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Mechanism of Formation of Palladium(II)–Allyl Complexes

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A kinetic study of the reaction of Na_2PdCl_4 with allyl alcohol in acidic aqueous solution giving $[\pi\text{—}C_3H_5PdCl_2]^{(-)}$ is reported. A mechanism consistent with the rate law is proposed in which the rate-determining step is the conversion of a π-olefin–palladium(II) complex into a σ-bonded hydroxo-alkyl complex, amounting to oxypalladation of allyl alcohol.

The chemistry of the allyl–palladium(II) complexes has received growing interest in the past decades in view of the structure and bonding problems involved and the catalytic applications which have often resulted in large-scale industrial processes.

A method of preparing $[\pi\text{-}C_3H_5PdCl]_2$ (C_3H_5 = allyl group) involves the reaction of allyl alcohol with $Na_2[PdCl_4]$ in 50% acetic acid, whereby palladium metal, propene, and an organic compound later identified as a mixture of hydrofurfuryl alcohol derivatives are also obtained as by-products beside the allyl–palladium complex (*1*):

$$CH_2{=}CH\text{—}CH_2OH + Na_2PdCl_4 \xrightarrow[50^\circ\,C]{50\%\ \text{acetic acid}} [\pi\text{—}C_3H_5PdCl]_2 + Pd^0 + C_3H_6 + \text{other products.} \quad (1)$$

We have carried out a kinetic investigation of the reaction of Na_2PdCl_4 with allyl alcohol in acidic aqueous solution to determine its mechanism. The major palladium product of the reaction investigated is $[\pi\text{-}C_3H_5PdCl_2]^-$. This reaction is probably as complicated as reaction (1). Although we cannot determine its stoichiometry, owing to the side reactions involving non-organometallic products, we felt that a kinetic treatment focused on the fate of the palladium complex could throw light on the mechanism of formation of $[\pi\text{-}C_3H_5PdCl]_2$. The spectrophotometric method employed was the most suited to this end, although it did not allow us to monitor the course of the overall reaction. The kinetic runs were carried out at 25°C in water at a constant ionic strength of 2 *M* with $NaClO_4$.

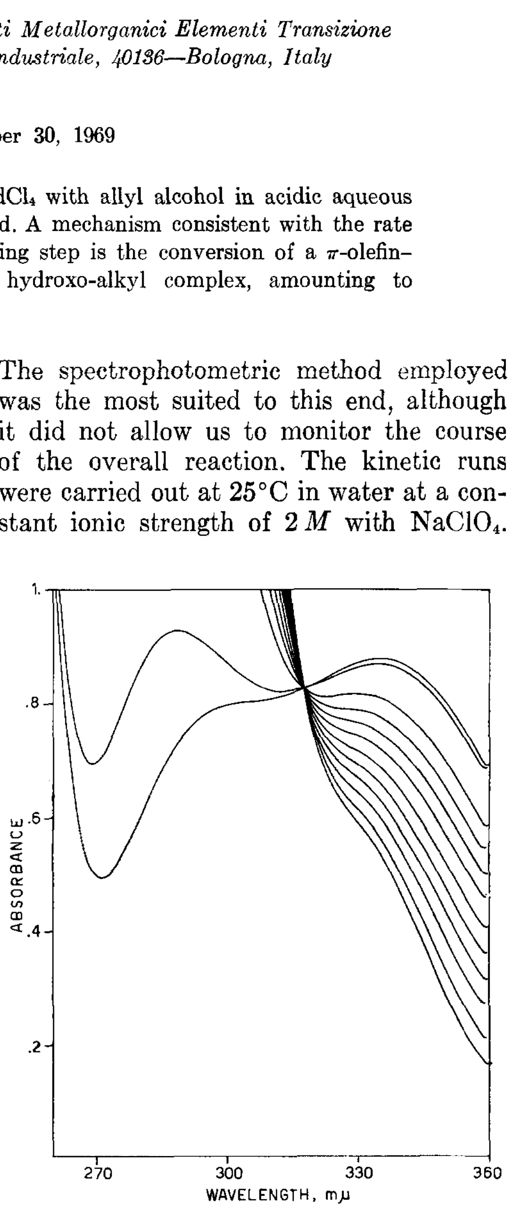


FIG. 1. Spectral changes in the reaction of Na_2PdCl_4 with allyl alcohol in methanol. $[PdCl_4^{2-}] = 10^{-3}\,M$; [allyl alcohol] $= 1.57 \times 10^{-2}\,M$; [HCl] $= 0.0984\,M$; [NaCl] $= 0.55\,M$; $[NaClO_4] = 1.35\,M$.

