

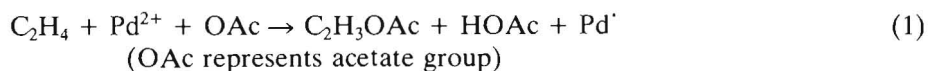
Kinetics and Mechanism of the Oxidation of Allyl Alcohol by Copper (II) Acetate in the Presence of Palladium (II) Chloride

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ABSTRACT. A kinetic study of the oxidation of allyl alcohol by copper (II) acetate in the presence of palladium (II) chloride is reported. The progress of the reaction was observed by measuring the disappearance of copper (II) acetate concentration spectrophotometrically. The reaction is first order with respect to allyl alcohol and palladium (II) chloride, inverse first order with respect to $[Cl^-]$ and zero order with respect to copper (II) acetate. The rate is found to increase linearly with acetic acid concentration.

Palladium (II) in acetic acid is known to oxidise ethylene to vinyl acetate (Stern and Spector 1961) and other olefins to a mixture of vinyl and allylic acetates, but copper (II) alone gives no reaction.



In several of the patents, copper (II) has been used as a redox system to render the reaction catalytic in palladium (II).



Palladium (II) chloride in the presence of potassium hexacyanoferrate (III) yields acetol ($CH_3-\underset{\underset{O}{||}}{C}-CH_2OH$) in the oxidation of allyl alcohol (Ahmad and Ashraf

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1979), but in a system containing palladium (II) chloride and copper (II) chloride in acetic acid, acetate esters of glycol and chloro-alcohols are formed (Henry 1966, 1972). It was further reported that the formation of chloro-alcohols arises from chloride ions of copper (Henry 1967) and not those of palladium. Hence, it is reasonable expected that the oxidation of such compounds by palladium (II) chloride in the presence of copper (II) acetate will afford only corresponding acetates. Thus, we were interested in the oxidation of allyl alcohol by this system with the idea of getting diacetin ($\text{AcOCH}_2\text{—CH—CH}_2\text{OH}$), yet, they usually yield a mix-



ture of mono and diacetin. This method provides a clean route for the formation of diacetin. Hence, it is also important to investigate the mechanism of this reaction, which is reported in this paper.

Experimental

All the chemicals used were Reagent (B.D.H.) grade. Allyl alcohol solution was standardized using the bromate-bromide procedure (Lucas and Pressman 1938). The ionic strength of the reaction mixture was maintained by the addition of sodium perchlorate solution. The reaction flask containing reactants was kept in the thermostat water bath at $60 \pm 0.1^\circ\text{C}$. After the reactants had reached thermostat temperature, the reaction was started by addition of the catalyst. The kinetics were followed by examining the concentration of copper (II) acetate spectrophotometrically. The optical density was measured by Bausch and Lomb Spectronic 20, at 785 nm, and the concentration of copper (II) acetate was read from the calibration graph. Every run was followed until the reaction was at least 70% complete. The plot of concentration of copper (II) acetate versus time were good straight lines. Pseudo-zero-order rate constants, k_{obsd} , were calculated from the slopes of these lines.

Identification of Products

For the qualitative identification of the products, a mixture containing 20 cm³ of 0.01 M allyl alcohol, 10 cm³ of 0.1 M acetic acid, 5 cm³ of 0.01 M copper (II) acetate, 55 cm³ of water and 10 cm³ of 6.56×10^{-4} M of palladium (II) chloride was heated in a thermostat bath at 60°C for about three hours. Thereafter, the reaction mixture was cooled to room temperature and repeatedly extracted with methylene chloride. The non-aqueous extract was dried over sodium sulphate, filtered and the solvent removed by distillation. The IR spectrum of the residue superimposed on the IR spectrum of a standard sample (B.D.H.) of diacetin. Moreover, their refractive indices were fairly identical $n_D^{23.8}$ 1.436 B.D.H. sample (Turner 1950) and $n_D^{23.8}$ 1.432 (product sample). Thus, the formation of diacetin was indicated.

In order to quantise the product, the following reaction mixture was used: 7 cm³ of allyl alcohol, 3 cm³ of palladium (II) chloride (2%), 1.5 cm³ of glacial acetic acid, 10 g of copper (II) acetate and water to make up the total volume of 100 cm³. This reaction mixture was heated at 60°C for about four hours and then allowed to cool to room temperature. Thereafter, it was extracted six times with 25 cm³ portions of methylene chloride. The extract was washed with water till it was acid free, dried over anhydrous sodium sulphate, filtered and the solvent removed by slow distillation. The residue was distilled under vacuum and its refractive index and IR spectrum were taken again which corresponded to the standard sample of diacetin. The presence of two ester groups in the product was verified by alkaline hydrolysis. Moreover, g.l.c. on a 20% carbowax 20 M column gave identical retention times both for the product obtained and the standard sample. Thus, the formation of diacetin was confirmed. The yield of diacetin from the experiment was 62%.

