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MECHANISM OF FORMATION OF PALLADIUM(II)-ALLYL COMPLEXES. THE REACTION OF $PdCl_4^{2-}$ WITH ALLYL ETHER

R. PIETROPAOLO, F. FARAONE and S. SERGI
Istituto di Chimica Generale Università di Messina-98100 Messina (Italy)
D. PIETROPAOLO
Istituto di Chimica Generale Facoltà di Chimica Industriale, Università di Bologna, Bologna (Italy)

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SUMMARY

A kinetic study of the reaction between $PdCl_4^{2-}$ and allyl ether in aqueous methanolic solutions is described. The rate law has the form:

$$k_{\text{obs}} = \frac{K \cdot [(CH_2{=}CHCH_2)_2O]}{[H^+] \cdot [Cl^-]^2}$$

A mechanism is proposed which involves a rate-determining nucleophilic attack of the OH^- coordinated to palladium(II) on the coordinated olefinic double bond of the allyl ether.

INTRODUCTION

The chemistry of π-allyl–palladium(II) complexes has received growing interest in view of the structure and bonding problems involved and their applications in homogeneous catalysis. The particular versatility of palladium(II) to give π-allyl complexes is well demonstrated by the several different methods by which they are obtained. It is interesting to mention the reactions of $PdCl_2$ with allyl chloride[1], allyl alcohol[2] or conjugated dienes[3].

A previous paper[4] reported the mechanism of the reaction between $PdCl_4^{2-}$ and allyl alcohol to give $[\pi\text{-}C_3H_5PdCl_2]^-$ in aqueous acidic solutions. On the basis of the first-order dependence on $CH_2{=}CHCH_2OH$, it was concluded that only one molecule of the olefin is coordinated to palladium(II) in the course of the reaction. However, Urry[5] has found that when $CH_2{=}CHCH_2OH$ reacts with Na_2PdCl_4 in the absence of solvent there is a second-order dependence of the rate on allyl alcohol concentration. A mechanism involving palladium alkyl hydrides was proposed. In order to elucidate the mechanism of formation of π-allyl complexes we have studied the reaction of allyl ether with $PdCl_4^{2-}$ to give $[\pi\text{-}C_3H_5PdCl_2]^-$ in aqueous methanolic solutions. Although this reaction is rather complex, we believed that a kinetic study might throw some light on the mechanism of formation of $[\pi\text{-}C_3H_5PdCl_2]^-$.

EXPERIMENTAL

The reactions were followed spectrophotometrically in the near UV region by recording spectral changes with time (see Fig. 1). An Optica CF4R spectrophotometer was used.

The reactions were carried out at 40° in methanol/water solutions maintained at constant ionic strength of 1 *M* with $LiClO_4$. The spectra of the initial and final palladium complexes were first determined with authentic samples, which were either available, as in the case of $PdCl_4^{2-}$, or were independently prepared[1], as with $[\pi\text{-}C_3H_5PdCl_2]^-$. Fresh solutions of distilled allyl ether were used.

All the reactions were followed in the presence of a large excess of LiCl, HCl and allyl ether in order to provide pseudo first-order conditions.

The observed rate constants, k_{obs} (sec^{-1}), were calculated from the slopes of plots of $\lg(A_t - A_\infty)$ *vs.* time, where A_t and A_∞ are the optical densities, at 360 nm, of the mixture at time *t* and after 10 half lives.

