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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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KINETIC STAGES OF THE OXIDATION OF ETHYLENE BY PALLADIUM CHLORIDE IN AQUEOUS SOLUTIONS

Earlier [1], in discussing the results of a study of the kinetics of oxidation of ethylene by palladium chloride in solutions containing 0.5 mole/liter NaCl, it was suggested that the reaction proceeds through the stage of deprotonation of the reacting π-complex, for example, of the complex of composition $C_2H_4PdCl(OH_2)_2^+$.

In order to obtain additional data on the mechanism of this reaction, we studied, by the method described earlier [1], the effect of chlorine ions on the reaction rate and measured the rate of oxidation of ethylene in acetic acid. In the concentration range of chlorine ions from 0.1 to 1.5 mole/liter, the reaction rate is directly proportional to the first powers of the concentrations of ethylene and palladium chloride. The observed second-order rate constant, at constant concentration of $HClO_4$ (0.5 mole/liter) and constant ionic strength of the solution (2.0 mole/liter LiCl–$LiClO_4$), varies inversely as the square of the concentration of chlorine ions (see Fig. 1). These results indicate that the reaction proceeds through the π-complex $C_2H_4PdCl_2OH_2$, and not $C_2H_4PdCl(OH_2)_2^+$.

Fig. 1. Dependence of the observed second-order rate constant on the concentration of chlorine ions (0.5 mole/liter $HClO_4$, 2.0 mole/liter LiCl–$LiClO_4$, 25°); it is represented by a straight line in the coordinates k^2–$1/[Cl^-]^2$.

It was already noted earlier [1] that the decrease in the rate of ethylene oxidation with increasing acid concentration may be associated both with participation of HO^- ions in the reaction and with the fact that the oxidative-reductive decomposition is preceded by deprotonation of the π-complex. Obviously, the hypothesis of Smidt [2], according to which the π-complex decomposes in the reaction of $C_2H_4PdCl_3^-$ with the HO^- ion, contradicts the experimentally observed dependence of the reaction rate on the concentration of chlorine ions.

However, the available kinetic data do not exclude a mechanism in which the complex $C_2H_4PdCl_2OH_2$ reacts with the HO^- ion.

Apparently, the main argument in favor of the participation of HO^- ions in the reaction is their increased nucleophilicity. In a $1M$ acid solution the concentration of H_2O is $5.5 \cdot 10^{15}$ times greater than the concentration of HO^-. There is no reason to expect that the ratio of the nucleophilic activities of HO^- ions and H_2O molecules (usually a quantity of the order of 10^6–10^9) can reach values greater than 10^{16}, as required by the hypothesis of the participation of HO^- ions in the reaction.

Table 1

H, %	[NaCl], mol/l	[HCl], mol/l	$[PdCl_2]\cdot 10^2$, mol/l	$[C_2H_4]\cdot 10^3$, mol/l	$k_1 \cdot 10^3$, sec^{-1}	$k_2 \cdot 10^2$, l/(mol·sec)	$(k_2)_{av}\cdot 10^2$, l/(mol·sec)	$\frac{k_2^{H_2O}}{k_2^{D_2O}}$
100	0,396	0,113	1,39	4,27	2,13	15,4		
100	0,396	0,113	1,42	4,29	2,15	15,1	15,2$\pm0,3|||100|0,396|0,113|3,25|5,28|4,83|14	
2,68	0,227	0,285	4,62	4,15	0,614	1,48		

The values of the isotope kinetic effect obtained by us (see Table 1) are also in contradiction with the hypothesis of the participation of HO^- ions in the reaction. The observed change in the reaction rate on going from water to deuterium oxide is a total effect, including the corresponding effects of the stages of formation and subsequent transformations of $C_2H_4PdCl_2OH_2$. It may be assumed that the equilibrium constants for the formation of the complex $C_2H_4PdCl_2OH_2$ from C_2H_4 and $PdCl_4^{2-}$ in water and in D_2O are close to one another, and, moreover, that the nucleophilicities of DO^- in D_2O and HO^- in H_2O are equal. Then it is easy to show that $k_2^{H_2O}/k_2^{D_2O} = K_w^{H_2O}/K_w^{D_2O}$ in the case where the rate-limiting step is the addition of HO^- to the coordinated olefin molecule in the formation of an intermediate product of the type $[Cl_2PdCH_2CH_2OH]^-$ or $[Cl_2PdCH(OH)CH_3]^{-*}$ (which then decomposes with formation of aldehyde). If the decomposition of the π-complex under the action of HO^- is rate-limiting according to a scheme analogous to Smith' s scheme ([2]), or if the decomposition of the organometallic compound is slow, then $k_2^{H_2O}/k_2^{D_2O} > K_w^{H_2O}/K_w^{D_2O}$. According to the data of work ([3]), in the case of a solution containing 98,92% D_2O, $K_w^{H_2O}/K_w^{D_2O} = 5,01$, and if HO^- ions participated in the reaction, one should consequently expect $k_2^{H_2O}/k_2^{D_2O} \geq 5,01$ instead of the observed value $4,05 \pm 0,15$.

