Oxidation of Some Alcohols by Silver (II) in Aqueous Phosphoric Acid

P. JAYA PRAKASH RAO, B. SETHURAM & T. NAVANEETH RAOI
Department of Chemistry, Osmania University.
Hyderabad 500 007

Received 14 October 1981; revised and accepted 10 December 1981

The oxidation of methyl, ethyl, n-propyl, isopropyl, n-butyl and benzyl alcohols by silver (II) in aqueous phosphoric acid is first order each in [Ag(II)] and [alcohol]. The reaction rate decreases with increase in [H3PO4] and is unaffected by added [Ag(II)] or [phosphate]. The acid dependence of the reaction rate is explained on the basis of hydrolysis of silver(II). A mechanism involving the formation of RCOH radicals in the rate determining step by free Ag+ as well as AgOH+ is postulated.

SILVER(II) has been used as an oxidant in the oxidation of organic compounds1–3. However, only a few kinetic studies on the silver(II) oxidation are reported4–6. The difficulty in studying the kinetics of Ag(II) oxidation arises because of its reaction with water in acid solutions7–11. The general mechanism of reduction of silver(II) by water involves first its disproportion into silver(III) and silver(I) (Eq. 1) followed by the reaction of silver(III) with water.

\[ 2\text{Ag(II)} \rightarrow \text{Ag(III)} + \text{Ag(I)} \]  

(1)

There are no reports on the kinetic studies involving Ag(II) in aqueous phosphoric acid medium in which it is known to be stabilized to a greater extent12. The present work aims at investigating the behaviour of Ag(II) in aqueous phosphoric acid and the importance of equilibrium(1) in the oxidation of some alcohols by Ag(II).

All the chemicals used were either BDH (AR) or of accepted grade of purity. The alcohols used were methyl, ethyl, n-propyl, isopropyl, n-butyl and benzyl alcohols. All the solutions were prepared in doubly distilled water. Silver(II) solution was always prepared a fresh in phosphoric acid from silver(II) oxide13 and standardised iodometrically6. The kinetics were followed by determining unreacted Ag(II) at definite time intervals iodometrically.

Isopropanol was chosen for determining stoichiometry because the first stage oxidation product, viz. acetone, reacted with Ag(II) to a negligible extent under similar conditions. It was found that two mol of Ag(II) were required for each mol of alcohol in accordance with Eq.(2) giving the corresponding keto compounds under conditions of [Ag(II)] < [alcohol] in the case of all the alcohols studied. The overall reaction can thus be written as

\[ 2\text{Ag(II)} + \text{R}_2\text{CHOH} \rightarrow 2\text{Ag(I)} + 2\text{H}^+ + \text{R}_2\text{CO} \]  

(2)

At constant [alcohol], [H3PO4] and [Ag(II)] and in the range of [Ag(II)] \approx 2.00 \times 10^{-1} to 6.90 \times 10^{-4} M, the reaction was first order in [Ag(II)] as revealed by the slope of the linear plot of log(initial rate) versus log [Ag(II)]. A similar first order dependence of rate on [alcohol] was also observed for all the alcohols. Thus the experimentally observed rate law could be written as

\[ -\frac{d[\text{Ag(II)}]}{dt} = k^\ast[\text{Ag(II)}][\text{R}_2\text{CHOH}] \]  

(3)

where \( k^\ast \) is the apparent second-order rate constant. At constant acidity, [Ag(II)] and [alcohol] the reaction rate was found to be independent of [Ag(II)] in the range 3.67 \times 10^{-2} to 12.5 \times 10^{-2} M. The rate of reaction was also found to be unaffected by the addition of KNO3 or any phosphate. For all the alcohols studied, the second-order rate constant (\( k^\ast \)) was found to be inversely dependent on [H3PO4] (Table 1).

