Chemistry

I. I. MOISEEV, M. N. VARGAFTIK, and Corresponding Member of the Academy of Sciences of the USSR Ya. K. SYRKIN

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Abstract

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I. I. MOISEEV, M. N. VARGAFTIK, and Corresponding Member of the Academy of Sciences of the USSR Ya. K. SYRKIN

ON THE MECHANISM OF THE REACTION OF PALLADIUM SALTS WITH OLEFINS IN HYDROXYL-CONTAINING SOLVENTS

The formation of carbonyl compounds in the reaction of olefins with palladium salts in aqueous solutions proceeds through the stage of interaction of a π-complex of the type $[\mathrm{Cl_3Pd}C_{nH_{2n}}]^-$ with water according to the equation:

$$[\mathrm{Cl_3Pd}C_{nH_{2n}}]^- + \mathrm{H_2O} = \mathrm{Pd} + 2\mathrm{HCl} + \mathrm{Cl}^- + C_{nH_{2n}}O.* \qquad (1)$$

In discussing the mechanism of this reaction, we proposed (^{1}) that, in the course of decomposition of the π-complex, a proton is split off from the carbon atom of the double bond and the π-complex is converted into an organometallic compound (in the case of ethylene, of the type $\mathrm{CH_2 = CH{—}PdCl_3^{2-}}$, I). In the reaction of I with water, vinyl alcohol is formed, which then isomerizes to the carbonyl compound.

Other authors (^{2}) consider that the first stage of reaction (1) is the addition of the $\mathrm{HO^-}$ ion to the strongly polarized olefin. Without entering into a detailed discussion of this question until more detailed data are obtained, we note that the participation of $\mathrm{HO^-}$ ions in this reaction appears to us unlikely. In particular, in our experiments (^{1}) the absolute concentration of $\mathrm{HO^-}$ ions was 10^{-12}—10^{-14} g-ion/l, whereas the concentration of such nucleophilic ions as $\mathrm{Br^-}$ or $\mathrm{Cl^-}$ exceeded the concentration of $\mathrm{HO^-}$ ions by 10^{10}—10^{12} times. Obviously, under these conditions, in addition to the reaction of the π-complex with $\mathrm{HO^-}$ ions, a competing reaction with halide ions should have proceeded to one degree or another, ultimately leading to the formation of organohalogen compounds fairly stable under the conditions of the process. Such a scheme cannot satisfactorily explain the high selectivity of the oxidation process, in which the yield of carbonyl compounds reaches 95-99%.

A more acceptable mechanism appears to be one according to which the charge of the nucleophilic particle attacking the C atom of the double bond of the olefin in the π-complex is not of substantial importance, and the addition of the $\mathrm{HO^-}$ ion occurs as a result of the reaction of the π-complex with solvent molecules:

$$\left[\mathrm{Cl_3Pd}\begin{array}{l}\cdots\mathrm{CH_2}\\ \cdots\mathrm{CH_2}\end{array}\right]^{-} + 2\mathrm{H_2O} \longrightarrow [\mathrm{Cl_3Pd{—}CH_2{—}CH_2{—}OH}]^{2-} + \mathrm{H_3O^+} \qquad (2)$$

(II)

The β-chloropallado-substituted ethanol (II) formed, judging for example by analogy with organomercury compounds, should readily enter into an acidolysis reaction with formation of the alcohol. The absence of alcohol among the reaction products is possibly explained by the fact that the conversion of II into the carbonyl compound proceeds faster than acidolysis. This conversion may proceed by two routes: 1) through an α-oxide, 2) through vinyl alcohol.

In the first case the reaction proceeds through an intramolecular nucleophilic substitution of the SN_i type:

$$\mathrm{Cl_3Pd{-}CH_2{-}CH_2OH} \longrightarrow [\mathrm{Cl_3Pd{-}CH_2{-}CH_2OH}]^{2-} \longrightarrow \mathrm{PdCl_3}^{-} + \mathrm{CH_2{-}CH_2OH}^{+}$$

$$\mathrm{PdCl_3}^{3-} \longrightarrow \mathrm{Pd} + 3\,\mathrm{Cl}^{-}$$

$$\mathrm{CH_2{-}CH_2OH}^{+} + \mathrm{H_2O} \longrightarrow \mathrm{CH_3{-}CHO} + \mathrm{H_3O}^{+}$$