The kinetics were followed spectrophotometrically in the near UV region by recording spectral changes with time. An isosbestic point was developed at **318** mμ indicating that only the starting Na_2PdCl_4 and the product $[\pi\text{-}C_3H_5PdCl_2]^-$ (see below) were present at appreciable concentrations as light-absorbing species in the wavelength range scanned (Fig. 1). The measurements were taken over a period of ca. 6 half-lives. Spectral assignments to starting and final palladium complexes were made on the basis of the spectra of authentic samples which were either available as such ($PdCl_4^{2-}$) or independently prepared (*1*) ($\pi\text{-}C_3H_5PdCl_2^-$). The concentration conditions were of different types:

1. constant concentrations of H^+ and Cl^-, with varying conc of allyl alcohol;
2. constant concentrations of Cl^- with varying conc of H^+ and allyl alcohol;
3. constant concentrations of H^+ with varying conc of Cl^- and allyl alcohol.

The Na_2PdCl_4 conc was always kept constant (10^{-3} *M*) and at least one tenth of the lowest concentration used for the other reactants. Under these pseudo-first-order conditions the rate of formation of the palladium product, as determined from the appearance of its spectrum, was of the form: $(d[\pi\text{-}C_3H_5PdCl_2^-])/dt = k_{obs}[PdCl_4^{2-}]$. The rate constants, k_{obs} (sec^{-1}), were determined as the slopes of plots of $\log(A_\infty - A_t)$ vs time (Table 1).

The experimental results are summarized as follows:

1. At constant $[H^+]$ and $[Cl^-]$ within each set of runs, the k_{obs} depends linearly on the conc of allyl alcohol (Fig. 2).
2. The slopes of plots of k_{obs} vs [allyl

TABLE 1

PSEUDO-FIRST-ORDER RATE CONSTANTS, k_{obs} (sec^{-1}), IN WATER AT 25°C

Na_2PdCl_4 conc = 10^{-3} *M*; ionic strength = 2*M*.

$CH_2{=}CHCH_2OH$, conc (10^{-2} *M*)	Conc (*M*) HCl	NaCl	$NaClO_4$	$10^5 k_{obs}$ (sec^{-1})
1.13	0.098	1.9	—	2.77
2.36	0.098	1.9	—	5.18
4.52	0.098	1.9	—	10
11.8	0.098	1.9	—	27
1.36	0.292	1.7	—	1.13
5.25	0.292	1.7	—	4.5
8.0	0.292	1.7	—	6.7
10.5	0.292	1.7	—	8.85
1.6	0.483	1.5	—	0.66
4.0	0.483	1.5	—	2.1
8.02	0.483	1.5	—	3.45
10.6	0.483	1.5	—	4.7
1.4	0.099	0.9	1	8.3
5.25	0.099	0.9	1	31.8
7.34	0.099	0.9	1	41.3
10.5	0.099	0.9	1	60.0
1.575	0.0984	0.55	1.35	19.5
5.11	0.0984	0.55	1.35	67.0
10.4	0.0984	0.55	1.35	127.0
1.55	0.0984	0.4	1.5	31.0
5.17	0.0984	0.4	1.5	98.0
10.35	0.0984	0.4	1.5	190.0

