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Oxidation of allyl alcohol by alkaline periodate in the presence of micro amounts of palladium(II)

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ABSTRACT: The oxidation of allyl alcohol by alkaline species of periodate, $H_2IO_6^{3-}$, was found to be catalysed by micro amounts of Pd(II) in 0.2 mol dm^{-3} alkali solution. The active species of the catalyst was found to be $PdCl^+$. A mechanism involving the interaction of the catalyst and substrate in prior equilibria leading to the formation of a π-complex is proposed and the rate is derived. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: allyl alcohol; oxidation; alkaline periodate; palladium(II) catalyst

INTRODUCTION

Allyl alcohol finds a number of industrial applications in the preparation of resins, plasticizers, pharmaceuticals and many organic compounds. Kinetic studies on the oxidation of allyl alcohol with different oxidants such as potassium permanganate, chromic acid, vanadium(V) and chloramine-T have been reported.[1] In alkaline medium, periodate is known to exist as different species involving multiple equilibria[2] and it is necessary to know the active form of the oxidant in the reaction system. Palladium(II) is known to catalyse various reactions.[3] Most studies using palladium(II) as a catalyst have employed it in the form of palladium(II) chloride[4] and the nature of its active form in such reactions remains obscure. Hence the effect of chloride on the reaction was studied in order to establish the active species of the catalyst.

EXPERIMENTAL

Reagent-grade chemicals and doubly distilled water were used throughout. Stock solutions of periodate were prepared by dissolving a known weight of KIO_4 (BDH) and used after keeping for 24 h. The solution was standardized iodimetrically.[5] Allyl alcohol was purified by the standard procedure and its concentration in aqueous solution was checked[6] by addition of an excess of chloramine-T followed by iodometric estimation of the excess. A palladium(II) stock solution was prepared by dissolving a known weight of palladium(II) chloride (Fischer) in 0.20 mol dm^{-3} hydrochloric acid and standardized[7] against EDTA. For some kinetic runs in the absence of chloride, the chloride ion in the palladium(II) stock solution was precipitated with $AgNO_3$ and removed by repeated centrifugation. The resulting clear palladium(II) solution contained less than 1.0×10^{-6} mol dm^{-3} Cl^- and Ag^+. Such extremely low concentrations of Cl^- and Ag^+ were found to have no significant effect on the reaction. The required chloride concentration between 0.5×10^{-5} and 1.5×10^{-4} mol dm^{-3} was maintained with NaCl. Iodate solution was prepared by dissolving a known amount of potassium iodate (Rechem) in water. $NaClO_4$ and NaOH were used to maintain the required ionic strength and alkalinity, respectively.

Kinetics

Runs were followed under pseudo-first-order conditions at a constant temperature of 25.0 ± 0.1°C. The reaction was initiated by addition of an allyl alcohol solution containing the required amounts of sodium hydroxide and sodium perchlorate to the periodate solution which also contained palladium(II) at the desired concentration. The reaction was followed by measuring the decrease in periodate concentration titrimetrically using sodium thiosulphate[5]. Such titrations were carried out at regular intervals.

The reaction was generally followed over a period longer than three half-lives. The first-order rate constants were obtained from the slope of log $[IO_4^-]$ versus time

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plots. The rate constants were reproducible to within ±5%. The effect of dissolved oxygen on the rate of the reaction was checked by preparing the reaction mixture and following the reaction in a nitrogen atmosphere. There was no significant difference between the results obtained in the presence of nitrogen and in the presence of air.