Fig. 2. Dependence of the observed second-order rate constant on temperature (0,5 mol/l NaCl, 0,275 mol/l $HClO_4$)

The kinetic data obtained in this work and earlier ([1]) indicate that the irreversible stage as a result of which the reaction products are formed is preceded

by the stages:

$$C_2H_4 + PdCl_4^{2-} = C_2H_4PdCl_3^- + Cl^-, \quad (1)$$

$$C_2H_4PdCl_3^- + H_2O = C_2H_4PdCl_2OH_2 + Cl^-, \quad (2)$$

$$C_2H_4PdCl_2OH_2 + H_2O = C_2H_4PdCl_2OH^- + H_3O^+. \quad (3)$$

* Here and below, for simplification, in the formulas of the organometallic compounds we omit a water molecule (probably occupying the 4th coordination site); in deriving the kinetic equation (10), the participation of water in stage (4) is taken into account.

It is unlikely that formation of the carbonyl compound from a molecule of C_2H_4 and an HO^- ion coordinated in $C_2H_4PdCl_2OH^-$ can occur in a single act, bypassing intermediate stages. In the oxidation of olefins by palladium salts, the carbonyl group is formed predominantly at the carbon atom to which the nucleophile adds in acid-catalyzed reactions, which indicates a substantial analogy between this reaction and other electrophilic-addition reactions. It may be assumed that the reason for this similarity is that the reaction proceeds through isomerization of the complex $C_2H_4PdCl_2OH^-$ into an organometallic compound of the type $[Cl_2PdCH_2CH_2OH]^-$, as a result of which addition of the electrophilic agent and the nucleophile occurs in accordance with Markovnikov' s rule. The carbonyl compound is formed upon irreversible decomposition of the organometallic compound:

$$C_2H_4PdCl_2OH^- = [Cl_2PdCH_2CH_2OH]^-, \quad (4)$$

$$\left[\begin{array}{l}\mathrm{Cl}\backslash\\ \mathrm{Cl}/\end{array}\ \mathrm{Pd{-}CH_2{-}CH{-}O{-}H}\right]^- + OH_2 = Cl^- + PdCl^- + CH_3CHO + H_3O^+. \quad (5)$$

The $PdCl^-$ ions, on interaction with the oxidizing agent, are rapidly oxidized, and in the absence of the latter decompose with formation of palladium.

If reactions (1) and (2) are close to equilibrium, the observed constant k_2 is related to the equilibrium constants K_1 and K_2 by the relation $k_2 = k_H K_1 K_2 / \Phi_1 \Phi_2$, where k_H is the rate constant of the reaction referred to the concentration of $C_2H_4PdCl_2OH_2$, Φ_1 is the ratio of the total concentration of palladium compounds to the equilibrium concentration of $PdCl_4^{2-}$, and Φ_2 is, correspondingly, the degree of complexation of ethylene. Analysis of the changes in Φ_1 and Φ_2, on the basis of previously obtained [4] data on complex-formation equilibria in solutions of $PdCl_4^{2-}$ and C_2H_4, shows that

changes in $\Phi_1\Phi_2$ during the kinetic experiment are comparatively small, but reach appreciable values when the initial concentrations of palladium salt and ethylene are varied over wide limits. Thus, if stages (1) and (2) were close to equilibrium, the reaction rate would not be proportional to the concentration of palladium salt, especially in the region of Cl^- ion concentrations of 0.1-0.5 mole/l. Thus, at $[Cl^-] = 0.1$; $[C_2H_4] = 10^{-3}$; $[Pd] = 10^{-2}$ mole/l, at equilibrium 90% of the olefin is bound in π-complexes. Increasing the palladium salt concentration by a factor of 3.07 (from $0.992 \cdot 10^{-2}$ to $3.05 \cdot 10^{-2}$ mole/l) should lead to an increase in the fraction of bound ethylene by 8%, i.e., change the rate only slightly. In reality, under these conditions the value of k_1 increases by a factor of 2.89 (from $2.21 \cdot 10^{-3}$ to $6.37 \cdot 10^{-3}$ sec^{-1}). Clear first-order behavior with respect to the palladium salt is observed over the entire investigated range of reactant concentrations at Cl^- ion concentrations from 0.1 to 1.5 mole/l.

