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STUDY OF THE MECHANISM OF REDUCTIVE DECOMPOSITION of π-ALLYL COMPLEXES OF PALLADIUM IN AQUEOUS SOLUTIONS BY THE TRACER ATOM METHOD

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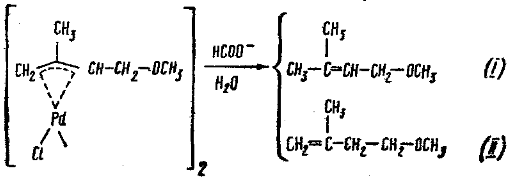
UDC 541.49:547.359.8:547.315.25

The reductive decomposition reaction seems to be one of the major reactions of π-allyl complexes of transition metals. The reductive decomposition of π-allyl complexes of palladium leads to the formation of olefins [1-5], unsaturated and saturated ethers [6, 7], esters, and aldehydes [8]. During a study of the mechanism of reductive decomposition of π-allyl complexes of palladium in alcoholic (methanol) solutions [9], we have established that the formation of the reaction products proceeds as the result of transfer of hydride ion from the reducing agent (methylate ion) to the allyl ligand of the complex. In [9], an intrasphere π-allyl hydride mechanism of the process was suggested which includes the introduction of methylate ion into the inner sphere of the complex, its intrasphere oxidation with the intermediate formation of a π-allyl hydride complex of palladium, and attack of the hydride ion on the allyl ligand with the formation of the reaction products.

Many reductive decomposition reactions of π-allyl complexes of palladium proceed in aqueous and aqueous alcoholic solutions [1-3, 5]. For the study of the mechanism of reductive decomposition in these media, in this work the decomposition of 1-(methoxymethyl)-2-methyl-π-allylpalladium chloride, $[(\pi\text{-}C_5H_8 \cdot OCH_3)PdCl]_2$, is studied in aqueous solutions under the action of a "mild" reducing agent, potassium formate.

The reaction was carried out at 40°C. Chloride ion (KCl) was introduced into the solution in order to raise the solubility of the complex. Reductive decomposition of the complex in aqueous solutions leads to the formation of metallic palladium and the unsaturated ethers 4-methoxy-2-methyl-1-butene (I) and 4-methoxy-2-methyl-2-butene (II):

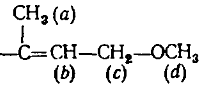


Study of the stoichiometry showed that the reaction is described by the equation

$$\frac{1}{2}[(\pi\text{-}C_5H_8\cdot OCH_3)\,PdCl]_2 + HCOO^- \xrightarrow[H_2O]{} (I—II) + Pd + Cl^- + CO_2,$$

M. V. Lomonosov Moscow Institute of Fine Chemical Technology. Yaroslav Polytechnic Institute. Translated from Teoreticheskaya i Éksperimental'naya Khimiya, Vol. 15, No. 3, pp. 319-323, May-June, 1979. Original article submitted July 3, 1978.

TABLE 1. Spectral Characteristics of the Product of Reductive Decomposition of the π-Allyl Complex of Palladium in Aqueous Deuterated Media

Reaction product	Reducing agent	Solvent	Intensities of proton signals				Total intensity
			H_a	H_b	H_c	H_d	
 $H_3C{-}\overset{CH_3(a)}{C}{=}CH{-}CH_2{-}OCH_3$ (a) (b) (c) (d)	$HCOO^-$	H_2O	6,0	1,0	2,0	3,0	12,0
	$HCOO^-$	D_2O	6,0	1,0	2,0	3,0*	12,0
	$DCOO^-$	H_2O	5,3	0,8	1,9	3,0*	11,0

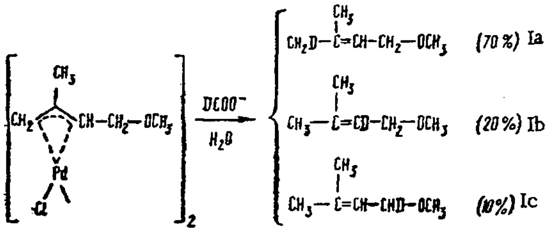
*During calculation of relative intensity, the intensity of the signal of protons of the CH_3O group was chosen as a standard.

whence it follows that the reaction products (I, II) are formed as the result of "finishing" of the allyl ligand of the complex by a hydrogen atom.