Results and Discussion

Trial and error plots of the rate data for runs with excess allyl alcohol concentration indicate that the reaction is zero order in copper (II) acetate. The copper (II) acetate concentration against time plot is a straight line and its slope yields k_{obsd} . Pseudo-zero-order rate constants for the oxidation of allyl alcohol are reported (Table 1). The plot of rate constant, k_{obsd} , and allyl alcohol concentration was a straight line and this shows first order dependence of rate on allyl alcohol concentration (Table 2). The concentration of palladium (II) chloride was varied in the range of $1.64 \times 10^{-5} M$ to $6.56 \times 10^{-5} M$ and a plot of k_{obsd} against concentration of Pd(II) yielded a straight line passing through the origin as shown in Fig. 1. This is indicative of first order dependence of rate on the catalyst concent-

Table 1. Pseudo-zero-order rate for the oxidation of allyl alcohol by copper (II) acetate in the presence of palladium (II) chloride.

[Allyl alcohol] = 0.10 M; [PdCl ₂] = 3.28 × 10 ⁻⁵ M; [CH ₃ COOH] = 10.00 × 10 ⁻³ M; Temp., 60°C	
[Cu(II)] × 10 ³ (M)	$k_{\text{obsd}} \times 10^7$ (Mole dm ⁻³ sec ⁻¹)
5.00	2.73
6.00	2.73
7.00	2.70
8.00	2.68
9.00	2.70
10.00	2.72

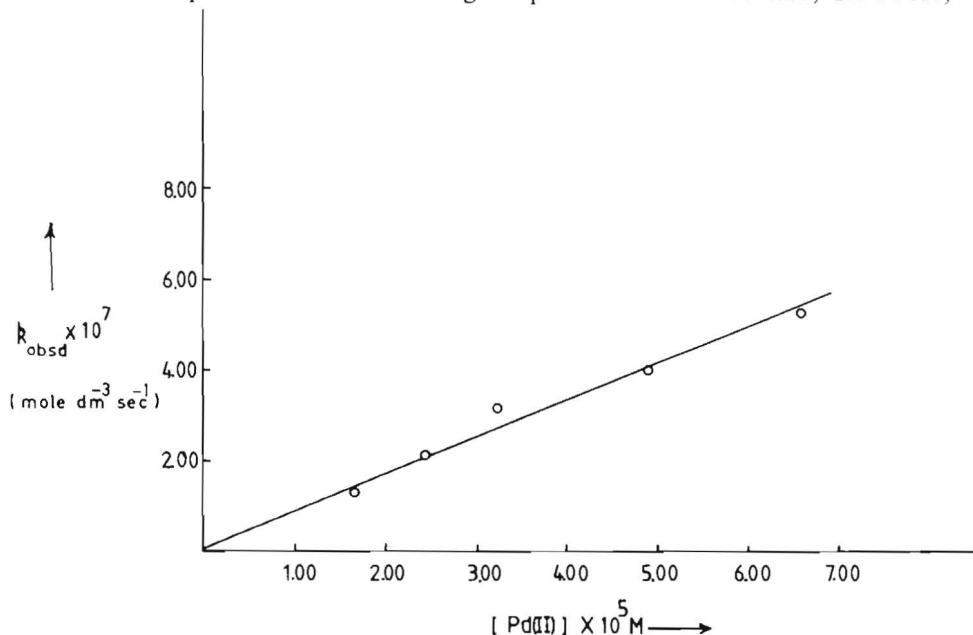
Table 2. First order dependence of palladium (II) chloride catalyzed oxidation rate on the concentration of allyl alcohol.

$[\text{PdCl}_2] = 3.28 \times 10^{-5} \text{ M}; [\text{Cu(II)}] = 5.00 \times 10^{-3} \text{ M};$ $[\text{CH}_3\text{COOH}] = 10.00 \times 10^{-3} \text{ M}; \text{Temp., } 60^\circ\text{C}$	
$[\text{Allyl alcohol}] \times 10^2 \text{ (M)}$	$k_{\text{obsd}} \times 10^7 \text{ (Mole dm}^{-3} \text{ sec}^{-1})$
7.50	2.06
10.00	2.73
12.50	3.58
15.00	4.20
17.50	4.85

ration. This also shows that there is no oxidation of allyl alcohol without palladium (II) chloride.

k_{obsd} is directly proportional to the concentration of acetic acid (Table 3). This shows first order dependence of rate on acetic acid concentration. The plot of k_{obsd} and $1/[\text{Cl}^-]$ is a straight line (Fig. 2) which suggests the inverse first order dependence of rate on chloride ion concentration.

