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Abstract

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OXIDATION REACTIONS OF OLEFINS

In the course of studying the interaction between palladous chloride and olefins, we carried out the following oxidation reactions of olefins to carbonyl compounds:

$$CH_2{=}CH_2 + H_2O_2 = CH_3CHO + H_2O \qquad (1)$$

$$CH_2{=}CH_2 + \tfrac{1}{2}O_2 = CH_3CHO \qquad (2)$$

$$CH_2{=}CH_2 + H_2O + 2O = \underset{\text{benzene ring}}{C_6H_6} = O - CH_3CHO + \text{quinone} \cdot \text{hydroquinone} \qquad (3)$$

All the reactions proceed in the presence of salts of divalent palladium, which play the role of oxidation catalysts.

Initially, the aim of our work was to study the reaction of Pd^II salts with olefins, as an example of reactions proceeding through the intermediate formation of π-complexes with labile bonds. Apparently, π-complexes of olefins and hydrocarbons of the acetylene series with transition elements are intermediate compounds in many reactions of unsaturated compounds. In particular, the addition of water to acetylene by the M. G. Kucherov reaction probably proceeds through a stage involving the formation of a π-complex of acetylene with divalent mercury ions (^1). There are grounds for believing that the formation of π-complexes also occurs in oxo-synthesis reactions, in some polymerization reactions of acetylene, and in others.

In this connection, the study of the properties of π-complexes of olefins with metals is of great theoretical interest. A representative of this class of compounds is Zeise' s salt (^2)–$K[PtCl_3C_2H_4]$. This stable compound, whose stability is due to the fact that, in addition to the donor–acceptor bond in the complex, a dative interaction probably also occurs (^{3,}4), as a result of which the effective positive charge on the carbon atoms of the olefin is lowered. Anderson (^5) showed that when an aqueous solution of Zeise' s salt is boiled, this complex decomposes with liberation of metallic platinum. Acetaldehyde was found in the reaction products. It may be thought that polarization of the C atoms of the double bond and, consequently, polarization of the C—H bond under the influence of the central atom is of substantial importance for this reaction. If this is so, then the reaction of the palladium analogue of Zeise' s salt with water should proceed faster because of the smaller ionic radius of Pd and, as may be supposed, the less pronounced ability of the 4*d* electrons of palladium for dative interaction in comparison with the 5*d* electrons of platinum.

Thus, there are grounds for believing that the reduction of palladium salts in aqueous solutions under the action of olefins or carbon monoxide (^6) proceeds through the formation and decomposition of the corresponding π-complexes. This

the reaction found application in the analysis of hydrocarbon gases as a qualitative reaction for olefins and CO (^7), and was also proposed for the separation of palladium from its aqueous solutions containing other noble metals (^8). Nevertheless, the chemistry of the reaction of olefins with palladium salts remained undisclosed. Phillips (^6) found that, upon reduction of palladium salts in aqueous solution by ethylene, acetaldehyde is formed. According to other authors, in the reaction of ethylene with $PdCl_2$, dichloroethane is formed (^7). With regard to the nature of the reaction products in the case of ethylene homologs, by the time this work was begun (end of 1957) there were no data in the literature.

The study of the reaction under conditions in which metallic palladium is formed is associated with difficulties caused by the scarcity of palladium salts and the high catalytic activity of the finely dispersed metallic powder, on the surface of which secondary processes may occur. It seemed expedient to carry out this reaction in the presence of an oxidizing agent which, without interacting with the olefin and the product of its transformation, would be capable of oxidizing palladium sufficiently rapidly, preventing its precipitation from solution. As an oxidizing agent of this kind, judging from the standard oxidation potentials (^9), hydrogen peroxide in acidified solutions, quinone, oxygen, and some other compounds may serve.

