PHYSICAL CHEMISTRY

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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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KINETICS OF THE OXIDATION OF CYCLOHEXENE BY PALLADIUM SALTS IN AQUEOUS SOLUTIONS

We have investigated the kinetics of the oxidation of cyclohexene to cyclohexanone by palladium salts in aqueous solutions in the temperature interval from 7.0 to 30.3° C. In the absence of an oxidizing agent this reaction proceeds according to equation (1)

$$C_6H_{10} + PdCl_2 + H_2O = C_6H_{10}O + Pd + 2HCl. \tag{1}$$

The study of this reaction under conditions in which metallic palladium precipitates and the concentration of H^+ and Cl^- ions changes is associated with considerable difficulties. Therefore the study of reaction (1) was carried out by us in the presence of an oxidizing agent—*p*-benzoquinone (2), which rapidly oxidizes the palladium atoms formed according to the equation

$$Pd + C_6H_4O_2 + 2HCl = PdCl_2 + C_6H_4(OH)_2. \tag{2}$$

Thus, the overall reaction occurring in solution is the oxidation of cyclohexene by *p*-benzoquinone according to the equation*

$$C_6H_{10} + H_2O + C_6H_4O_2 = C_6H_{10}O + C_6H_4(OH)_2. \tag{3}$$

Fig. 1. Change in the potential of the quinone—hydroquinone system during kinetic experiments.
1—$C_{PdCl_2} = 0.41 \cdot 10^{-3}$ g-mol/l;
2—$C_{PdCl_2} = 0.68 \cdot 10^{-3}$;
3—$C_{PdCl_2} = 2.14 \cdot 10^{-3}$.

Under the conditions of the kinetic study (olefin concentration $1.8 \cdot 10^{-3}$—$2.0 \cdot 10^{-2}$ g-mol/l, quinone $1.1 \cdot 10^{-2}$—$4.0 \cdot 10^{-2}$ g-mol/l, palladium chloride $0.13 \cdot 10^{-3}$—$2.14 \cdot 10^{-3}$ g-mol/l) reaction (1) proceeds more slowly than reaction (2), as is indicated by the absence of formation of metallic palladium and by the constancy of the pH of the solution during the experiment. Thus, the rate of reaction (3) is determined by the rate of reaction (1). Special experiments showed that under these conditions quinone does not enter into any side reactions with the olefin, cyclohexanone, hydroquinone, or palladium chloride. Similarly, hydroquinone does not react with the listed components of the reaction system. All this proves that the change in the concentration of quinone and hydroquinone is due only to the course of reactions (1) and (2), and by from the change in the quinone concentration with time one can unambiguously judge the rate of reaction (1).

As is evident from equation (3), the amount of olefin that has reacted is equal to the amount of hydroquinone formed. This makes it possible to follow the course of the reaction by determining the concentrations of quinone and hydroquinone, for example by measuring the oxidation-reduction potential of the quinone—hydroquinone system. This method was used in the present work. The measured value of the potential is related to the activities of the reduced and oxidized forms by the Nernst equation. In sufficiently dilute solutions, as was the case in our experiments, the ratio of activities may be replaced by the ratio of concentrations. At constant hydrogen-ion concentration, changes in the potential are described by the equation

$$E = E_0 - \frac{RT}{2F} \ln \frac{C_{\mathrm{x}}}{C}. \tag{4}$$

For the measurements, samples of the reaction solution were taken and diluted 25-fold with a $1N$ NaCl solution containing 0.01 gram-mole/liter hydrochloric acid. The potential was measured with a platinum plate electrode of area 25 cm^2. A saturated calomel electrode served as the reference electrode. The measurement was carried out by a compensation circuit using an R-307 potentiometer and a GZS-47 mirror galvanometer. The accuracy of the measurements was $3 \cdot 10^{-5}$ V.

Fig. 2. Change in the logarithm of the olefin concentration with time: I—$C_{\mathrm{c1}} = 0.13 \cdot 10^{-3}$ g-mole/l; II—$C_{\mathrm{PdCl_2}} = 0.22 \cdot 10^{-3}$; III—$C_{\mathrm{PdCl_2}} = 0.39 \cdot 10^{-3}$; IV—$C_{\mathrm{PdCl_2}} = 0.47 \cdot 10^{-3}$; V—$C_{\mathrm{PdCl_2}} = 2.14 \cdot 10^{-3}$.

Preliminary experiments showed that the potential of the quinone—hydroquinone system is practically independent of the concentration of palladium

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* Special experiments showed that the yield of cyclohexanone under the conditions in which the kinetics were studied is 93-98% based on olefin.

Fig. 2. Change in the logarithm of the olefin concentration with time: I—$C_{\text{c1}} = 0.13 \cdot 10^{-3}$ g-mole/l; II—$C_{\text{PdCl}_2} = 0.22 \cdot 10^{-3}$; III—$C_{\text{PdCl}_2} = 0.39 \cdot 10^{-3}$; IV—$C_{\text{PdCl}_2} = 0.47 \cdot 10^{-3}$; V—$C_{\text{PdCl}_2} = 2.14 \cdot 10^{-3}$.

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chloride or olefin. At constant acidity, the potential values fully coincide with the values calculated from equation (4), within the range of the ratio C_{x}/C from 1 to 10^4. Since the change in potential with time is unambiguously determined by the course of the oxidation-reduction reaction (3), the change in potential can be used to judge the change in olefin concentration in the experiment.

