Kinetics and mechanism of palladium (II) catalysed oxidation of allyl alcohol by N-chloro succinimide in aqueous alkaline medium

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The title reaction is the first order in [NCS] in the presence of palladium(II) catalyst. The order in [allyl alcohol] is less than unity whereas that in [Pd(II)] is unity. Increase in [OH] accelerates the reaction rate while added product, succinimide, retards the reaction rate. Increase in ionic strength and t-butanol content in reaction medium have negligible effect. The mechanism involving the hypochlorite ion as the reactive species of the oxidant has been proposed. The reaction constants of individual steps involved in the reaction mechanism have been evaluated.

Kinetic studies on the oxidation of allyl alcohol with different oxidants such as potassium permanganate, chromic acid, vanadium(V), manganese pyrophosphate, silver(III), chloramine-T, etc. have been reported. N-chlorosuccinimide (NCS) has been used as an oxidizing agent and analytical reagent especially in the acid medium. However, work on oxidation reactions of NCS in alkaline medium is scanty. Palladium(II) is known to catalyse various reactions. Most studies using palladium(II) as a catalyst have employed it in the form of palladium(II) chloride and the nature of its active form in such reactions remains obscure. Hence, the effect of chloride in the reaction was studied in order to establish the active species of the catalyst. Allyl alcohol oxidation by NCS is very slow in both acid and alkaline media. Pd(II) does not catalyse the reaction in acid medium but pronounced catalysis is observed in alkaline medium. We have undertaken the systematic study of title reaction with a view to find out mechanism aspects and to know the active form of NCS in alkaline medium.

Experimental
Reagent grade chemicals and doubly distilled water were used throughout. Aqueous solution of N-chlorosuccinimide (SRL) was prepared always afresh and standardized iodometrically. Allyl alcohol (AA) (Kochlight) was purified and its solution was standardized by addition of excess of chloramine-T, followed by iodometric titration. A Pd(II) stock solution was prepared by dissolving a known weight of palladium chloride (Fischer) in 0.20 mol dm⁻³ hydrochloric acid and standardized against EDTA. For some kinetic runs in the absence of chloride, the chloride ion in the Pd(II) stock solution was precipitated with AgNO₃ and removed by repeated centrifugation. The resulting clear Pd(II) solution contained less than 1 x 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 was maintained with NaCl. t-Butanol (Baker) was distilled before use. Succinimide was prepared by known method and recrystallised and its solution was prepared in doubly distilled water. NaClO₃ and NaOH were used to maintain the required ionic strength and alkalinity respectively.

Kinetics
The reaction was carried out under pseudo-first order conditions where [AA] was always ten or more fold excess over [NCS] at constant temperature of 27± 0.1 °C. The reaction was initiated by mixing the required quantities of thermally equilibrated solutions of [NCS] and [AA] which also contained the required quantities of Pd(II), NaOH and NaClO₃. The progress of the reaction was followed by iodometric determination of the unreacted oxidant in aliquots (5 ml each) of the reaction mixture withdrawn at regular time intervals. The pseudo-first order rate constants were obtained from the plots of log[NCS] versus time. Most of the kinetic runs were followed to more than 80% completion of the reaction and rate constants were reproducible 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 nitrogen atmosphere. No significant difference between the results are observed. Added carbonate showed no effect on the reaction rate.
Results and discussion

Stoichiometry and reaction products

Different reaction mixtures containing different sets of reactant concentrations at constant alkalinity and ionic strength were kept to react for 24 hours at 27±1.0°C and then analysed. The remaining NCS was assayed iodometrically. Under the condition [AA]>[NCS], the unreacted allyl alcohol was estimated. Succinimide was the main product as detected by the method reported4 and another product acrolein was evidenced by test5. Test for acrylic acid was negative. The results was in agreement with 1:1 stoichiometry.

\[
RNCI + CH\equiv CH\equiv CH\cdot OH + OH^- \rightarrow CH\equiv CH\equiv CHO + RNH\cdot Cl^- + H_2O
\]

where \( R = C_3H_5O_2 \).

Reaction order

Order in each reactant was obtained from log-log plot of rate constant versus concentration. The order in [NCS], was unity in the concentration range 1.0 \times 10^{-4} to 1.0 \times 10^{-2} mol dm^{-3} at fixed [AA], [Pd(II)], [NaOH] and ionic strength. The rate constants increased with increase in [AA] and the order in [AA] was found to be less than unity (0.4). The reaction rate increased with increase in [Pd(II)] and the order in [Pd(II)] was found to be unity. The rate of the reaction increased with increase in [OH^-] at constant ionic strength (Table 1).

Addition of ten fold excess of the product, succinimide, at constant ionic strength decreased the rate of reaction. The initial addition of Cl^- and acrolein has no effect on the reaction rate. Change in the ionic strength (NaClO_4) and dielectric constant (\( \varepsilon \)) of reaction medium did not affect the rate significantly.