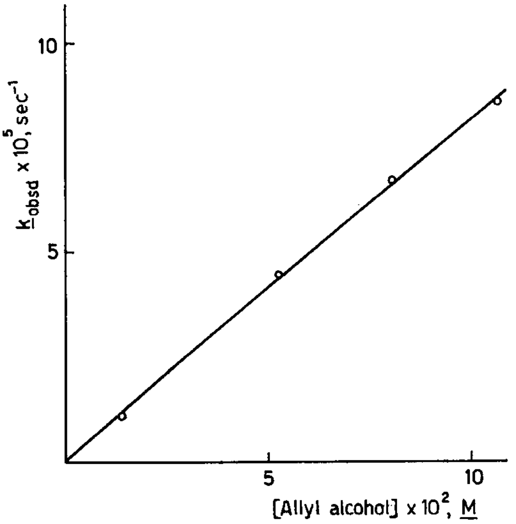


FIG. 2. Plot of k_{obs} (sec^{-1}) vs allyl alcohol conc at constant [H^+] and [Cl^-]. [HCl] = 0.292 *M*, [NaCl] = 1.7 *M*.

alcohol] at constant [Cl^-] depend linearly on 1/[H^+] (see Fig. 3).

3. The slopes of plots of k_{obs} vs [allyl alcohol] at constant [H^+] depend linearly on 1/[Cl^-]^2 (see Fig. 4).

Based on these findings the kinetic law takes the form:

$$k_{obs} = \frac{k[C_3H_5OH]}{[H^+][Cl^-]^2}. \qquad (2)$$

Under our experimental conditions (high Cl^- conc) the reaction product is [π-$C_3H_5PdCl_2$]$^{(-)}$ formed by splitting of the chloride bridge in [π-C_3H_5PdCl]$_2$ by the excess Cl^- (*2*). The rate law (2) can be accounted for by the mechanism shown in Fig. 5.

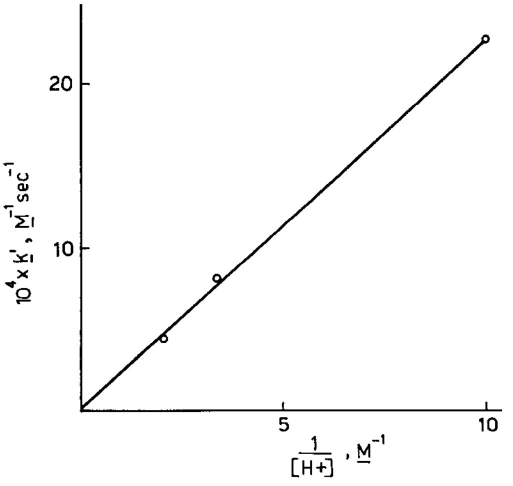


FIG. 3. Dependence of the slopes of plots of k_{obs} vs [allyl alcohol] (k') on 1/[H^+] at constant [Cl^-].

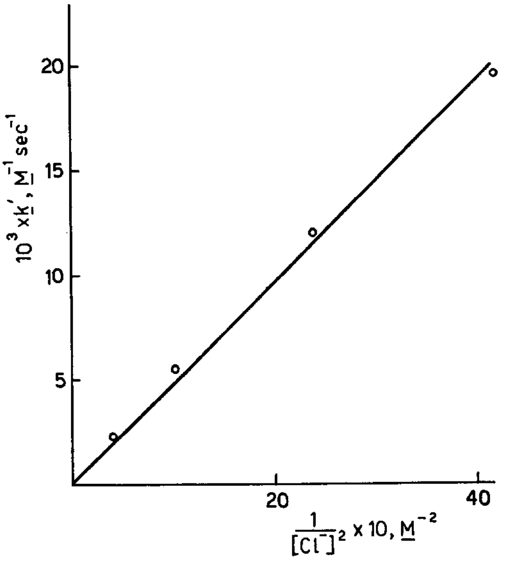


FIG. 4. Dependence of the slopes of plots of k_{obs} vs [allyl alcohol] (k') on 1/[Cl^-]^2 at constant [H^+].