RESULTS

Stoichiometry

Different sets of reaction mixtures containing different amounts of reactants at constant alkalinity and ionic strength were allowed to react for about 24 h in closed containers. When $[IO_4^-] > [AA]$, the remaining IO_4^- was assayed iodometrically,[5] whereas under the condition, $[AA] > [IO_4^-]$, when the IO_4^- had fully reacted, the unreacted allyl alcohol was estimated[6] as mentioned above. Under the condition $[IO_4^-] > [AA]$, the total oxidant was determined by iodometry and, after accounting for the remaining oxidant concentration, the concentration of IO_3^- formed was derived. Acrolein was found to be the main product, as evidenced by a spot test,[8,9] and test for acrylic acid[10] was negative. The results showed a ratio of consumption of oxidant to reductant of 1:1 [equation (1)].

$$CH_2 = CHCH_2OH + IO_4^- \xrightarrow{Pd(II)} CH_2 = CHCHO + IO_3^- + H_2O \qquad (1)$$

The concentration of the catalyst, palladium (II), remained unchanged at the end of the reaction, as found by estimating it as the palladium azide complex[11] at 315 nm ($\varepsilon = 12\,000$ dm^3 mol^{-1} cm^{-1} ± 10%).

Reaction orders

As the periodate oxidation of allyl alcohol in alkaline medium proceeded with a measurable rate in the absence of palladium (II), the catalysed reaction is understood to occur in parallel paths with contributions from both the catalysed and uncatalysed paths. Thus, the total rate constant (k_T) is equal to the sum of the rate constants of the catalysed (k_C) and uncatalysed (k_U) reactions, so $k_C = k_T - k_U$. Hence the order of reaction was found from log–log plots of k_C versus concentration. The order in both $[IO_4^-]$ and [Pd(II)] was found to be unity, whereas it was less than unity for substrate and alkali in the ranges given (Table 1).

Table 1. Effect of variations in [AA], $[IO^-{}_4]$, [Pd(II)] and $[OH^-]$ on palladium(II)-catalysed periodate oxidation of allyl alcohol in aqueous alkaline medium at 25°C and ionic strength 0.6 mol dm^{-3}

10^2[AA] (mol dm^{-3})	$10^2[10^-{}_4]$ (mol dm^{-3})	10^5[Pd(II)] (mol dm^{-3})	$10[OH^-]$ (mol dm^{-3})	$10^5 k_T$ (s^{-1})	$10^5 k_U$ (s^{-1})	$10^4 k_C$ (s^{-1}) Expt.	Calc.[a]
2.0	4.0	6.8	2.0	14.6	3.37	1.1	1.1
4.0	4.0	6.8	2.0	28.5	6.47	2.2	2.1
6.0	4.0	6.8	2.0	41.7	9.50	3.2	3.3
10.0	4.0	6.8	2.0	66.2	15.0	5.1	5.3
15.0	4.0	6.8	2.0	93.4	21.0	7.2	7.8
20.0	4.0	6.8	2.0	117.3	26.2	9.1	10.2
30.0	4.0	6.8	2.0	157.9	28.9	12.9	13.5
40.0	4.0	6.8	2.0	195.6	31.6	16.4	16.9
4.0	1.0	6.8	2.0	28.47	6.47	2.2	2.1
4.0	2.0	6.8	2.0	28.50	6.40	2.2	2.1
4.0	3.0	6.8	2.0	28.46	6.46	2.2	2.1
4.0	4.0	6.8	2.0	29.50	6.48	2.3	2.1
4.0	6.0	6.8	2.0	28.67	6.47	2.2	2.1
4.0	10.0	6.8	2.0	28.97	6.47	2.2	2.1
4.0	4.0	0.35	2.0	7.97	6.47	0.2	0.1
4.0	4.0	0.70	2.0	9.47	6.47	0.3	0.2
4.0	4.0	1.00	2.0	10.47	6.47	0.4	0.3
4.0	4.0	5.00	2.0	22.80	6.47	1.6	1.6
4.0	4.0	6.9	2.0	28.47	6.47	2.2	2.1
4.0	4.0	10.0	2.0	39.47	6.47	3.3	3.2
4.0	4.0	6.8	0.5	10.18	2.38	0.8	0.7
4.0	4.0	6.8	1.0	18.12	4.12	1.4	1.3
4.0	4.0	6.8	1.5	23.70	5.40	1.8	1.8
4.0	4.0	6.8	2.0	28.47	6.47	2.2	2.1
4.0	4.0	6.8	3.0	36.10	8.10	2.8	2.7
4.0	4.0	6.8	5.0	45.30	10.00	3.5	3.4

[a] Calculation of rate constants was on the basis of rate law (12) and $K_5 = 3.30$ dm^3 mol^{-1}, $K_6 = 1.85$ dm^3 mol^{-1} and $k = 126$ dm^3 mol^{-1} s^{-1}.