The formation of vinyl alcohol may occur during the conversion of II through a five-membered cyclic active complex:

$$[\mathrm{PdCl_2(CH_2{=}CH{-}OH)ClH}] \longrightarrow \mathrm{PdCl_2}^{2-} + \mathrm{CH_2{=}CHOH} + \mathrm{HCl}$$

Substantial data on the mechanism of decomposition of the π-complex can be obtained by studying the reaction between $PdCl_2$ and olefins in nonaqueous solutions. Obviously, in this case it may be possible to isolate the corresponding derivatives of the intermediate compounds formed when the reaction is carried out in water. Thus, if the reaction proceeds through α-oxides, then in a solution of an alcohol or a carboxylic acid one may expect the formation of simple or complex ethers of glycols. If the reaction proceeds through vinyl compounds, one may expect the formation of simple or complex vinyl ethers or products of their

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* It is not excluded that, in reality, it is not the complex anion that is directly decomposed, but complexes of the type $Cl_2PdC_{nH_{2n}}$ or $[ClPdC_{nH_{2n}}]^+$ activated by solvent. In that case the reaction equations and the schemes of the activated complexes (see below) change their form accordingly.

transformation. Smidt and co-workers (^{2}) reported that palladium chloride is not reduced by the action of olefins upon it in glacial acetic acid. These solutions absorb olefins, and the excess of olefin relative to the amount dissolving in the absence of $PdCl_2$ is equivalent to the amount of dissolved $PdCl_2$. This fact may be regarded as evidence for the reversible formation in these solutions of a π-complex between $PdCl_2$ and the olefin.

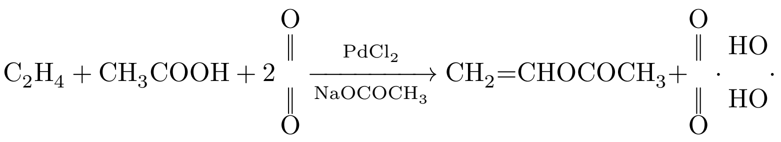
The absence of a reduction reaction in glacial acetic acid may be associated with various causes, including the possibility that the interaction between $PdCl_2$ and the olefin under these conditions terminates with the formation of a complex whose structure differs from that formed in the reaction of $PdCl_2$ with olefins in water. To test this assumption we attempted to carry out the reaction between the complex $(PdCl_2 \cdot C_2H_4)_2$, synthesized by Kharash' s method (^{3}), and glacial acetic acid. Our experiments showed that this compound, which reacts instantly even with atmospheric moisture, remains unchanged in a solution of glacial acetic acid for ten days. At the same time, the complex $(PdCl_2 \cdot C_2H_4)_2$ rapidly decomposes with separation of metallic palladium in solutions of ethyl alcohol, benzyl alcohol, and phenol.

It may be thought that the main reason impeding decomposition of the π-complex in acetic acid is the "acidic character" and the lowered nucleophilicity of the solvent molecules, which are more inclined to eliminate a proton than to form onium ions. As a result, the first stage of decomposition of the π-complex is hindered. If this is so, then addition to the solution of lyate ions (for example, in the form of an alkali-metal salt) may make possible the reaction of the π-complex with the acid. The experiments we carried out showed that palladium chloride in acetic acid solutions containing sodium acetate is reduced by ethylene according to the equation:

$$C_2H_4 + PdCl_2 + 2\,CH_3COONa \longrightarrow CH_2{=}CH{-}OCOCH_3 + 2\,NaCl + Pd + CH_3COOH \cdot \tag{3}$$

The yield of vinyl acetate, based on reacted ethylene, is 97%. The complex $(PdCl_2 \cdot C_2H_4)_2$ also reacts with sodium acetate in glacial acetic acid to form vinyl acetate. In the presence of substances capable—

···oxidize the metallic palladium formed upon reduction, reaction (3) can evidently be used as a preparative method for obtaining complex vinyl ethers. Thus, for example, in the presence of *p*-benzoquinone, simultaneously with reaction (3) the oxidation of palladium takes place. The overall reaction may be represented by the equation:

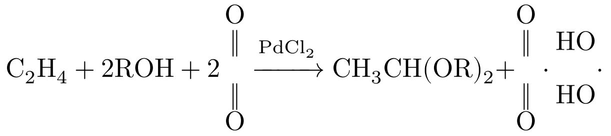


$$C_2H_4 + CH_3COOH + 2\begin{array}{c}O\\ \|\\ \\ \|\\ O\end{array} \xrightarrow[NaOCOCH_3]{PdCl_2} CH_2{=}CHOCOCH_3 + \begin{array}{c}O\\ \|\\ \\ \|\\ O\end{array} \cdot \begin{array}{c}HO\\ \\ HO\end{array} \cdot$$

If one assumes that in alcohol the decomposition of the π-complex proceeds analogously to the decomposition in acetic acid, then one should expect that the product of the reaction of $PdCl_2$ with ethylene in an alcoholic solution should be a vinyl ether or the product of addition to it of an alcohol molecule (a reaction catalyzed by traces of acids and by metal halides (^{4})). Our experiments showed that $(PdCl_2 \cdot C_2H_4)_2$ reacts rapidly with alcohol. The main product of the reaction is an acetal:

$$(PdCl_2 \cdot C_2H_4)_2 + 4C_2H_5OH \rightarrow 2Pd + 4HCl + 2CH_3CH(OC_2H_5)_2. \tag{4}$$

In the presence of *p*-benzoquinone, the reduction of $PdCl_2$ by ethylene in alcoholic solutions is accompanied by oxidation of metallic palladium, which makes it possible to use this reaction for obtaining acetals directly from olefins:



$$C_2H_4 + 2ROH + 2\begin{matrix}O\\ \|\\ \\ \|\\ O\end{matrix} \xrightarrow{PdCl_2} CH_3CH(OR)_2 + \begin{matrix}O\\ \|\\ \\ \|\\ O\end{matrix} \cdot \begin{matrix}HO\\ \\ HO\end{matrix}.$$

Copper salts may also be used as oxidants in alcoholic solutions, just as was done in carrying out the reaction in aqueous solutions (^{1,2}).

The data we have obtained substantially support the point of view according to which decomposition of the π-complex in hydroxyl-containing solvents proceeds through the intermediate formation of vinyl compounds. In water this is vinyl alcohol, which isomerizes to acetaldehyde; in acetic acid, vinyl acetate; in alcohol, a simple vinyl ether, which subsequently adds an alcohol molecule with formation of an acetal. Evidently, the data obtained in this work are difficult to explain if one assumes that the reaction proceeds through α-oxy compounds.

It should be noted that our data do not answer the question of which of the two reactions—the conversion of the π-complex into I or II—is the first step of decomposition. Both mechanisms, in particular, satisfactorily explain both the absence of reaction in glacial acetic acid and the fact that in the presence of CH_3COO^- ions the reaction of the π-complex with acetic acid becomes possible. However, the weak point of the mechanism that includes reaction (2) as the first stage is the assumption that conversion of II into a vinyl compound proceeds faster than the acidolysis of II.

Experimental Part

1. Interaction of the complex $(PdCl_2 \cdot C_2H_4)_2$ with nonaqueous solvents.

a) 2.05 g (0.005 g-mol) of the complex $(PdCl_2 \cdot C_2H_4)_2$, obtained from the palladium compound with benzonitrile by the method of Kharash (^{3}), is mixed with 1.58 g (0.034 g-mol) of absolute alcohol. Strong heating and rapid precipitation of metallic palladium are observed. After 2 hours the solution is filtered and distilled. A fraction is isolated ···

with b.p. 102-104°/758 mm, yield 0.74 g, d_4^{20} 0.8252, n_D^{20} 1.3818. b) 2.05 g (0.005 g-mole) of the complex $(PdCl_2 \cdot C_2H_4)_2$ is mixed with 1.5 ml (0.025 g-mole) of glacial acetic acid. No changes are observed over the course of 10 days. c) 2.05 g (0.005 g-mole) of the complex $(PdCl_2 \cdot C_2H_4)_2$ is mixed with 1.5 ml (0.025 g-mole) of glacial acetic acid and 0.41 g (0.005 g-mole) of anhydrous sodium acetate. Rapid precipitation of metallic palladium is observed. After 3 hours the solution is filtered off, washed with water, dried with magnesium sulfate, and distilled. A fraction with b.p. 72–73° is isolated; yield 0.51 g, d_4^{20} 0.9341, n_D^{20} 1.3958.