This mechanism involves formation of a π complex of palladium(II) with allyl alcohol acting as an olefin (**I**) via fast pre-equilibrium steps. This aquo complex is converted to the *cis*-hydroxocomplex (**II**) in a prerate-determining acid–base equilibrium. The rate-determining step involves nucleophilic attack of coordinated hydroxyl group onto the olefinic double bond with formation of a β,γ-dihydroxoalkyl σ-bonded palladium complex (**III**). Fast reaction of **III** with a further molecule of allyl alcohol gives the final π-allyl complex (**IV**). The most peculiar feature of this mechanism, viz, the conversion **II** → **III** is a rather common type of oxypalladation reaction which is now generally accepted as the critical step of many oxydation reactions of unsaturated organic compounds by palladium(II) salts (*3*, *4*). The easy breakdown of the σ alkyl derivative (**III**) is attributed to the great tendency of palladium(II) to form π-allyl complexes. An alternative mechanism that could be conceived of would involve fast preliminary formation of a palladium complex of diallyl ether, viz, $Pd[(CH_2CHCH_2)_2O]Cl_2$, which

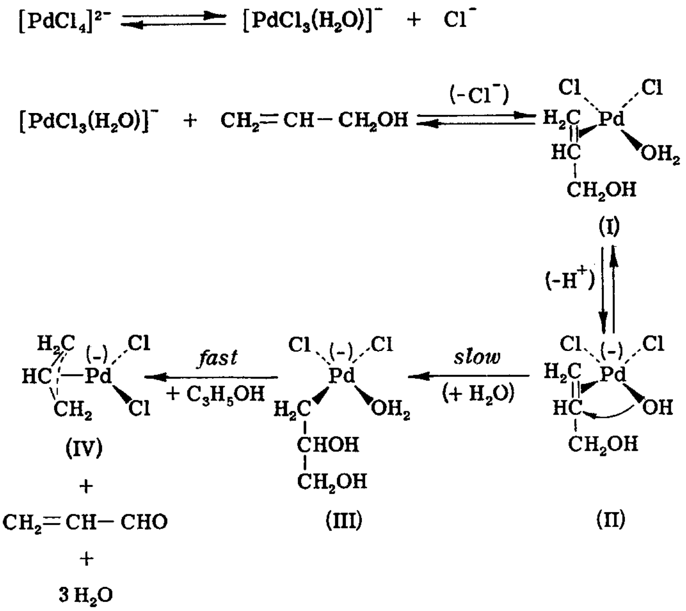
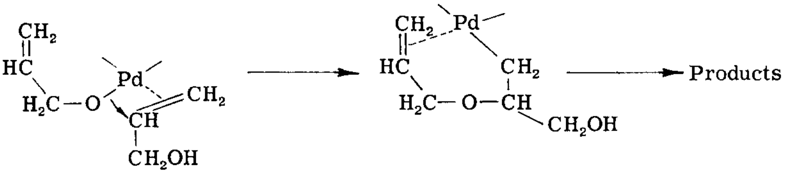


FIG. 5. Proposed reaction mechanism.

would then break down to give the π-allyl-palladium complex **IV** and acrolein. This mechanism, however, must be rejected on the basis of the following arguments: (i) the reaction rate would be second order in allyl alcohol concentration, which is at variance with our rate law (2); (ii) we have independently studied the reaction of Na_2PdCl_4 with diallyl ether and found that it produces $[\pi\text{-}C_3H_5PdCl_2]^-$ at a much slower rate than does the reaction of Na_2PdCl_4 with allyl alcohol examined in this work under the same experimental conditions. Kinetic data on the reaction with diallyl ether will be reported in a future publication.

As for the formation of furfuryl derivatives of reaction (1) in a side reaction, this may occur through interaction of two molecules of allyl alcohol via a palladium(II) organometallic complex. The reaction scheme generally accepted for reaction (1) has been suggested by Hafner *et al.* (*5*) based on nonkinetic observations and on the basic chemistry of organometallic palladium compounds [for a comprehensive review see Ref. (*4*)]. Apart from finer details, this route requires the presence of *two* molecules of allyl alcohol bonded to palladium which rearrange via two *cis* insertions to form the furfuryl moiety:



It is worth mentioning that the reaction of Na_2PdCl_4 with allyl alcohol in the absence of solvent has been reinvestigated recently on both a preparative and a mechanistic basis (*6*). A second-order dependence of rate on the allyl alcohol concentration was found. A mechanism involving palladium alkyl-hydrides was proposed to explain the formation of the various reaction products beside $[\pi\text{-}C_3H_5PdCl]_2$.

ACKNOWLEDGMENT

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