The available evidences4–8,11,12 indicate uncomplexed Ag(II) as the reactive species, though in strong acid media Ag(II) is known to be coordinated with the anion and its greater stability in phosphoric acid medium may be attributed to the stronger ligating properties of phosphate. The nondependence of reaction rate on added phosphate also supports this assumption. Like many metal ions in their higher oxidation states Ag(II) gets hydrolysed (Eq. 4) to a significant extent even at high acidities11.

\[ \text{Ag}^{2+} + \text{H}_2\text{O} \rightarrow \text{AgOH}^+ + \text{H}^+ \]  

(4)

<table>
<thead>
<tr>
<th>Table 1 — Effect of Varying Acidity on Ag(II)–Methanol Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Ag(II)}] = 1.34 \times 10^{-3} \text{ M}; [\text{MeOH}] = 0.05 \text{ M}; [\text{Ag(0)}] = 3.67 \times 10^{-4} \text{ M}; \text{ temp.} = 303 \text{ K} )</td>
</tr>
<tr>
<td>([\text{H}_3\text{PO}_4] ) (M)</td>
</tr>
<tr>
<td>1.62</td>
</tr>
<tr>
<td>1.92</td>
</tr>
<tr>
<td>2.12</td>
</tr>
</tbody>
</table>

612
Acid-base equilibria of this type are generally very rapid and we assume both Ag^{2+} and AgOH^{+} to be the reactive species. These two species may have different reactivities since they are differently protonated and the acid dependence of the reaction rate may be treated on the basis of this difference in reactivity.

The possible involvement of protonated alcoholic species in the reaction has been ruled out in view of very low pK_a values for R_2CHOH^+ (e.g., -1.94 for EtOH^+ at 25°C, ref. 16). The free radical nature of the reaction was confirmed by the observed induced polymerisation of acrylonitrile. However, it is not possible to give any kinetic evidence about the a-C-H or O-H bond rupture in the oxidation of simple alcohols as the alkoxyl radicals, if produced, are rapidly converted into the tervalent carbon radicals in accordance with Eq. (5).

\[ R_2CHO + R_2CHOH \rightarrow R_2CHO + R_2COH \ldots (5) \]

The involvement of Ag(III) in the reaction has also been ruled out since the order in [Ag(II)] was strictly one and not two as it should be if equilibrium (i) and Ag(III) as reactive species are considered. This is further supported by the fact that the reaction rate is unaffected by changes in [Ag(I)].

Based on the facts gathered, the mechanism of oxidation of alcohols by Ag(II) can be represented by Scheme 1 and the rate law by Eq. (6).

\[
\begin{align*}
K & \quad Ag^{2+} + H_2O \quad AgOH^+ + H^+ \quad \ldots (i) \\
fast & \\
Ag^{2+} + R_2CHOH \rightarrow R_2COH + Ag^+ + H^+ \quad \ldots (ii) \\
AgOH^+ + R_2CHOH \rightarrow R_2COH + Ag^+ + H_2O \quad \ldots (iii) \\
\text{fast} & \\
Ag(II) + R_3COH \rightarrow Ag^+ + \text{products} \quad \ldots (iv)
\end{align*}
\]

Scheme 1

\[
\begin{align*}
\frac{d[Ag(II)]}{dt} = & \quad \frac{k_1 + k_2K[H^+]}{[Ag(II)]_0[R_2CHOH]} \\
& \quad \frac{1 + K[H^+]}{K[H^+]}
\end{align*}
\]

where \([Ag(II)]_0 = [Ag^{2+}] + [AgOH^+]\)

Comparison of Eq. (6) with the observed rate law (Eq. 3) gives

\[ k^* = \frac{k_1 + k_2K[H^+]}{1 + K[H^+]}. \]

From the recently reported pK value (5.35) for equilibrium (i) in Scheme 1 and the experimental [H^+] range used, K/[H^+] may be neglected in compari-

---

**Fig. 1** — (A) Plot of \( k'' \times 10^4 \) versus \( 1/[H^+] \) under the conditions [Ag(II)] = 1.34 × 10^{-2} M; [MeOH] = 0.05 M; [Ag(O)] = 3.67 × 10^{-3} M; temp. = 303 K. (B) Plot of \( 3 + \log k''^{\text{obs}} \) versus \( 3 + \log k^{\text{obs}} \).
TABLE 2—SECOND-ORDER RATE CONSTANTS AND ACTIVATION PARAMETERS