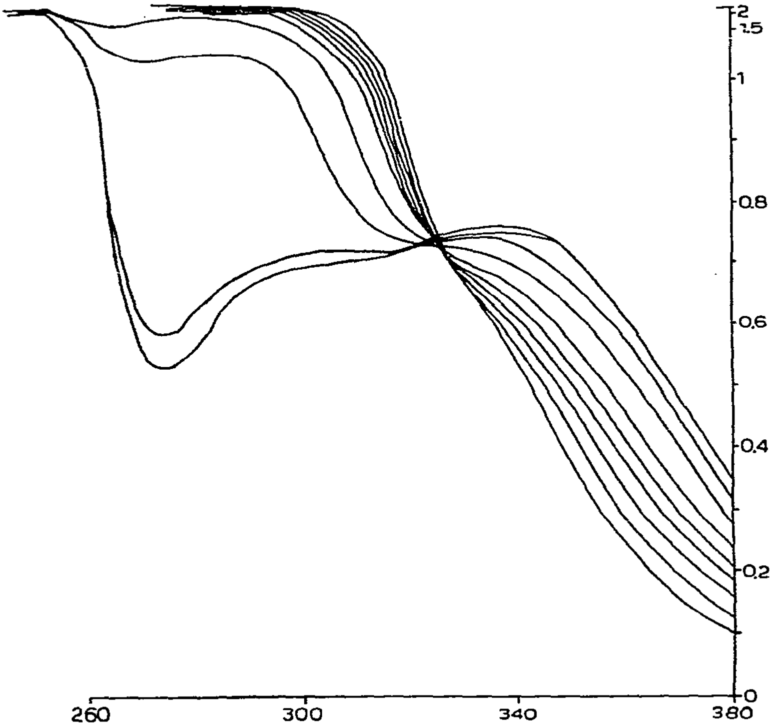


Fig. 1. Spectral changes in the reaction of Na_2PdCl_4 with allyl ether in water/methanol solutions. $[PdCl_4^{2-}] = 10^{-3}$ *M*; [allyl ether] $= 10^{-1}$ *M*; $[H^+] = 0.0985$ *M*; $[Cl^-] = 0.302$ *M*; $[ClO_4^-] = 0.7$ *M*.

RESULTS AND DISCUSSION

Table 1 lists values of the pseudo first-order constants, k_{obs} (sec^{-1}) obtained for the reaction of allyl ether with $PdCl_4^{2-}$.

Concentrations were varied in three different ways:

TABLE 1

PSEUDO FIRST-ORDER RATE CONSTANTS, k_{obs}, FOR THE REACTION OF $PdCl_4^{2-}$ WITH ALLYL ETHER IN WATER/METHANOL SOLUTIONS AT 40° $[PdCl_4^{2-}] = 10^{-3}$ *M*; IONIC STRENGTH = 1 *M*.

$10^2 \cdot [(CH_2{=}CHCH_2)_2O]$	$[H^+]$	$[Cl^-]$	$[ClO_4^-]$	H_2O (%)	$10^5 \cdot k_{obs}$ (sec^{-1})
4.6	0.0985	1		10	3.1
10.2	0.0985	1		10	8.1
19.9	0.0985	1		10	14.6
29.57	0.0985	1		10	23.1
11.57	0.207	1		10	3.9
22.14	0.207	1		10	7.2
30.16	0.207	1		10	10.8
5.55	0.305	1		10	1.5
23.62	0.305	1		10	5.4
30.0	0.305	1		10	8.0
5.29	0.098	0.508	0.5	10	16.0
9.8	0.098	0.508	0.5	10	26.0
15.8	0.098	0.508	0.5	10	43.0
19.66	0.098	0.508	0.5	10	50.0
24.95	0.098	0.508	0.5	10	60.0
3.4	0.0985	0.3	0.7	10	16.9
6.86	0.0985	0.3	0.7	10	39.0
10.2	0.0985	0.3	0.7	10	61.0
14.9	0.0985	0.3	0.7	10	82.0
19.6	0.0985	0.3	0.7	10	103.0
1.14	0.102	0.153	0.845	10	21.0
5.2	0.102	0.153	0.845	10	119.0
9.1	0.102	0.153	0.845	10	178.0
5.1	0.0984	0.498	0.5	5	5.4
10.3	0.0984	0.498	0.5	5	12.8
22.8	0.0984	0.498	0.5	5	25.0

(1). Constant concentrations of H^+ and Cl^-, with varying concentrations of allyl ether.
(2). Constant concentrations of Cl^- with varying concentrations of H^+ and allyl ether.
(3). Constant concentrations of H^+ with varying concentrations of Cl^- and allyl ether.

The Na_2PdCl_4 concentration was kept constant (10^{-3} *M*) throughout. The results can be summarized as follows:

(1). At constant $[H^+]$ and $[Cl^-]$, within each set of runs, the values of k_{obs} depend linearly on the concentration of allyl ether (Fig. 2).
(2). The slopes, k', of the plots of k_{obs} *vs.* [allyl ether] at constant $[Cl^-]$ depend linearly on $1/[H^+]$ (Fig. 3).
(3). The slopes k'', of plots of k_{obs} *vs.* [allyl ether] at constant $[H^+]$ depend linearly on $1/[Cl^-]^2$ (Fig. 4).
(4). The rate decreases when the concentration of water is lowered.