Table 2. Effect of [Cl^-] on [Pd(II)] species[a] and rate constant on palladium(II)-catalysed periodate oxidation of allyl alcohol in aqueous alkaline medium at 25 °C[b]

10^5 [Cl^-] (mol dm^{-3})	α_0	$10^2\alpha_1$	$10^2\alpha_2$	$10^4\alpha_3$	$10^7\alpha_4$	10^5k_C (s^{-1})
0.0	1.00	-	-	-	-	5.5
0.5	0.95	4.8	0.07	0.01	0.001	9.2
1.0	0.91	9.1	0.28	0.05	0.012	12.8
5.0	0.64	31.7	4.90	4.30	5.150	29.3
10.0	0.43	43.2	13.40	23.30	56.150	42.3
15.0	0.31	46.6	21.70	56.70	204.700	47.5

[a] α_0, α_1, α_2, α_3 and α_4 are the fractions of the total [Pd(II)] of the species Pd^{2+}, $PdCl^+$, $PdCl_2$, $PdCl_3^-$ and $PdCl_4^{2-}$, respectively. Error ±3%.
[b] [IO_4^-] = 4.0×10^{-3}, [AA] = 4.0×10^{-2}, [Pd(II)] = 5.2×10^{-5}, [OH^-] = 0.2, mol dm^{-3} and ionic strength I = 0.6 mol dm^{-3}.

Effect of added chloride

Although, the stock solution of palladium(II) contained chloride, for this series of runs a palladium(II) solution which did not contain chloride was used. When the chloride content of the reaction mixture containing palladium(II) was increased gradually, the rate of reaction also increased, which is ascribable to the formation of chloride complexes of palladium(II). The order in Cl^- concentration under such conditions was found to be less than unity (Table 2). Palladium(II) is known to form different chloride complexes[12] of the general formula $Pd(Cl)_n^{(2-n)+}$ with *n* having values from 1 to 4, as shown in the equilibria (2) – (5).

$$Pd^{2+} + Cl^- \overset{K_1}{\rightleftharpoons} PdCl^+ \qquad (2)$$

$$PdCl^+ + Cl^- \overset{K_2}{\rightleftharpoons} PdCl_2 \qquad (3)$$

$$PdCl_2 + Cl^- \overset{K_3}{\rightleftharpoons} PdCl_3^- \qquad (4)$$

$$PdCl_3^- + Cl^- \overset{K_4}{\rightleftharpoons} PdCl_4^{2-} \qquad (5)$$

The total palladium(II) concentration, $[Pd(II)]_T$, is the sum of the different palladium(II) species, Pd^{2+}, $PdCl^+$, $PdCl_2$, $PdCl_3^-$ and $PdCl_4^{2-}$, the complexes having cumulative equilibrium constants[12], β_5, β_6, β_7 and β_8 having values of 1.0×10^4, 3.0×10^7, 5.4×10^9 and 1.3×10^{11}, respectively, and the total palladium(II) concentration being calculated using the equation

$$[Pd(II)]_T = [Pd(II)]_f\ (1 + \beta_5\,[Cl^-] + \beta_6\,[Cl^-]^2 + \beta_7\,[Cl^-]^3 + \beta_8\,[Cl^-]^4) \qquad (6)$$

The approximate concentrations of chloride species of palladium(II) were calculated after accounting for the competing equilibria.[13] The variations of the concentrations of such species with increasing chloride concentration are given in Table 2 along with the rates of the respective catalysed reactions and it is found that there is a parallelism only between rates and $PdCl^+$ concentrations [written as Pd(II) in the mechanism for brevity].