Our experiments showed that dilute hydrochloric acid solutions of palladium chloride containing 3-5% hydrogen peroxide at 40-45° slowly absorb ethylene and propylene with the formation, respectively, of acetaldehyde and acetone. Metallic palladium does not precipitate in this case. Thus, under these conditions the reaction of reduction of a palladium salt by an olefin is accompanied by oxidation of the palladium formed thereby with hydrogen peroxide:

The overall reaction is the oxidation of an olefin by hydrogen peroxide to a carbonyl compound. However, along with the main reaction, decomposition of hydrogen peroxide into oxygen and water occurs in the solutions. The rate of this reaction increases with increasing temperature much more rapidly than the rate of the main process. These circumstances, as well as the ability of hydrogen peroxide to oxidize carbonyl compounds, make it difficult to study the reaction of palladium salts with olefins under these conditions.

p-Benzoquinone is a reagent that makes it possible to carry out the oxidation of olefins sufficiently rapidly under very mild conditions. The hydroquinone formed in the reaction does not reduce palladium salts in acidic solutions. The disadvantages inherent in this oxidizing agent include the difficulties associated with isolating the oxidation products from the reaction mixture because of the volatility of quinone and hydroquinone.

Oxygen, in the absence of other substances, oxidizes metallic palladium very slowly. We therefore attempted to find an oxidizing agent that would be capable of oxidizing metallic palladium, while its reduced form would be oxidized by oxygen.

We succeeded in showing that salts of cupric oxide in halide solutions can be used as such an oxidizing agent. In solutions of nitrate or sulfate salts, oxidation of metallic palladium by cupric salts is thermodynamically impossible. In halide solutions, formation of acid complexes of the type PdX_4^{2-} takes place. As a result, the standard oxidation potential $E^0_{\mathrm{Pd^{II}/Pd^0}}$ is lowered. On the other hand, in the presence of halide ions, reduction of divalent copper ions proceeds to cuprous salts Cu_2X_2; in this case, as a result of stabilization of the reduced form, the oxidation potential $E^0_{\mathrm{Cu^{II}/Cu^{I}}}$ increases.

From a comparison of the standard oxidation–reduction potentials (^9), it can be seen that the change in the standard free energy for

the reaction of oxidation of metallic palladium by Cu^{2+} ions in chloride solutions is 3700 cal/mole, and in bromide solutions 1850 cal/mole, which corresponds to values of the equilibrium constant at 25° of, respectively, $2.2 \cdot 10^{-3}$ and $2.2 \cdot 10$.

Thus, thermodynamic factors favor the oxidation reaction of palladium to a greater extent in bromide solutions than in chloride solutions. Owing to the positive value of ΔS of the reaction, the value of the equilibrium constant increases with increasing temperature both for bromides and for chlorides. In our experiments cupric bromide was used as the oxidation catalyst.

In experiments on the oxidation of olefins with oxygen, the gas mixture was passed through a solution of palladium salts and cupric oxide at 90°. The gas was dispersed by means of a glass filter. After the reactor, the gas passed through a system of scrubbers in which the reaction products were trapped by water. In this way we obtained acetone from propylene (identified by the melting points of the semicarbazone, thiosemicarbazone, and 2,4-dinitrophenylhydrazone) and, in small amounts (up to 5% of the total carbonyls), propionaldehyde (determined polarographically). By the same method, acetaldehyde was obtained from ethylene, and methyl ethyl ketone from butenes-2. Our data in this part are in complete agreement with the data of Smith et al. (10), whose work appeared in print by the time this part of the study was completed. Smith et al., by a somewhat different route, likewise achieved the oxidation of olefins with oxygen in the presence of palladium and copper salts.

Thus, when a mixture of an olefin and oxygen is passed through a solution containing palladium salts and cupric oxide, the following reactions take place:

$$PdX_4^{2-} + C_2H_4 + H_2O = Pd + CH_3CHO + 2H^+ + 4X^- \qquad (4)$$

$$Pd + 2Cu^{2+} + 6X^- = PdX_4^{2-} + Cu_2X_2 \qquad (5)$$

$$\frac{Cu_2X_2 + {}^1/{}_2O_2 + 2H^+ + 2X^- + 2CuX_2 + H_2O}{C_2H_4 + {}^1/{}_2O_2 = CH_3CHO} \qquad (6)$$

For the conditions of stationarity to be satisfied, the rates of reactions (4), (5), and (6) must be equal to one another. The interaction of the olefin with Pd^II (4) proceeds through the stage of formation of a π-complex and, probably for this reason, depends strongly on the concentration of ions capable of forming stable acidocomplexes of the type PdX_4^{2-}. This circumstance makes it possible, by using an excess of halide ions (characteristic for each olefin) and by varying the concentration of Cu^II and the partial pressure of oxygen, to maintain a stationary regime in the reactor.