The source of the hydrogen atoms which "finish" the allyl ligand into unsaturated ethers in the reaction studied may be either the solvent (water) or the reducing agent (formate ion). In connection with this, two series of tests were carried out on the reductive decomposition of the π-allyl complex: 1) under the action of undeuterated potassium formate HCOOK in deuterium oxide (D_2O); b) under the action of deuterated potassium formate DCOOK in water.

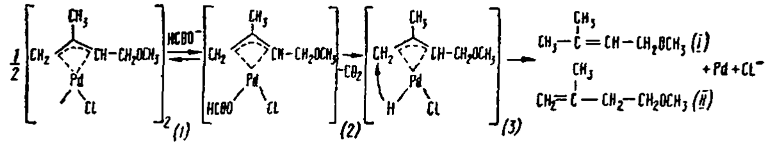
The solution of deuterated potassium formate in water was prepared by neutralization of formic acid labeled with deuterium on the formyl group (DCOOH) by a KOH solution. One of the products of reductive decomposition (4-methoxy-2-methyl-2-butene) was isolated by the method of preparative chromatography and analyzed by the PMR method. From the data given in Table 1 it follows that the reductive decomposition of the complex under the action of $HCOO^-$ ion in deuterium oxide leads to the formation of an ether which does not contain the deuterium "tracer."

Upon carrying out the reaction under the action of the deuterated formate ion $DCOO^-$ in water, a deuterated ether is formed which contains one atom of deuterium per molecule. It should be noted that in this case a change occurs in the integrated intensities of the proton signals in the PMR spectra, not for one, but simultaneously for several carbon atoms of the allyl ligand. This is evidence that the deuterium occurs, not on any one carbon atom, but is "delocalized" over the molecule; i.e., isomers with different positions of the deuterium in the molecule are formed as the result of the reaction (isotopic isomers a, b, and c, see Scheme 1).



Scheme 1

The results obtained provide evidence that the mechanism of reductive decomposition of the π-allyl complex of palladium in aqueous solutions is associated with the transfer of hydrogen from the reducing agent (formate ion) to the allyl ligand of the complex. A satisfactory explanation of the processes which occur is found in the scheme of the mechanism (Scheme 2),

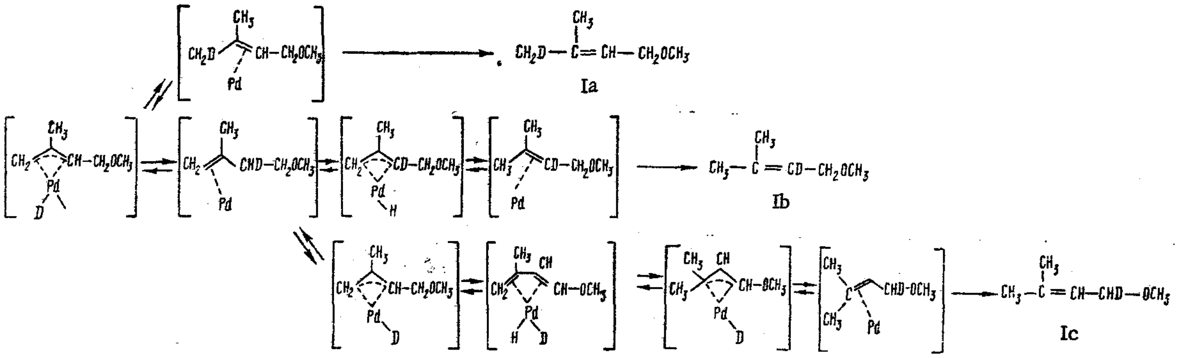


Scheme 2. Mechanism of the reductive decomposition of π-allyl complexes of palladium.

the basic stages of which seem to be: a) the introduction of the reducing agent into the inner coordination sphere; b) its intrasphere oxidation with the intermediate formation of a hydride complex of palladium; c) attack of the hydride ion on the allyl ligand with the formation of reaction products I and II. This mechanism is consistent with the mechanism of reductive decomposition of π-allyl complexes of palladium in alcohol solutions [9].