Initial addition of the products, IO_3^- and acrolein, each in the concentration range 1.0×10^{-3} – 8.0×10^{-3} mol dm^{-3}, did not affect the rate of the reaction significantly. The variation in the ionic strength of the medium led to no substantial increase in the rate of the reaction. The effect of solvent polarity of the medium was studied by increasing the *tert*-butanol content in the reaction medium, which showed a negligible change in the rate of the reaction.

Test for free radicals

The intervention of free radicals in the reaction was examined as follows. The reaction mixture to which a known quantity of acrylamide had been added initially was kept for 24 h in an inert atmosphere. On diluting the reaction mixture with methanol a copious precipitate resulted, suggesting the possibility of free radical intervention in the reaction.

DISCUSSION

The activity of periodate as an oxidizing agent varies greatly as a function of pH and is capable of subtle control. In acidic solution, it is one of the most powerful oxidizing agents known, whereas in alkaline solution it is slighly less so. However, in an aqueous alkaline medium and in the pH range employed in the present study, periodate cannot exist as $H_4IO_6^-$ because, in aqueous solution, periodate is involved in the following equilibria, depending on the pH of the solution:

$$H_5IO_6 \rightleftharpoons H_4IO_6^- + H^+ \qquad (7)$$

$$H_4IO_6^- \rightleftharpoons H_3IO_6^{2-} + H^+ \qquad (8)$$

$$H_3IO_6^{2-} \rightleftharpoons H_2IO_6^{3-} + H^+ \qquad (9)$$

The species $H_4IO_6^-$ exists near pH 7.0. Hence, under the alkaline conditions employed in the present system, the main species would be expected to be trihydrogenparaperiodate, $H_3IO_6^{2-}$, and dihydrogenparaperiodate, $H_2IO_6^{3-}$. At higher concentrations, periodate can also undergo dimerization. The observed fractional order in alkali concentration may be understood in terms of $H_2IO_6^{3-}$ as the main species in alkaline medium with the

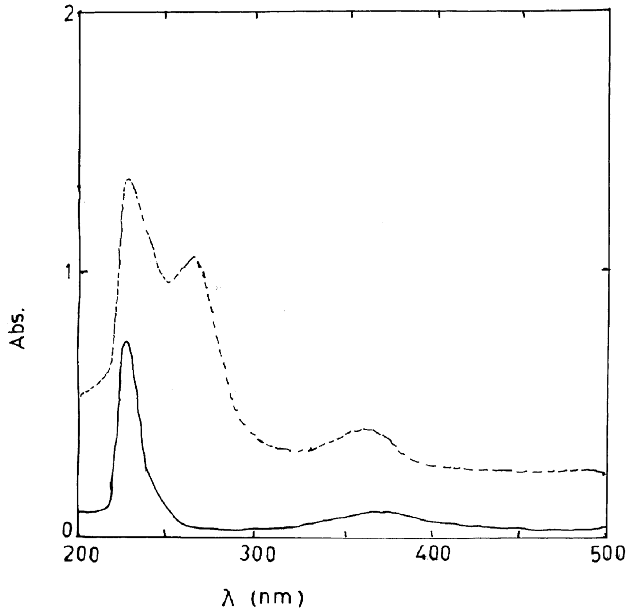


Figure 1. Spectra of (solid line) Pd(II) in alkali and (dashed line) Pd(II) + allyl alcohol in alkali

following equilibrium, which is also supported by earlier work:[14]

$$H_3IO_6^{2-} + OH^- \overset{K_5}{\rightleftharpoons} H_2IO_6^{3-} + H_2O \qquad (10)$$

The periodate oxidation of allyl alcohol in aqueous alkaline medium proceeds with a measurable rate in the absence of the catalyst, palladium (II). Hence, in the presence of catalyst the reaction is understood to occur in parallel paths with contributions from the uncatalysed and catalysed paths.