It should be noted that the reaction of oxidation of lower olefins with oxygen to carbonyl compounds may apparently also be of practical interest. Under the conditions of our experiments, with one of the catalyst samples containing 0.02 mole/liter $PdCl_2$, 0.16 mole/liter $CuBr_2$, and 0.04 mole/liter $CuCl_2$, at a temperature of 90° and a space velocity of 100 liters per 1 liter of catalyst per hour, the conversion of ethylene was 25%, and the yield of acetaldehyde based on reacted ethylene was more than 95%. When a mixture containing 75% propylene and 25% oxygen was passed through a solution containing 0.02 mole/liter $PdCl_2$, 0.15 mole/liter $CuBr_2$, and 0.15 mole/liter $CuSO_4$ at 90° and a space velocity of 100–150 liters per 1 liter of catalyst per hour, the conversion of propylene was 15–17%, and the yield of carbonyl compounds based on reacted propylene was 95–96%. When a stoichiometric mixture of oxygen with butenes-2 (cis and trans) was passed through this same solution at a rate of 65 liters per 1 liter of catalyst per hour, the conversion of the olefins was 15%.

Replacement of hydrogen atoms at the double bond by methyl groups leads to a decrease in the reaction rate in the series: $CH_2 = CH_2 > CH_3CH = CH_2 >$ cis- and trans-$CH_3CH = CHCH_3 \gg (CH_3)_2C = CHCH_3$. In this same sequence—

the stability of complexes of divalent platinum with olefins decreases (11). This circumstance permits the assumption that the retardation of the reaction is at least partly connected with a decrease in the complex-formation constant, which enters as a factor into the observed rate constant.

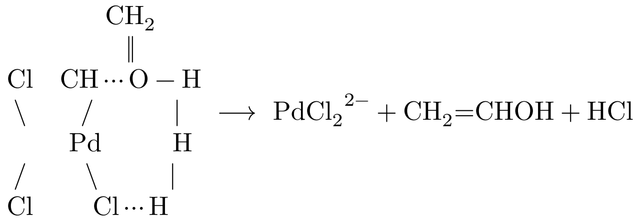
Thus, in all the cases of oxidation studied, the overall reaction consists of the stages of formation and decomposition of a π-complex, as well as the oxidation reaction of palladium atoms formed during decomposition of the π-complex.

The experimental data presently available are insufficient for judging the mechanism of this reaction. However, it seems advisable to us to state some assumptions concerning the mechanism of this transformation.

It may be assumed that the first act in the decomposition of the π-complex is the cleavage of a proton from the strongly polarized carbon atom of the olefin

$$\left[\begin{array}{lr} & \cdots\ \mathrm{C} \\ \mathrm{Cl_3Pd} & \vdots \\ & \cdots\ \mathrm{C} \end{array}\right]^{-} + \mathrm{H_2O} \rightarrow [\mathrm{Cl_3Pd - C \equiv CH_2}]^{2-} + \mathrm{H_3O^+} \qquad (7)$$

with transformation of the π-complex into an organometallic compound, which, on reaction with water, possibly through a five-membered complex, is converted according to the scheme:



(8)

$$\mathrm{PdCl_2}^{2-} \rightarrow \mathrm{Pd} + 2\mathrm{Cl}^-$$

$$\mathrm{CH_2{=}CHOH} \rightarrow \mathrm{CH_3CHO}.$$

In conclusion, we note that in the case of certain olefins, interaction with palladium salts leads to the formation of complex compounds, the synthesis and properties of which have been described earlier (12).

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