The results are consistent with the following rate law:

$$k_{obs} = \frac{K \cdot [(CH_2{=}CHCH_2)_2O]}{[H^+] \cdot [Cl^-]^2}$$

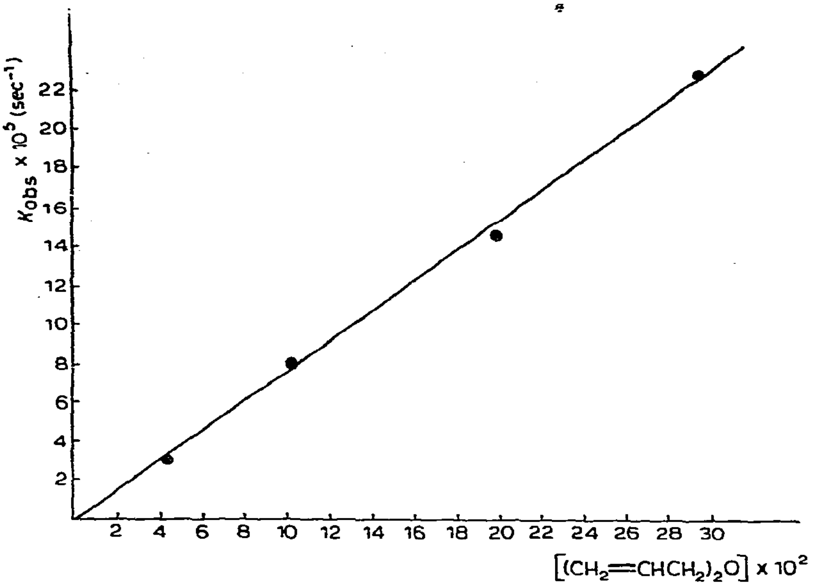


Fig. 2. Plot of k_{obs} (sec^{-1}) *vs.* allyl ether concn. at constant $[H^+]$ and $[Cl^-]$; $[H^+]=0.0985$ *M*; $[Cl^-]=1$ *M*.

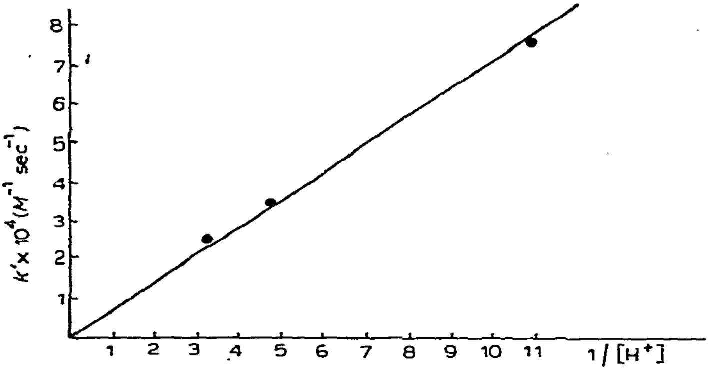


Fig. 3. Dependence of the slopes, k'; of plots of k_{obs} *vs.* [allyl ether] on $1/[H^+]$ at constant $[Cl^-]$.

In order to obtain additional evidence for the mechanism of the reaction, we studied the kinetics of the reaction between $CH_2{=}CHCH_2OH$ and $PdCl_4^{2-}$ under the conditions used for the allyl ether reaction; the reaction involving allyl alcohol gives the same product $[\pi\text{-}C_3H_5PdCl_2]^-$. The results are listed in Table 2, and show that the values of the rate constants, k_{obs} are about half those obtained with allyl ether under the same conditions.

Furthermore, the rate decreases when less water is present in the solution. These findings are consistent with the mechanism shown in Scheme 1. This mechanism is rather similar to that previously formulated for the reaction of allyl alcohol with $PdCl_4^{2-}$ in water, and involves formation of a π-complex of palladium(II) with allyl ether in a fast pre-equilibrium.

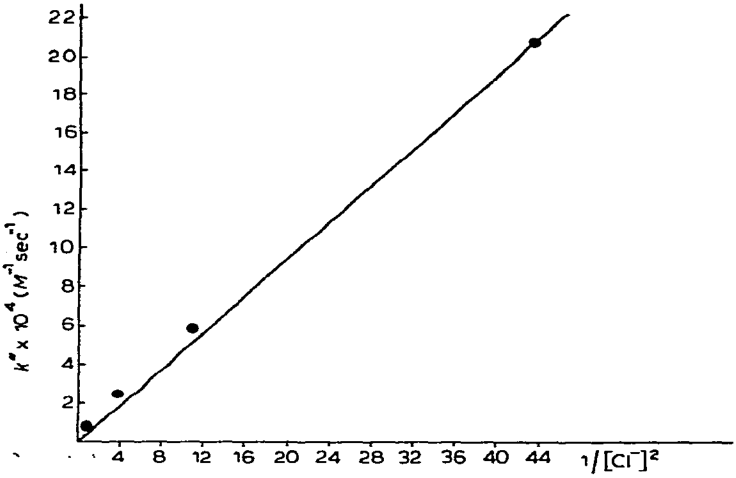


Fig. 4. Dependence of the slopes, k'', of plots of k_{obs} *vs.*[allyl ether] on $1/[Cl^-]^2$ at constant $[H^+]$.

