Palladium η³-Allyl Complex with Sorbic Acid: Kinetics and Mechanism of Protodemetalation in Aqueous Solutions

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Abstract—The allyl complex di- μ -chloro-bis[(1,2,3- η)-1-carboxy-3-(1-hydroxyethyl)allyl]dipalladium (which is a hydroxyl-containing palladium η^3 -allyl complex based on sorbic acid) has been synthesized from *trans,trans*-2,4-hexadienic (sorbic) acid and Na₂PdCl₄ in an aqueous solution. The complex has been isolated from the reaction solution and has been characterized by IR, ¹H NMR, and ¹³C NMR spectroscopy. Its composition has been determined by elemental analysis. The protodemetalation kinetics of the complex in aqueous solutions has been studied. The rate of this reaction obeys a second-order equation, first-order with respect to each reactant. A reaction mechanism has been derived from protodemetalation kinetics and data characterizing the state of the reactants.

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INTRODUCTION

Palladium η^3 -allyl complexes can readily be obtained from dienes and are used as catalysts in the synthesis of various polyfunctional compounds [1]. The functionalized η^3 -allyl complexes (containing functional groups in the allyl ligand) are of special interest [2, 3]. The ratio of the formation and decomposition rates of intermediate η^3 -allyl complexes governs the efficiency of catalytic systems based on palladium(II) salts. Protodemetalation (acidic decomposition) is a decomposition route possible for these complexes.

The purpose of the present work is to synthesize an allyl complex from sorbic acid and Na₂PdCl₄, determine its structure, and study its protodemetalation kinetics.

EXPERIMENTAL

The hydroxyl-containing palladium η^3 -allyl complex with sorbic acid was synthesized according to an original procedure.

A weighed sample of sorbic acid crystals was added to a 0.1 M aqueous solution of $PdCl_2$ (palladium : sorbic acid = 1 : 1 mol/mol) containing sodium chloride (0.5 mol/l). The reaction was conducted for 72 h at 22– 24°C. Sorbic acid was not dissolved completely. The color of the solution changed with time from reddish brown to lemon-yellow, and the fine white crystals of sorbic acid in the precipitate turned into bulky conglomerates of yellow crystals of the allyl complex. The allyl complex was decanted from the reaction mixture, purified by repeated washing with acetone, and dried in vacuo. The complex is poorly soluble in water, *n*hexane, methanol, acetone, and chloroform. It is moderately soluble in DMF and acetone and well soluble in pyridine. The complex was characterized by elemental analysis and IR, UV, ¹H NMR, and ¹³C NMR spectroscopy.

¹H and ¹³C NMR spectra were recorded on a Bruker DPX-300 spectrometer operating at 300 MHz.

IR spectra were recorded as KBr pellets on a Specord M-80 spectrophotometer.

UV-vis spectra of aqueous solutions were obtained on a He λ ios- α spectrometer.

Protodemetalation kinetics were studied by colorimetry and ¹H NMR spectroscopy in concentration intervals of 0.08–0.13 mol/l and 0.3–1.6 mol/l for the allyl complex and HCl, respectively, at 15–30°C.

The ionic strength was maintained constant and the Cl^- and H_3O^+ concentrations were kept unchanged or were varied by using the HCl–NaCl–NaClO₄ system.

In colorimetric measurements, the reaction rate was monitored as the absorbance of reaction solutions using a KFK-2 photoelectrocolorimeter with a temperature-controlled measurement cell and a $\lambda_{max} = 490$ nm light filter. The current concentration of the allyl complex was calculated as

$$[\eta^3] = [\eta^3]_0 - \frac{\Delta D}{(\varepsilon_{\rm Pd} - \varepsilon_{\rm n^3})l},$$

where $[\eta^3]$ and $[\eta^3]_0$ are the current and initial concentrations of the allyl complex, $\Delta D = D - D_0$ is the incre-

[†] Deceased.

ment of the absorbance of the reaction solution over the absorbance at the initial moment of the reaction (D_0) , $\varepsilon_{Pd} = 123.8 \ l \ mol^{-1} \ cm^{-1}$ and $\varepsilon_{n^3} = 26.6 \ l \ mol^{-1} \ cm^{-1}$ are

the molar extinction coefficients of $PdCl_4^{2-}$ and the allyl complex, and *l* is the absorbing layer thickness. This formula was derived from optical balance equations, taking into account that the reaction solution contains two colored substances, namely, Na₂PdCl₄ and the allyl complex.

In NMR spectroscopic measurements, the reaction rate was monitored as the integrated intensities of the signals from the methyl groups of the allyl complex and sorbic acid.

RESULTS AND DISCUSSION

The reaction of conjugated dienes with palladium salts in polar media can yield η^3 -allyl complexes with various structures [1–3]. In the case of sorbic acid, one would have expected the formation of various, primarily positional, isomers because of the possibility of the formation of an allyl fragment in different places of the conjugation chain.

We found that the interaction of sorbic acid with Na_2PdCl_4 in aqueous and aqueous-acetone solutions in the presence of NaCl affords an allyl complex via the reaction



The reaction proceeds in its specific way to yield a single η^3 -allyl complex. This complex was isolated from the reaction media.

The following elemental composition was determined for the allyl complex synthesized: C, 26.5%; H, 3.3%; Pd, 39.6%; Cl, 13.2%.

For $[(\eta^3-C_6H_9O_3)PdCl]_2$ anal. calcd. (%): C, 26.6; H, 3.3; Pd, 39.3; Cl, 13.1.