The experimental results observed are well accommodated by the rate law.

$$\text{rate}_{\text{cat}} = \text{rate}_{\text{total}} - \text{rate}_{\text{uncat}}$$

$$= \frac{kK_5K_6[AA]_T[10_4^-]_T[Pd(II)]_T[OH^-]_T}{1 + K_5[OH^-] + K_6[AA] + K_5K_6[AA][OH^-]} \qquad (11)$$

Where the right-hand side represents the catalysed path. $\text{Rate}_{\text{total}}$, rate_{cat} and $\text{rate}_{\text{uncat}}$ are the total reaction rate contributed from both the catalysed and uncatalysed reactions, catalysed reaction only and uncatalysed reaction only, respectively. In terms of rate constants,

$$\frac{\text{rate}}{[10_4^-]} = k_C = k_T - k_U$$

$$= \frac{kK_5K_6[AA]_T[10_4^-]_T[Pd(II)]_T[OH^-]_T}{1 + K_5[OH^-] + K_6[AA] + K_5K_6[AA][OH^-]} \qquad (12)$$

The results suggest complex formation between the catalyst and substrate, which in turn reacts with alkaline species of the oxidant in the rate-determining stage followed by one more fast step to yield the products. The main active species of oxidant was found to be $H_2IO_6{}^{3-}$. Evidence for complex formation was obtained from the absorption spectra of both palladium(II) and the palladium(II)–allyl alcohol complex, which indicate a first downward shift of about 10 nm due to the participation of d-electrons of palladium(II) species in bonding and another peak due to a $\pi - \pi^*$ transition of the ligand, marked by a shift of wavelength from about 227 to 264 nm (Figure 1) which clearly supports complex formation. Furthermore, a plot of $1/k_C$ versus 1/[AA] gives a straight line with a non-zero intercept supporting the formation of a palladium(II)–allyl alcohol complex. Bond cleavage takes place at C-1. The experimental rate law indicates a mechanism as shown in Scheme 1.

$$H_3IO_6^{2-} + OH^- \overset{K_5}{\rightleftharpoons} H_2IO_6^{3-} + H_2O$$

$$Pd(II) + CH_2 = CHCH_2OH \overset{K_6}{\rightleftharpoons} \text{complex(C)}$$

$$\text{Complex(C)} + H_2IO_6^{3-} \xrightarrow[\text{slow}]{k}$$
$$CH_2 = CH\dot{C}HOH + H_2IO_6^{4-} + Pd(II) + H^+$$

$$CH_2 = CH\dot{C}HOH + H_2IO_6^{4-} + OH^- \xrightarrow[\text{fast}]{}$$
$$CH_2 = CHCHO + H_2IO_6^{5-} + H_2O$$

Scheme 1

Scheme 1 also involves the intervention of free radicals, which is supported by the polymerization of acrylamide induced when it is added to the reaction system. Thus, Scheme 1 leads to the rate law (12) which explains all the observed orders and can be verified by rearrangement to the form

$$\frac{[Pd(II)]}{k_C} =$$
$$\frac{1}{kK_5K_6[AA][OH^-]} + \frac{1}{kK_6[AA]} + \frac{1}{kK_5[OH^-]} + \frac{1}{k} \qquad (13)$$

The proposed rate law (12) may be thus, verified by the linear plots of $Pd(II)/k_C$ versus $1/[OH^-]$ and $Pd(II)/k_C$ versus 1/[AA] at a constant concentration of palladium (II) (Figure 2). From the slopes and intercepts of these plots, K_5, the equilibrium constant for the formation of alkaline species of the oxidant, K_6, the formation constant of the complex between the catalyst and substrate, and k, the rate constant of the rate-limiting stage, were found to be 3.30 ± 0.1 dm^3 mol^{-1}, 1.85 ± 0.02 dm^3 mol^{-1} and 126 ± 2 dm^3 mol^{-1} s^{-1}, respectively. Using these values, the rates under different conditions were evaluated and were found to be in good agreement with the experimental data (Table 1). The value of K_5 obtained is similar