TABLE 2

PSEUDO FIRST-ORDER RATE CONSTANTS, k_{obs}, FOR THE REACTION OF $PdCl_4^{2-}$ WITH ALLYL ALCOHOL IN WATER/METHANOL SOLUTIONS AT 40°

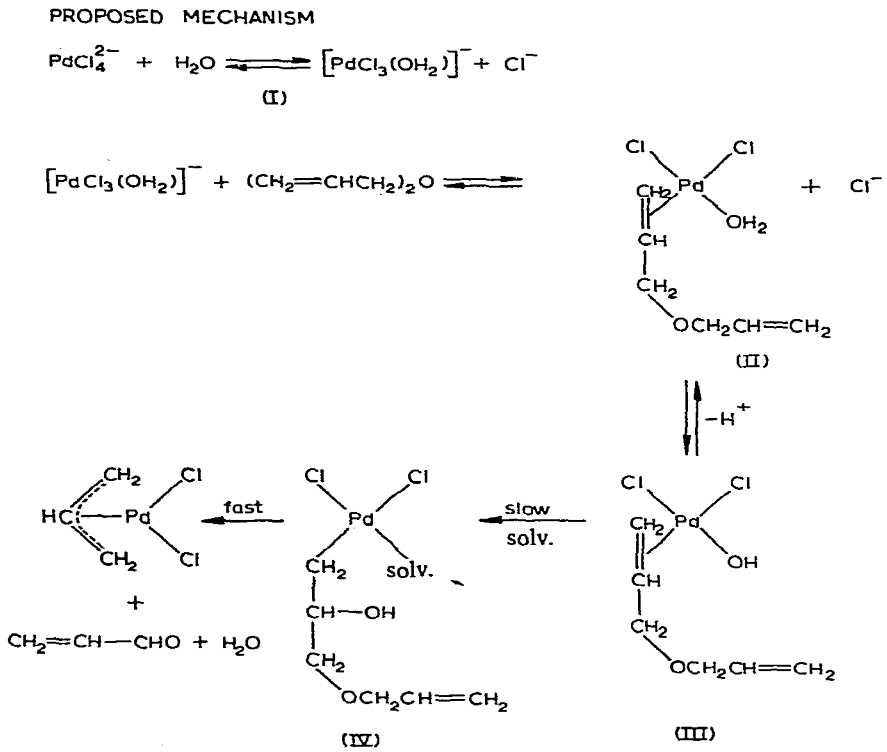
$[PdCl_4^{2-}] = 10^{-3}$ *M*; ionic strength = 1 *M*.

$10^2 \cdot [(CH_2{=}CHCH_2)_2OH]$	$[H^+]$	$[Cl^-]$	$[ClO_4^-]$	H_2O (%)	$10^5 \cdot k_{obs} (sec^{-1})$
1	0.099	0.495	0.5	10	1.4
4.1	0.099	0.495	0.5	10	7
10	0.099	0.495	0.5	10	15.8
2	0.0984	0.498	0.5	5	1
9.8	0.0984	0.498	0.5	5	4.2
25.5	0.0984	0.498	0.5	5	10.5

The aquo complex (II) is converted to a *cis*-hydroxo complex (III) in a fast acid-base pre-equilibrium. The rate-determining step of the reaction is the nucleophilic attack of the OH^- coordinated to Pd^{II}on the olefinic double bond of the allyl ether to give a hydroxo alkyl complex (IV). This then reacts rapidly to give the π-allyl palladium(II) complex. An essential feature of this reaction is the conversion (II) → (III), which is considered to be a very common step in many oxidation processes of unsaturated hydrocarbons in the presence of palladium(II)[6]. It is also noteworthy that allyl ether, which is a bidentate olefin, behaves as a monodentate species under the conditions used.

An alternative mechanism, involving the coordination of both double bonds of allyl ether to palladium(II), does not account for the linear dependence of the rate on $1/[H^+]$ nor for its marked dependence on the water concentration. This last dependence is, on the other hand, nicely accounted for in Scheme 1 since water plays an important role in the solvation equilibrium. Additionally, the fact that the values k_{obs} of the reaction of allyl alcohol with $PdCl_4^{2-}$ are only about half of those for allyl ether, under the same conditions, can be attributed to the fact that allyl ether offers

SCHEME 1



one more coordination site than does $CH_2{=}CHCH_2OH$.

Finally, we note that complexes of allyl ether with transition metal complexes, such as $Pt[(CH_2{=}CHCH_2)_2O]Cl_2$, have been reported. The special behaviour of allyl ether in its reactions with $PdCl_4^{2-}$ can be related to the remarkable tendency of palladium(II) to give π-allyl complexes.

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