Study of the reaction by the tracer atom method has also allowed expression of a suggestion as to the mechanism of attack of the hydride ion on the allyl ligand (Scheme 2, step 3). Let us examine this mechanism as an example of the formation of one of the products, 4-methoxy-2-methyl-2-butene (I). As could have been assumed, formation of this product should occur as the result of attack of the hydride ion in position 1 of the allyl ligand (Scheme 1). However, analysis of the PMR spectra showed that in this case several isotopic isomers are formed with different positions of the deuterium in the molecule (Ia-Ic). Formation of the isotopic isomer Ia (Scheme 1) serves as a demonstration of "direct" attack of deuterium (hydride ion) in position 1 of the allyl ligand. Formation of the isomers Ib (Ic) themselves provides evidence of the attack of deuterium in position 3 (4) of the allyl ligand and subsequent migration of the hydrogen atom from position 3 (4) to position 1 ("ricochet" mechanism).

For explanation of the "ricochet" mechanism, we suggested that the reaction products are not formed directly from the π-allyl hydride complex, but by the step of intermediate formation of a π-olefin (π-diolefin) complex of Pd(0). The formation of such complexes has been postulated in the reactions of isomerization and hydridation of olefins and dienes [10-12]. The fact of migration of hydrogen along the carbon chain of the allyl ligand and the formation of products with different locations of deuterium in the molecule find an explanation on the basis of mutual transformations of the π-allyl hydride and π-olefin complexes of palladium (Scheme 3).



Scheme 3. Mechanism of attack of hydride ion on the allyl ligand in the reductive decomposition reaction.

EXPERIMENTAL

The π-allyl complex of palladium $[(\pi\text{-}C_5H_8 \cdot OCH_3)PdCl]_2$ was synthesized from isoprene and palladium chloride in methanol by the method of [13]. Found, %: C 29.88; H 4.60. Calculated for $C_{12}H_{22}Cl_2O_2Pd_2$, %: C 29.93; H 4.53. The structure of the complex was confirmed by the results of PMR spectroscopy.

Reduction of the complex by potassium formate in water was carried out at 40-50°C. Additionally, chloride ion (KCl, 3.0 moles/liter) was introduced in order to increase the solubility of the complex. Concentrations of the reagents were: complex 0.015-0.03 mole/liter, potassium formate 1.0-2.0 moles/liter. After completion of the reaction (~1 h), the reaction mixture was separated from metallic palladium by filtration, and the reaction product was extracted with diethyl ether. The ether solution was dried over sodium sulfate, and the extractant was then distilled off.

Gas-liquid chromatographic analysis and preparative separation of the reaction products were carried out on a "Tsvet-4" chromatograph under the following conditions: katharometer; 25% di(2-ethylhexyl) ester of sebacic acid on Chromosorb W (particle size 60-80 mesh); length of column 3 m; helium carrier gas. In experiments on separation, the components upon exit from the chromatograph were condensed in special traps cooled by liquid nitrogen.

The deuterium content in the reaction product was determined from the ratio of integrated intensities of the proton signals on a Bruker WP-60 spectrometer. The spectra were taken in CCl_4 (0.01-0.05 mole/liter) by use of hexamethyldisiloxane as an internal standard, 100-150 scannings being done for each measurement. The accuracy of determination of amount of deuterium amounted to ±10%.

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DIMER – MONOMER EQUILIBRIUM IN BENZENE SOLUTIONS OF TRICHLOROPHOSPHAZO-o-CHLOROPHENYL

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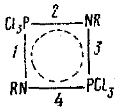
and V. G. Yurchenko

UDC 536.11

In contrast to trichlorophosphazosulfonylaryls and trichlorophosphazocarbacyls, many trichlorophosphazoaryls and trichlorophosphazoalkyls $Cl_3P=NR$ (R = Alk, Ar) are dimerized [1]. The following cyclic structure, involving partially delocalized $p_\pi-d_\pi$ bonds, was proposed for dimeric phosphazo compounds [1, 2]:



(1)

Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev. Translated from Teoreticheskaya i Éksperimental'naya Khimiya, Vol. 15, No. 3, pp. 324-329, May-June, 1979. Original article submitted January 12, 1979.