It has been reported by previous workers (Henry 1967) that the palladium (II) chloride in the presence of acetic acid gives palladium chloroacetate, ClPdOAc ,

**Fig. 1.** First order dependence of rate on Pd(II) concentration

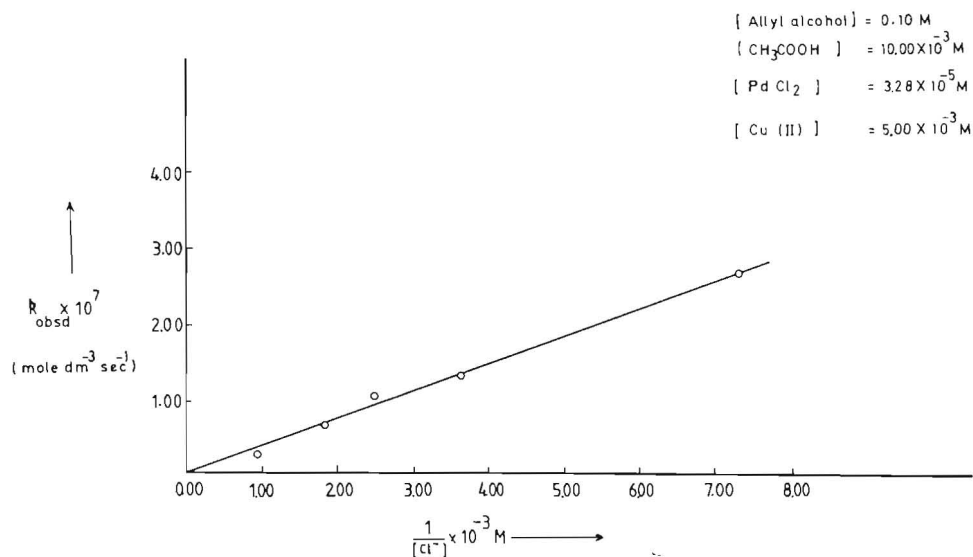


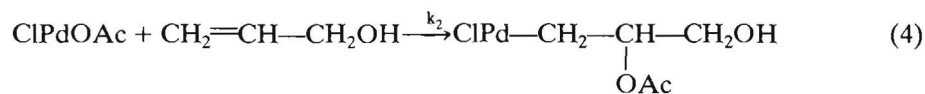
Fig. 2. Inverse first order dependence of rate on chloride ion concentration

Table 3. First order dependence of palladium (II) chloride catalyzed oxidation rate on the concentration of acetic acid.

[PdCl₂] = 3.28 × 10⁻⁵ M; [Cu(II)] = 5.00 × 10⁻³ M; [Allyl alcohol] = 0.10 M; Temp., 60°C	
[CH ₃ COOH] × 10 ³ (M)	$k_{\text{obsd}} \times 10^7 \text{ (Mole dm}^{-3} \text{ sec}^{-1})$
5.00	1.40
7.50	2.07
10.00	2.72
12.50	3.42
15.00	4.22



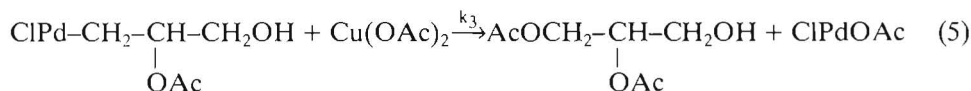
which attacks allyl alcohol to yield complex I,



(I)

A similar σ -bonded complex was proposed by Grinstead (1961) in the oxidation of ethylene by thallium (III) ions. Moreover, the formation of such an intermediate has also been reported in our recent study (Ahmad and Ashraf 1979).

This complex I in the presence of copper (II) acetate yields diacetin and reproduces ClPdOAc which may attack another molecule of allyl alcohol.



In the equations (3) to (5), the formation of complex I is considered to be rate determining step and hence,

$$\text{Rate of reaction} = k_2[\text{ClPdOAc}][\text{CH}_2=\text{CH}-\text{CH}_2\text{OH}] \quad (6)$$

From the equilibrium 1,

$$[\text{ClPdOAc}] = \frac{K_1[\text{PdCl}_2][\text{HOAc}]}{[\text{Cl}^-]} \quad (7)$$

where,

$$K_1 = \frac{k_1}{k_{-1}}$$

Substituting the value of concentration of ClPdOAc into equation (6), we get,

$$\text{Rate of reaction} = \frac{k_2 K_1 [\text{PdCl}_2][\text{HOAc}][\text{CH}_2=\text{CH}-\text{CH}_2\text{OH}]}{[\text{Cl}^-]} \quad (8)$$

This equation (8) explains the order of the reaction with respect to palladium (II) chloride, allyl alcohol, acetic acid, chloride ion and copper (II) acetate concentrations.

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حركات وآليات أكسدة كحول الأليل بواسطة أسيتات النحاس (II) في وجود كلوريد البلا ديوم (II)

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تمت دراسة آليات وحركات أكسدة كحول الأليل بواسطة أسيتات النحاس (II) في وجود حفاز من كلوريد البلا ديوم (II) وتمت متابعة التفاعل بقياس نقصان تركيز أيونات النحاس (II) ضوء كيميائياً. هذا التفاعل من التفاعلات ذات الرتبة الأولى بالنسبة لكحول الأليل وبالنسبة لكلوريد البلا ديوم، وفي الرتبة صفر بالنسبة لأسيتات النحاس ومن معكوس الرتبة الأولى بالنسبة لتركيز أيون الكلوريد؛ كما وجد أن معدل التفاعل يزيد خطياً مع زيادة تركيز حمض الخليك.