Found, %: C 55.50; 55.66; H 7.38; 7.26
$C_4H_6O_2$. Calculated, %: C 55.80; H 7.03

The IR spectrum is identical with the spectrum of vinyl acetate (bands: 1775, 1660, 1438, 1377, 1298, 1226, 1146, 1025, 980, 955, 880, and 851 cm^{-1}).

2. Reaction of palladium chloride with ethylene in a solution of glacial acetic acid containing sodium acetate. A solution of 8.88 g (0.05 g-mole) of anhydrous palladium chloride and 8.2 g (0.10 g-mole) of anhydrous sodium acetate in 60 ml of glacial acetic acid is saturated with dry ethylene for 16 h at 20°. After absorption of 560 ml (at 765 mm) of ethylene (0.0235 g-mole), the precipitated palladium is filtered off and the fraction 96–118° is distilled off (24 ml). The content of unsaturated compounds, determined with Kaufmann reagent, is 0.0228 g-mole (97% based on absorbed ethylene). The resulting fraction is distilled on a column (33 theoretical plates), and the fraction 72–86° is isolated, washed with water, dried with magnesium sulfate, and distilled. Yield 0.84 g, b.p. 72.4–72.9°/755 mm, d_4^{20} 0.9340, n_D^{20} 1.3958. The IR spectrum is identical with the spectrum of vinyl acetate (see 1c).

3. Oxidation of ethylene by *p*-benzoquinone in an acetic-acid solution in the presence of palladium chloride. A solution of 0.178 g (0.001 g-mole) of anhydrous palladium chloride and 8.2 g (0.1 g-mole) of anhydrous sodium acetate in 125 ml of glacial acetic acid is mixed with 27 g (0.25 g-mole) of *p*-benzoquinone and, with shaking, saturated with dry ethylene for 63 h at 18°. After absorption of 2100 ml (at 765 mm) of ethylene (0.0885 g-mole), the solution is filtered and a fraction with b.p. 85–118° (60 ml) is distilled from the filtrate. After redistillation with a dephlegmator, the content of unsaturated compounds, determined with Kaufmann reagent, is 0.0877 g-mole (99.2% based on absorbed ethylene). The resulting mixture is separated on a column (33 theoretical plates); the fraction with b.p. 72–86° is washed with water, dried with magnesium sulfate, and distilled. Yield 3.27 g, b.p. 72.5–72.9°/758 mm, d_4^{20} 0.9341, n_D^{20} 1.3959; the IR spectrum is identical with the spectrum of vinyl acetate (see 1c).

4. Oxidation of ethylene by *p*-benzoquinone in an alcoholic solution in the presence of palladium chloride. To a solution of 0.500 g (0.00281 g-mole) of anhydrous PdCl in 29 ml, 23 g (0.5 g-mole) of absolute alcohol, 25 ml of absolute ether and 54 g (0.5 g-mole) of *p*-benzoquinone are added. The mixture is saturated, with shaking, with dry ethylene for 6 h at 18°. After absorption of 5500 ml (at 765 mm) of ethylene (0.233 g-mole), 50 ml of ether is added, the mixture is filtered, the filtrate is washed with 10% aqueous KOH solution until discoloration ceases, dried with magnesium sulfate, and distilled. Yield 19.9 g (72.4% based on reacted ethylene), b.p. 102–104°, d_4^{20} 0.8252, n_D^{20} 1.3816.

Moscow Institute of Fine Chemical Technology
named after M. V. Lomonosov

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1. I. I. Moiseev, M. N. Vargaftik, Ya. K. Syrkin, DAN, **130**, 821 (1960).
2. J. Smidt et al., Angew. Chem., **71**, 176 (1959).
3. M. S. Kharash, R. C. Seyler, F. R. Mayo, J. Am. Chem. Soc., **60**, 882 (1938).
4. M. F. Shostakovskii, *Simple Vinyl Ethers*, Publishing House of the Academy of Sciences of the USSR, 1952.

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