect of the amount of catalyst on the rate of quinone reduction by carbon monoxide. Stirring intensity—600 strokes/min; solvent—water-dioxane (3 : 7); HCl—0.25%; 1, 2—$PdCl_4^{2-}$; 3—Pd/C.

Fig. 2. Dependence of the rate of quinone reduction on the time of saturation of the catalyst. Pd/C—50 mg; stirring intensity—600 strokes/min; temperature —20° C; solvent—water-dioxane (3 : 7); HCl—0.35%; 1—CO; 2—H_2.

The reaction proceeds at the maximum rate when a weighed portion of quinone is introduced into the reaction vessel beforehand (Fig. 2). The activity of Pd/C decreases sharply after 10 minutes of saturation. More prolonged shaking in an atmosphere of hydrogen leads to a further gradual decrease in the reaction rate; saturation with carbon monoxide, on the contrary, even somewhat activates the catalyst, as a result of which the reduction rates after 6 hours differ by more than a factor of two.

Fig. 3

Figure 3: Fig. 3

Fig. 4. Effect of the acidity of the medium on the rate of quinone reduction. Pd/C—50 mg; stirring intensity—600 strokes/min; solvent—water-dioxane (3:7); 1—HCl; 2—HCl, saturation time—10 min; 3—H2SO4

Figure 4: Fig. 4. Effect of the acidity of the medium on the rate of quinone reduction. Pd/C—50 mg; stirring intensity—600 strokes/min; solvent—water-dioxane (3:7); 1—HCl; 2—HCl, saturation time—10 min; 3—H2SO4

The decrease in catalyst activity upon saturation probably occurs because the limiting stage is the dissolution of Pd (reaction 4). Sorbed CO and H_2, being active reducing agents, hinder oxidation of the metal, with hydrogen proving to be more toxic (Fig. 2, 2).

Fig. 3. Adsorption equilibrium on the Pd/C catalyst. Pd/C—100 mg; stirring intensity—600 strokes/min; temperature—20° C; 1—solvent—water-dioxane (3 : 7); 2—the same + 0.35% HCl; 3—the same + 5% HCl.

To determine the strength of the adsorption bond of these gases with Pd/C, the suspension was shaken in an atmosphere of carbon monoxide until a constant potential was reached; then the reactor was blown through with a stream of hydrogen, and the catalyst was saturated.

It is known from the literature that, in the gas phase, carbon monoxide is adsorbed on metals more strongly than hydrogen (15,16). Figure 3 shows that the potential of the catalyst rather rapidly reaches the value of the reversible hydrogen-

under these conditions and, consequently, in solution the sorbed CO is readily displaced from the surface by hydrogen. On the contrary, a considerable time (6-8 h) is required in order to obtain the carbon monoxide potential again. As in the gas phase (16), the carbon monoxide potential is 280-350 mV more positive than the reversible hydrogen potential, depending on the pH of the solution.

It is interesting to note that saturation of the catalyst with carbon monoxide affects not only the rate of quinone reduction, but also the character of the dependence of the reaction rate on the acidity of the medium. Figure 4 presents such a dependence for catalysts not subjected to the action of CO and preliminarily saturated for 10 minutes.

Fig. 4. Effect of the acidity of the medium on the rate of quinone reduction. Pd/C—50 mg; stirring intensity—600 strokes/min; solvent—water-dioxane (3:7); 1—HCl; 2—HCl, saturation time—10 min; 3—H_2SO_4.

Quinone on an unpoisoned catalyst is reduced at the maximum rate in a 0.25% HCl solution, and on a poisoned catalyst—in a 0.1% solution. It should be emphasized that at low concentrations of hydrochloric acid (0.05 and 0.1%) the "poisoned" catalyst proved to be more active (by factors of 8.7 and 1.2, respectively). In an H_2SO_4 solution, after the initial jump, the reaction rate slowly increases with increasing acid concentration. According to the literature (17), in sulfuric-acid solutions no appreciable complex formation occurs and therefore the oxidation–reduction potential of the system

$$\mathrm{Pd}^{2+} + 2e \rightleftarrows \mathrm{Pd},$$

equal to +0.82 V (18). The oxidation–reduction potential of quinone is +0.71 V, and at an oxidized-form concentration of 99.99% it is 0.856 V (19); therefore the process is evidently limited by the stage of palladium dissolution. A decrease in pH should promote an increase in the overall rate of the process, which is also observed in the experiment (Fig. 4, 3).

The dependence of the rate of quinone reduction on the concentration of HCl is more complicated. Formation of a monomeric or dimeric palladium chloride complex is accompanied by a decrease in the oxidation–reduction potential of system (5) to +0.62 V (20); therefore the rate of reaction (4), which controls the process in weakly acidic media, is much higher under these conditions.

However, at sufficiently high HCl concentrations, Cl^- ions begin to inhibit the process of formation of complex II and its hydrolysis (the descending branches of curves 1 and 2, Fig. 4). The sharp maximum indicates a change in the rate-limiting stages. Evidently, in this case the inequality $W_2 < W_4$ or $W_3 < W_4$ is satisfied.

In 5% HCl, after quinone reduction no precipitation of metallic Pd is observed, and in a 16.9% solution quinone is not quantitatively reduced. The same inhibiting effect of the Cl^- ion is observed in the oxidation reaction of ethylene in the presence of aqueous solutions of palladium salts (4,21,22), and the limiting HCl concentrations at which the reactions cease coincide numerically (17). The rates of both reactions increase with increasing H_2SO_4 concentration (17) and do not depend on the initial quinone concentration (22).

This analogy in the regularities of the reaction under study—the oxidation of CO—and of the well-studied process with C_2H_4, due to the presence in these mole-

in molecules of bonds of the same type and of the π-complexes they form with palladium salts confirms the validity of the proposed mechanism for the catalytic reduction of quinone by carbon monoxide in the liquid phase.

Kazakh State University
named after S. M. Kirov

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