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Oxidation of Palladium with Allyl Bromide and Iodine in Dimethylformamide

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Abstract—The kinetic features of palladium oxidation with allyl bromide and iodine in dimethylformamide were determined. The apparent equilibrium constants, enthalpies, and entropies of reactant adsorption on the palladium surface were calculated.

An interest in oxidation of palladium with halogens and various halohydrocarbons [1–5] is due to both theoretical (detailed elucidation of the reaction mechanism) and applied (recovery of palladium from production wastes) problems. However, some features of previous studies [1–5] could affect their results. For example, in [3] the reaction mixture was in contact with air. In [5], the reaction was performed at a temperature at which the oxidant could react with the ligand at a noticeable rate to give products reactive toward palladium. Furthermore, the kinetic features of the reactions were not studied in [1–5].

Our goal was to study the kinetics of palladium oxidation with allyl bromide and iodine in dimethylformamide (DMF).

Figures 1 and 2 show how the rate V of the developed process depends on the allyl bromide concentration C_{Ox} at a constant ligand concentration C_{L} and on the ligand concentration at a constant oxidant concentration. The shape of the kinetic curves, in combination with data of [6], shows that the reaction is described by the Langmuir–Hinshelwood scheme [7], with the adsorption of the oxidant and ligand on the palladium surface occurring on active centers of different nature.

$$\mathrm{Ox} + \mathrm{S}_1 \xrightleftharpoons{K_{\mathrm{Ox}}} \mathrm{Ox(S_1)}, \qquad (1)$$

$$\mathrm{L} + \mathrm{S}_2 \xrightleftharpoons{K_{\mathrm{L}}} \mathrm{L(S_2)}, \qquad (2)$$

$$\mathrm{Ox(S_1)} + \mathrm{L(S_2)} \xrightarrow{k} \text{Products}. \qquad (3)$$

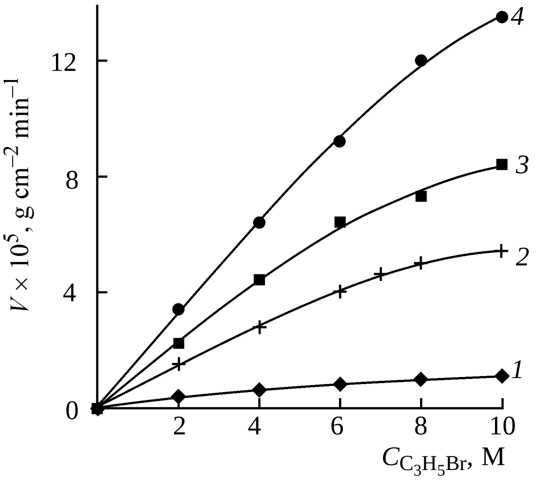

Fig. 1. Rate of palladium oxidation as a function of allyl bromide concentration in DMF–*p*-xylene (C_{DMF} 1.7 M). Temperature, K: (*1*) 323, (*2*) 333, (*3*) 338, and (*4*) 343; the same for Fig. 2.

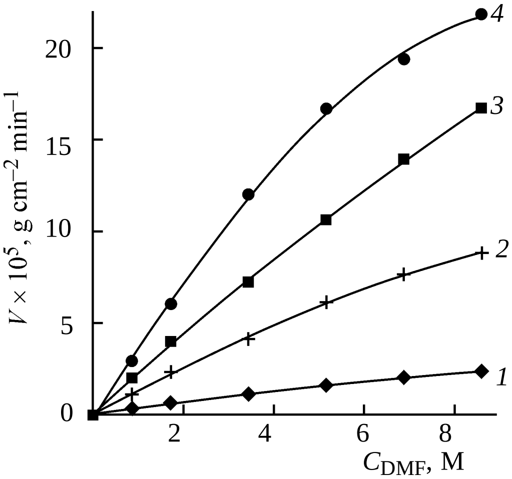

Fig. 2. Rate of palladium oxidation as a function of DMF content in the reaction mixture. Inert solvent *p*-xylene, $C_{\mathrm{C_3H_5Br}}$ 4.0 M.

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Here, K_{Ox} and K_L are the equilibrium constants of adsorption of the oxidant and ligand, respectively; k is the rate constant of the reaction on the metal surface.

In this case, the expression for the reaction rate has the form

$$V = k' \frac{S_{01}S_{02}K_{Ox}K_LC_{Ox}C_L}{(1 + K_{Ox}C_{Ox})(1 + K_LC_L)}, \qquad (4)$$

where S_{01} and S_{02} are the numbers of the corresponding adsorption centers per unit surface area; $k = k'S_{01}S_{02}$.

Treatment of the kinetic data in the coordinates $1/V = f(1/C_{Ox})$ at C_L = const and $1/V = f(1/C_L)$ at C_{Ox} = const allowed calculation of the apparent equilibrium constants of reactant adsorption on the metal surface and of the reaction rate constants. From the temperature dependences of these quantities, we determined the apparent activation energy of the process and the apparent enthalpy and entropy of adsorption of the oxidant and ligand on the palladium surface.