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>$k'' \times 10^5$ (M$^{-1}$ sec$^{-1}$)</th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^\ddagger$ (J K$^{-1}$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl alcohol</td>
<td>1.36</td>
<td>68.6</td>
<td>-69.5</td>
</tr>
<tr>
<td>Isopropyl alcohol</td>
<td>4.48</td>
<td>72.4</td>
<td>-46.5</td>
</tr>
<tr>
<td>Ethyl alcohol</td>
<td>5.11</td>
<td>73.2</td>
<td>-42.5</td>
</tr>
<tr>
<td>n-Propyl alcohol</td>
<td>19.2</td>
<td>81.2</td>
<td>-13.0</td>
</tr>
<tr>
<td>n-Butyl alcohol</td>
<td>23.9</td>
<td>81.2</td>
<td>-2.07</td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td>106</td>
<td>57.3</td>
<td>-72.6</td>
</tr>
</tbody>
</table>

From the data presented in Table 2 the order of reactivities of alcohols is methyl < isopropyl < ethyl < n-propyl < n-butyl < benzyl. The increase in reactivity from methyl to n-butyl may be attributed to the $+1$ effect of the alkyl groups which result in a higher electron density at the alpha carbon leading to a decrease in the bond energy for the $\alpha$C-H homolytic cleavage. The lower reactivity of isopropanol could be due to steric effects which hinder the approach of Ag(II) to the reaction site. The very high reactivity observed for benzyl alcohol is probably due to formation of resonance stabilized benzylic radical in the slow step.

The data in Table 2 also show that these reactions are entropy-controlled. This contention receives support from the existence of isokinetic phenomenon as evidenced by the linear Exner's plot (Fig. 1B) for the aliphatic alcohols and also the isokinetic temperature ($\beta$) evaluated from it (246.2 K) which is far below the experimental temperature range (278-303K) employed.

References


Kinetics of Oxidation of Some Primary Alcohols by Aqueous Chlorine

V. P. Kudesia* & S. K. Mukherjee
Department of Chemistry, D. N. College, Moorut

Received 27 December 1978; revised 30 April 1981; rerevised 31 December 1981; accepted 4 February 1982

Oxidation of primary alcohols (method, ethanol, propanol and butanol) by aqueous chlorine follows first order in substrate, first order in chlorine, half order in $H^+$ at lower $[H^+]$ and first order in $H^+$ at higher $[H^+]$ except in the case of methanol and ethanol where the order in substrate is zero, other things being the same. Added chloride enhances the rate of the reaction while sulphates decrease the rate. The activation parameters have been calculated and a suitable mechanism proposed.

Our earlier studies¹ on the kinetics of oxidation of propan-2-ol by aq. chlorine, have been extended to a host of primary alcohols in order to delineate the role of chlorine species in these reactions.

All the chemicals used (BDH or E. Merck, AR grade) were purified by usual methods and their purity checked by standard methods². $D_2O$ of isotopic impurity $>99.45\%$ was supplied by Bhabha Atomic Research Centre, Bombay. The chlorine solution was prepared by the reaction of $KMnO_4$ with $HCl$ in cold. All other solutions were prepared in deionised water. Reactions were followed at $35 \pm 0.05^\circ C$ in bottles wrapped with aluminium foils by estimating the amount of chlorine in the reaction mixture at regular intervals of time.

The initial rates, $k_0$ were calculated in each case by plotting $x/t$ against $x$ ($x$ being the number of mol per litre of chlorine consumed) and extrapolating to $x = 0$. Linear plots were obtained up to 50-60% of the reaction and the estimated probable error in $k_0$ for various runs were within ±3%.

The reaction is first order each in $[Cl]_2O$ and $[alcohol]$ except for methyl and ethyl alcohols where the order in $[Cl]_2O$ and $[alcohol]$ is one and zero respectively. The results are summarised in Tables 1 to 3. The probable oxidising species existing in aqueous solution of chlorine are $Cl_2$, $HOCl$ and $Cl_2$- and their concentrations depend upon the concentration of chlorine solution, $H^+$ and $Cl^-$ (if added).