Table 1

Time, min	Olefin concentration, mole/l, $C \cdot 10^4$	$\lg C$	$k_1 \cdot 10^3$, s^{-1}
0	5.90	$\bar{4},7709$	0.750
10	3.76	$\bar{4},5752$	0.755
20	2.39	$\bar{4},3784$	0.754
30	1.52	$\bar{4},1818$	0.747
40	0.97	$\bar{5},9868$	0.746
50	0.62	$\bar{5},7924$	$k_1^{\text{avg}} = 0.750 \pm 0.005 \cdot 10^{-3}$

An example of the drop in potential during a kinetic experiment is shown in Fig. 1. The different curves correspond to different concentrations of palladium chloride. The change in olefin concentration with time is given in Table 1.

As is evident from this table, the rate of oxidation of the olefin obeys a first-order equation with respect to the olefin concentration. First order with respect to the olefin is maintained during the kinetic experiments up to

up to conversions of 95-98%. The observed rate constant k_1 does not change when the initial concentration of the olefin is varied in the range from $1.8 \cdot 10^{-3}$ to $2 \cdot 10^{-5}$ g-mole/l. The value of k_1 also does not depend on the initial concentration of quinone or on the concentration of cyclohexanone. The values of k_1 vary in proportion to the concentration of palladium chloride within the limits from $1.3 \cdot 10^{-4}$ to $2.14 \cdot 10^{-3}$ g-mole/l (Figs. 2 and 3). Thus, the rate of the reaction of oxidation of cyclohexene by palladium salts obeys a second-order equation—first order in the olefin and in PdCl_2.

Table 2

Fig. 3. Dependence of the value of the first-order rate constant k_1 on the concentration of $PdCl_2$

Figure 3: Fig. 3. Dependence of the value of the first-order rate constant k_1 on the concentration of $PdCl_2$

C_{HClO_4}, g-mole/l	k_2, $l^2 \cdot sec^{-1} \cdot mole^{-1}$	C_{HClO_4}, g-mole/l	k_2, $l^2 \cdot sec^{-1} \cdot mole^{-1}$
0.005	1.58	0.10	1.61
0.01	1.50	0.20	1.57
0.02	1.67	0.50	1.60
0.05	1.60	–	–

All kinetic experiments were carried out in aqueous solutions of $HClO_4$.* In order to investigate the influence of hydrogen ions on the rate of oxidation, a series of experiments was performed in which the concentration of $HClO_4$ was varied from 0.005 to 0.5 g-mole/l. The results of these experiments are given in Table 2.

In the presence of the neutral salt $NaClO_4$ (in an amount from 0.01 to 1.0 g-mole/l), at a constant concentration of $HClO_4$ (0.1 g-mole/l), the value of the second-order constant k_2 remains constant. Thus, the reaction rate depends neither on the concentration of hydrogen ions nor on the ionic strength of the solution.

The existence of proportionality between the oxidation rate and the concentrations of the palladium salt and of the olefin is the first kinetic confirmation of the previously stated assumption ($^{1-3}$) that the reaction proceeds through the formation of a π-complex. The data obtained by us are insufficient, however, for judging the detailed mechanism of this reaction. The presence of second order, the absence of a salt effect and of an effect of hydrogen ions, in particular, can be reconciled with equal success both with the assumption that the rate-limiting step is formation of the π-complex and with a scheme according to which complex formation is an equilibrium step (assuming that $K_{eq} \ll 10^3$), while the decomposition of the π-complex limits the reaction. It should be noted, however, that the values $\Delta H^{\#} = 13$ kcal/mole and $\Delta S^{\#} = -3.7$ e.u., calculated from the data on the temperature dependence of k_2 in the range 7.0-30.3° C, are close to those usually observed for substitution reactions in complexes of divalent platinum.

Fig. 3. Dependence of the value of the first-order rate constant k_1 on the concentration of $PdCl_2$

Another important question relating to the reaction mechanism is the question of the active form of the palladium salt. In solutions of $PdCl_2$ containing no other substances capable of ionization with formation of Cl^- ions, one may assume the existence of $PdCl_2$ molecules, hydrated Pd^{2+} ions, $PdCl^+$, and also $PdCl^-$. The absence of thermodynamic data does not make it possible to estimate accurately the concentrations of these forms. The instability constant of the $PdCl_4^{2-}$ complex at 25° (^{4}) is $5 \cdot 10^{-13}$ $\mathrm{mole}^4 \cdot \mathrm{l}^{-4}$. With respect to the instability constants of the particles $PdCl^+$ (K_{I}), $PdCl_2$ (K_{II}), $PdCl^-$ (K_{III}), and $PdCl_4^{2-}$ (K_{IV})— one can assume only that $K_{\mathrm{I}} \ll K_{\mathrm{II}} < K_{\mathrm{III}} < K_{\mathrm{IV}}$. As follows from Fig. 4, the first-order rate constant at a constant concentration of Pd^{II} of 0.00458 g-mole/l decreases sharply with increasing concentration of Cl^- ions introduced with NaCl. This course of the curve may be explained by a change in the ratio between the ions of divalent palladium as the concentration of Cl^- ions is increased. Further discussion of this question requires additional kinetic and thermodynamic studies, to which a separate publication will be devoted.

* The choice of $HClO_4$ is explained by the fact that ClO_4^- ions have the least tendency toward complex formation.

Fig. 4. Dependence of the logarithm of the first-order constant k_1 on the ratio $C_{Cl^-}/C_{Pd^{II}}$ at a constant concentration of Pd^{II} (0.00458 g-mole/l)

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