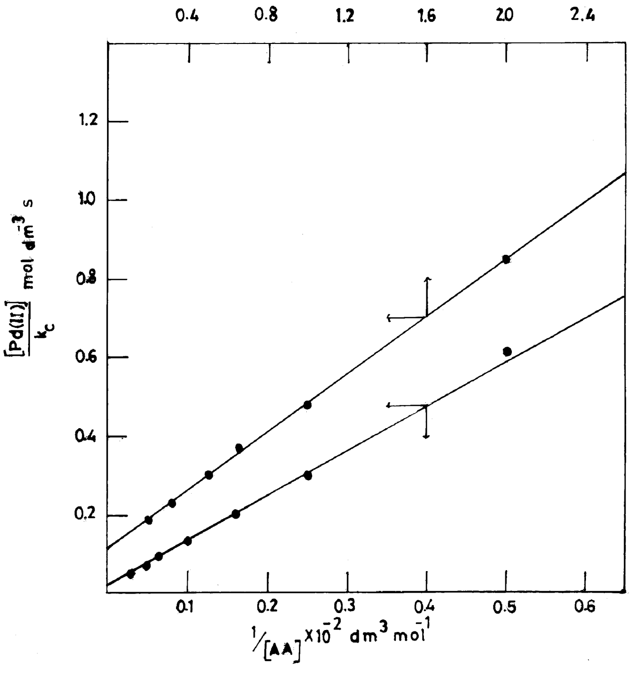
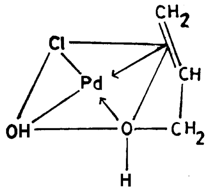


Figure 2. Verification of rate law (12). Conditions as in Table 1

to that of the uncatalysed reaction since the same pre-equilibrium is involved in the two reaction schemes.

The increase in rate with increase in chloride concentration may be understood as being due to the palladium (II) complex, [$PdCl^+$], as stated earlier. This species of palladium (II) in the presence of chloride has also been observed earlier.[15] The complex between the active form of the catalyst, $PdCl^+$, and the substrate, allyl alcohol, is a type of π-complex[16] which may be of the form.



The negligibly small effects of ionic strength and polarity on the reaction are presumably due to the fact that the reaction is between a neutral and a charged species (Scheme 1).

Effect of temperature

The rate constants, *k*, of the slow step in Scheme 1 were obtained from the slopes and intercepts of the of Pd(II)]/k_C versus 1/[AA] and versus 1/[OH^-] at four different temperatures and least-squares analysis of the data led to the activation parameters given in Table 3. The difference in the activation parameters for the catalysed and uncatalysed reactions (Table 3) explains the catalytic effect on the reaction. The catalyst, Pd (II), alters the path of the reaction by lowering the energy barrier, that is, it provides an alternative pathway with lower activation parameters for the reaction involving the formation of an intermediate complex (π-complex), as proposed in Scheme 1.

Table 3. Effect of temperature on Pd(II)-catalysed and uncatalysed periodate oxidation of allyl alcohol[a]

Parameter	Catalysed reaction	Uncatalysed reaction
$\Delta H^{\neq}$ (kJ mol^{-1})	46.5 ± 2.0	= 57.5 ± 2.0
$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	−47.0 ± 3.0	=−110.0 ± 3.0

[a] $[IO_4^-] = 4.0 \times 10^{-3}$, $[AA] = 4.0 \times 10^{-2}$, $[OH^-] = 0.2$, $[Pd(II)] = 6.8 \times 10^{-5}$ mol dm^{-3} and ionic strength 0.6 mol dm^{-3}. Temperature: 25, 30, 35 and 45°C. Error ± 4%.

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