The ¹H NMR spectrum of the hydroxyl-containing palladium η^3 -allyl complex with sorbic acid was recorded for a C₅D₅N solution. The following NMR data (δ , ppm; *J*, Hz) were obtained: H(2) d, 4.09, J_{23} 10.82; H(3) dd, 6.94; J_{34} 11.26; H(4) dd, 4.57, J_{45} 2.37; H(5) dq, 4.65, J_{56} 6.42; H(6) d, 1.63. It was demonstrated by the double resonance method that the sorbic acid molecule is coordinated to the metal atom through the carbon atoms in positions 2, 3, and 4 of the carbon chain. The spin–spin coupling constants $J_{23} = 10.82$ and $J_{34} = 11.26$ Hz indicate the *syn* orien-

tation of both substituents at the terminal carbon atoms of the allyl moiety.

The ¹³C NMR spectrum of the complex in C_5D_5N is characterized by the following chemical shifts (δ , ppm): C(1) 173.75, C(2) 110.82, C(3) 65.17, C(4) 90.15, C(5) 66.55, C(6) 23.35.

The IR spectrum of the allyl complex was obtained for a sample as a KBr pellet. The short-wavelength region exhibits a narrow peak characteristic of the stretching vibrations of an alcoholic OH group not involved in hydrogen bonding. The stretching vibrations of the CO group show themselves as a narrow band at 1700 cm⁻¹. The spectrum contains no bands characteristic of a system of conjugated bonds such as in the spectrum of sorbic acid.

UV–vis spectra were recorded for the allyl complex in water and in aqueous solutions containing different concentrations of NaCl. When the allyl complex is dissolved under these conditions, it is monomerized and chloride ions are inserted into the coordination sphere of palladium to form a dichloro complex. In the presence of at least 0.5 mol/l of chloride ions, the allyl complex exists mainly as the dichloro species.

The introduction of HCl into an aqueous solution of the allyl complex in the presence of NaCl results in the acidic decomposition of the complex, yielding sorbic acid and the tetrachloropalladate ion according to the stoichiometric equation



The reaction occurs under mild conditions and proceeds at a rather high rate at an acid concentration of 0.5 mol/l and 20°C .

Kinetic studies have shown that the protodemetalation of the hydroxyl-containing palladium η^3 -allyl complex with sorbic acid in aqueous solutions obeys a second-order rate equation that is first-order with respect to the η^3 -complex and first-order with respect to the hydronium ion.

The finding that the reaction is first-order with respect to the allyl complex was verified by establishing pseudo-zero-order conditions with respect to HCl (1000-fold excess of acid over the allyl complex). A linear time dependence of the logarithm of the allyl complex concentration is observed up to 80–85%. The reaction is first-order with respect to the allyl complex throughout the HCl concentration, ionic strength, and temperature ranges examined.

The first order of the reaction with respect to H_3O^+ was verified by a series of experiments carried out under pseudo-zero-order conditions with respect to HCl at a variable initial HCl concentration. The ionic strength of the solution and the concentration of chloride ions were maintained at 4.0 mol/l.

The study of the influence of the chloride ion concentration on the reaction rate has demonstrated that the variation of the chloride ion concentration between 0.7 and 4.0 mol/l at a constant ionic strength (I = 4.0 mol/l) insignificantly changes the apparent second-order rate constant k_2^{app} (from 2×10^{-4} to $2.8 \times 10^{-4} \text{ 1 mol}^{-1} \text{ s}^{-1}$). This result indicates that the chloride ion is involved only in elementary steps subsequent to the rate-determining step of the reaction. The slight increase in k_2^{app} caused by an increase in the chloride ion concentration within the indicated limits may be a consequence of structural changes in the solvation shell of the reacting species due to the replacement of Cl⁻ by ClO₄⁻ under

conditions of a high salt background. Thus, the kinetic data obtained can be described by

Thus, the kinetic data obtained can be described by the rate equation

$$r = k^{\text{app}}[\eta^3][\text{H}_3\text{O}^+],$$
 (1)

where $[H_3O^+]$ is the concentration of hydronium ions.

The temperature dependence of the apparent second-order rate constant at 15–30°C is satisfactorily described by the Arrhenius equation. The activation parameters derived from this dependence are $\Delta H^{\neq} =$ 74.8 ± 4.0 kJ/mol and $\Delta S^{\neq} = -46 \pm 8$ J mol⁻¹ K⁻¹.

All of the kinetic and spectroscopic data can be interpreted in terms of the following reactions:







A comparison between the structural characteristics of the η^3 -allyl moiety of the initial complex and those of the resulting *trans,trans*-hexadienic (sorbic) acid indicates that the organic ligand undergoes minimum structural changes in the course of the reaction.

Evidently, the inner-sphere transformation of the η^3 allyl ligand into sorbic acid reduces to the elimination of the hydroxide ion and is, therefore, the heterolytic cleavage of the C–O bond. This is accompanied by a change in the coordination mode of the bidentate organic ligand: the η^3 -allyl complex turns into an η^4 diolefin complex. The intermediate formation of similar structures is assumed to occur during the formation and acidic decomposition of other palladium allyl complexes based on conjugated dienes [1]. Next, the organic ligand is displaced from the coordination sphere of palladium with the intermediate formation of an anionic η^2 -monoolefin complex of palladium.

We believe that step (I) is the rate-determining step of the reaction. Ligand substitution reactions in the coordination sphere of palladium are known to proceed at high rates and to require no substantial activation energy. Furthermore, the absence of a noticeable influence of the chloride ion concentration on the apparent second-order rate constant indicates that the chloride ion is involved only in elementary steps that follow the rate-determining step and, therefore, does not appear in the rate equation.

Although the above reaction mechanism is consistent with all of the results obtained, it is tentative to a considerable extent. Other explanations are also possible for the observed kinetic regularities. However, the mechanism presented seems to be most plausible.

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