Effect of added chloride

Palladium(II) is known to form different chloride complexes\(^6\) of the general formula Pd(Cl)\(^n\)\(^{+n}\) with \( n \) having values from 1 to 4. Hence the effect of chloride on the reaction rate was studied. Although the stock solution of Pd(II) contained chloride, for this series of runs, a Pd(II) solution which did not contain chloride was used. However, it was found that chloride has no effect on the reaction rate. Hence palladium chloride complexes are precluded in the title reaction.

Test for free radicals

The reaction mixture to which a known quantity of acrylonitrile had been added initially and was kept for 24 hours in an inert atmosphere. On diluting the reaction mixture with methanol, no copious precipitate resulted indicating the absence of free radicals.

Effect of temperature

Kinetics were studied at 27, 32, 37, and 42°C with [NCS]= 5 \times 10^{-2} mol dm\(^{-3}\), [AA]= 5 \times 10^{-2} mol dm\(^{-3}\), [OH^-] = 1.0 \times 10^{-3} mol dm\(^{-3}\) and 1= 0.1 mol dm\(^{-3}\). The rate constants of the slow step \( (k) \) were obtained from the intercept of plot of [Pd(II)]/k vs. [NH]. Plots at four different temperatures and least squares analysis of the data led to the following values; 

\[
E_a = 57 \pm 3 \text{ kJ mol}^{-1}, \quad \Delta S^\circ = 54 \pm 2 \text{ J K}^{-1} \text{ mol}^{-1}, \quad \Delta H^\circ = 55 \pm 2 \text{ kJ mol}^{-1} \text{ and } \Delta G^\circ = 72 \pm 4 \text{ kJ mol}^{-1}. 
\]

The reaction is first order each in [NCS] and 1[Pd(II)] and less than unity both in [AA] and [OH^-]. The results suggest the complex formation between the catalyst and substrate. As platinum group metals have the ability to form complexes with organic substrates highly enhanced
rates substantiate the formation of [Pd(II)*-AA] complex which slowly reacts with [NCS] species in the rate determining step to give products. It is also noteworthy that the reaction is not influenced by chloride ions, to be expected in Pd(II) catalysed reactions. However in alkaline solutions, Pd(II) is mostly present as hydroxylated species (shown as Pd(II)* for simplicity) which is in accordance with earlier work and not as its chloride complex as in other cases.

Taking all the experimental results into consideration, a mechanism as in Scheme 1 (Eqs 1-3) may be proposed.

\[ \text{NCS} + \text{NaOH} \overset{K_1}{\rightleftharpoons} \text{NaOCl} + \text{NH(CH}_2\text{CO)}_2 \]  
\[ \text{Pd(II)*} + \text{AA} \overset{K_2}{\rightleftharpoons} [\text{Pd(II)*-AA}] \text{Complex (C)} \]  
\[ C + \text{OCI}^- \rightarrow \text{Pd(II)} + \text{acrolein} + \text{Cl}^- + \text{H}_2\text{O} \]

\[ \text{C + OCI}^- \rightarrow \text{Pd(II)} + \text{acrolein} + \text{Cl}^- + \text{H}_2\text{O} \] 

Scheme 1

The structure of the complex (C) might be given as;

Attempts to obtain spectral evidence for catalyst substrate complex were not successful. The interaction might be quite feeble. However, a kinetic evidence for complex formation can be obtained. Such catalyst-substrate complex formation have also been reported earlier. Presumably the Pd(II)*-AA species is a type of π-complex. Scheme 1 leads to rate Eq.(4)

Strictly, the factor \( 1 + K_3 \text{[Pd(II)]} \) should also be there in the denominator of RHS of Eq. (5). In view of low concentration of Pd(II) used, this term is approximated to unity. Finally the Eq. (5) may be verified by the linear plots of \( \text{[Pd(II)]/k_{obs}} \) versus \([\text{HN}]\) and \( \text{[Pd(II)]/k_{obs}} \) versus \(1/[\text{AA}]\) as shown in Fig.1.

From the slopes and intercepts of such plots \( K_1, K_2 \) and \( k \) were evaluated and found to be 11.03, 47 (dm\(^3\)/mol/\(\text{sec}\)) and 1.245 (mole/dm\(^3\)/sec) respectively.
mol$^{-1}$ and 4.83 dm$^3$ mol$^{-1}$s$^{-1}$ respectively. Using these values, experimental rates can be regenerated.

Negligible effect of ionic strength and dielectric constant on reaction rate might be due to involvement of neutral substrate in the reaction. The modest energy of activation and entropy of activation support the involvement of complex transition state in the catalysed reaction. The activation energy calculated for Pd(II) catalysed reaction explains the catalytic effect.

References