T, K	323	333	338	343
$K_{Ox} \times 10^2$	8.3	4.3	3.3	2.4
$K_L \times 10^2$	4.3	3.1	2.8	2.2
k, g cm^{-2} min^{-1}	3.5×10^{-4}	2.9×10^{-3}	7.1×10^{-3}	2.1×10^{-2}

$$E_a\ 187 \pm 11,\ -\Delta H^{Ox}_{ads}\ 57 \pm 2,\ -\Delta H^{L}_{ads}\ 28 \pm 11\ \text{kJ mol}^{-1};$$
$$-\Delta S^{Ox}_{ads}\ 47 \pm 3,\ -\Delta S^{L}_{ads}\ 27 \pm 9\ \text{J mol}^{-1}\ \text{K}^{-1}$$

After reaction completion, the unchanged metal was removed, and the liquid phase was distilled off at reduced pressure. The remaining oily liquid was analyzed for the bromine content. The analysis results show that 1 mol of metal reacts with 1 mol of allyl bromide. Thus, in agreement with [1], the reaction follows the scheme

$$2Pd + 2C_3H_5Br \longrightarrow (C_3H_5PdBr)_2. \qquad (5)$$

An NMR study [8] showed that the halide bridges in allylpalladium halides are broken in the presence of dimethyl sulfoxide, and the allyl ligand becomes σ-coordinated. A similar process apparently occurs in DMF.

A part of the oily liquid was hydrolyzed by boiling with water, and the released propylene was determined chromatographically. Its amount was 0.47 mol per mole of dissolved palladium, which, in agreement with [9], corresponds to 94% yield of allylpalladium halide.

The dependence of the rate of palladium oxidation with iodine in DMF on the iodine concentration has a peculiar shape with a sharp maximum (Fig. 2). At the oxidant concentration corresponding to the maximum, the metal removed from the mixture has a dull surface, whereas at higher iodine concentrations the palladium surface becomes covered with a dense black precipitate, apparently preventing further reaction. This fact did not allow determination of the formal kinetics of the process. The yield of PdI_2 was determined at the initial iodine concentration corresponding to the maximum in the plot $V = f([I_2])$. After removal of the liquid phase at reduced pressure and recrystallization of the residue from acetone, the IR spectrum of the product contained no bands assignable to N–H vibrations (2450 cm^{-1}) in the dimethylammonium ion $(CH_3)_2NH_2^+$, and the content of palladium and iodine was consistent with the formula PdI_2 (found, %: Pd 29.1; I 69.8. Calculated, %: Pd 29.5, I 70.5). The yield of PdI_2 was 93% based on the dissolved metal. The difference between our results and those obtained in [5] is due to different reaction conditions.

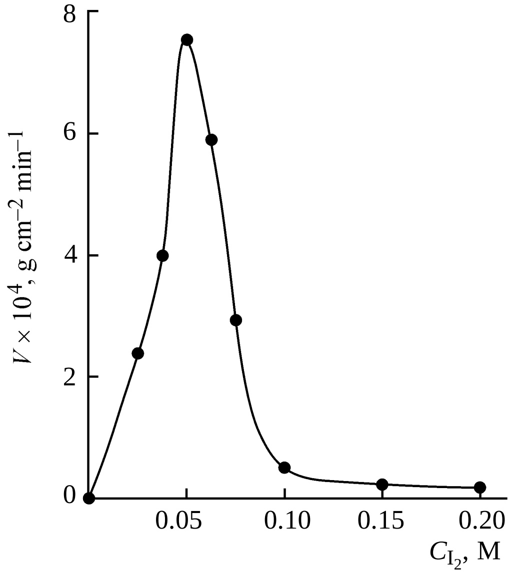

Fig. 3. Rate of palladium oxidation in DMF at 333 K as a function of the initial iodine concentration.

EXPERIMENTAL

The IR spectra were recorded on an IKS-29 spectrophotometer.

Palladium wire (ultrapure grade, 99.999% main substance, 0.2 mm in diameter) was used without additional treatment. Crystalline I_2 was of chemically pure grade. Allyl bromide (pure grade) and DMF were purified and dried by common procedures [10]. Liquid reactants, if necessary, were degassed before use by repeated freeze–pump–thaw cycles. The content of palladium [11] and bromine [12] in the reaction product was determined photometrically with an SF-46 spectrophotometer. Iodine was determined by argentometric titration [13]. Propylene was determined chromatographically (Tsvet-106 chromatograph, thermal conductivity detector, 1000 × 5-mm glass column packed with activated carbon, column and detector temperatures 150°C, carrier gas helium, flow rate 40 ml min^{-1}). The kinetic measurements were performed by the resistometric method [14] modified to exclude contact with air.

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