Thus, stages (1) and (2) are not equilibrium stages; the concentrations of palladium π-complexes under the conditions of kinetic experiments are small, and, consequently, changes in the concentration of $PdCl_4^{2-}$ during the experiment may be neglected. Under this condition, from the balance equation

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

$$+ [C_2H_4PdCl_2\overline{OH}] + [Cl_2\overline{P}dCH_2CH_2OH] \qquad (6)$$

it follows:

$$\frac{d[C_2H_4PdCl_3^-]}{dt} + \frac{d[C_2H_4PdCl_2OH_2]}{dt} + \frac{d[C_2H_4PdCl_2\overline{OH}]}{dt} + \frac{d[Cl_2\overline{P}dCH_2CH_2OH]}{dt} = 0. \qquad (7)$$

The rates in the left-hand side of equation (7) can be expressed through the concentrations and rate constants of the stages in which, respectively, $C_2H_4PdCl_3^-$, $C_2H_4PdCl_2OH_2$, etc., are formed or consumed. Substituting these expressions into (7), we obtain:

$$\alpha_1[C_2H_4][PdCl_4^{2-}] - \beta_1[C_2H_4PdCl_3^-][Cl^-] = \alpha_5[Cl_2\overline{P}dCH_2CH_2OH], \qquad (8)$$

where α_1 and β_1 are the rate constants of stage (1) in the forward and reverse directions, and α_5 is the rate constant of stage (5). These constants include the activity coefficients of the reacting substances and activated complexes.

The left-hand side of equation (8) is the observed rate of formation of $C_2H_4PdCl_3^-$, and the right-hand side is the rate of formation of the reaction

products. Obviously, equation (8) is satisfied either in the case where stage (1) limits the reaction, or when the reaction proceeds in a stationary regime. The first condition contradicts the experimentally established dependence of the reaction rate on the concentrations of H_3O^+ and Cl^-. Consequently, the totality of the data obtained by us indicates that the reaction proceeds in a quasi-stationary regime.

Analysis of the sequence (1-5) according to M. I. Temkin[5], under the condition that stage (3) is quasi-equilibrium, leads to the equation:

$$w = \frac{[C_2H_4][PdCl_4^{2-}]}{\frac{1}{\alpha_1} + \frac{\beta_1}{\alpha_1\alpha_2}[Cl^-] + \left(\frac{\beta_1\beta_2}{\alpha_1\alpha_2K_3\alpha_4} + \frac{\beta_1\beta_2\beta_4}{\alpha_1\alpha_2\alpha_4K_3\alpha_5}\right)[Cl^-]^2[H_3O^+]}. \quad (9)$$

From the data of this work[1] and Fig. 1 it is seen that, in the coordinates k_2–$1/[H_3O^+]$ and k_2–$1/[Cl^-]^2$, the experimental data fall well on a straight line passing through the origin. Consequently, the first and second terms of the denominator are negligibly small in comparison with the last. This agrees with the known data[4,6] that the formation of the complex $C_2H_4PdCl_3^-$ and the subsequent substitution of chlorine in the trans position by a water molecule are fast reactions, whereas the equilibrium constant of the acid dissociation of the complex $C_2H_4PdCl_2OH_2$ (K_3) is a quantity of the order of 10^{-3}-10^{-5} mol/l.

After the corresponding simplifications and certain transformations, from equation (9) we obtain:

$$k_2 = \frac{K_1'K_2'K_3'K_4'\alpha_5'}{\left(1 + \frac{\alpha_5'}{\beta_4'}\frac{f_4^{\neq}}{f_5^{\neq}}a_{H_2O}\right)} \cdot \frac{f_{C_2H_4}f_{PdCl_4^{2-}}a_{H_2O}^4}{f_{Cl^-}^2 f_{H_3O^+}f_5^{\neq}} \cdot \frac{1}{[H_3O^+][Cl^-]^2}, \quad (10)$$

where $K_i' = \alpha_i'/\beta_i'$ are the equilibrium constants of the corresponding stages, expressed in terms of activities, while α_5' and β_4' are, respectively, the rate constants of reaction (5) in the forward direction and reaction (4) in the reverse direction; $f_4^{\neq}$ and $f_5^{\neq}$ are the activity coefficients of the activated complexes in stages (4) and (5).

The equation obtained for the observed second-order rate constant agrees well with the experimentally established dependence of k_2 on ionic strength and on the concentrations of acid[1] and chloride ions.

The second-order rate constant increases with increasing temperature in the interval 10-40°, obeying the Arrhenius equation (see Fig. 2). The observed activation parameters are $\Delta H^{\neq} = 16.8$ kcal/mol, and $\Delta S^{\neq} = -6.4$ entropy units.

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