Kinetics of Oxidation of Benzoin by Ceric Ammonium Nitrate in Aqueous Acetic Acid

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The kinetics of oxidation of benzoin by ceric ammonium nitrate (CAN) has been studied in aqueous acetic acid. The reaction exhibits a first order dependence on [CAN]. The dependence of the rate of oxidation on [benzoin] presents certain interesting features. A break in the log $k_{obs}$ versus log [benzoin] plot has been observed. Further, at higher concentrations of benzoin added nitric acid accelerates the rate of oxidation while a retardation in the rate of oxidation is noticed at lower concentrations of benzoin with increase in [HNO$_3$]. These facts have been explained by involving a dual mechanistic pathway for the oxidation of benzoin via the keto or the enol form.

Two different reaction courses, viz. fragmentation or direct oxidation are available in the oxidation of alcohols by ceric ammonium nitrate (CAN). Cyclopropyl carbinols and primary benzylic alcohols are oxidized to the corresponding carbonyl compounds$^{1,2}$. 2 - Aryl -1-phenylethanol s undergo C - C bond fission to yield fragmentation products whereas alkylphenyl carbinols afford a mixture of benzaldehyde and alkyl phenyl ketones$^{3,4}$. These results are of pertinent interest in the CAN oxidation of benzoin, which has a benzylic alcohol function also may thus give rise to one or both type of products. In a preparative reaction Tse Lok Ho has shown that benzoin splits into benzaldehyde and benzoic acid when reacted with CAN in aqueous acetonitrile$^5$. We wish to report here some interesting features observed in the kinetics of oxidation of benzoin by CAN.

Materials and Methods

Ceric ammonium nitrate (Fluka AG) was used as such. A 3% solution of ferroin indicator (BDH, LR) in water was found suitable in this study. Ceric ammonium sulphate (BDH, LR) was dissolved in 1·0M H$_2$SO$_4$ and standardized using ferrous ammonium sulphate. Benzoin (Aldrich) was used as such.

The kinetic runs were made in water-acetic acid mixtures at constant ionic strength. The reactions, studied in the temperature range 50-60°, were followed by studying the rate of disappearance of Ce(IV) ions by quenching the reaction mixture in a known excess of ferrous sulphate and estimating the unreacted FeSO$_4$ by back titration with ceric ammonium sulphate using ferroin as the indicator.

Results and Discussion

The linearity of the plot of log ($b-x$) versus time clearly reveals that the CAN oxidation of benzoin follows a first order kinetics with respect to [Ce(IV)] (Fig. 1).

Fig. 1 — First order plot for the disappearance of Ce(IV)

The order with respect to benzoin was determined by varying the [benzoin] at fixed values of [Ce(IV)], [HNO$_3$], [NaNO$_3$] and at a constant composition of the solvent system. At lower ranges of benzoin concentration the rate of oxidation shows unit dependence on [benzoin]. At intermediate concentrations of benzoin a fractional order dependence is observed and at very high concentrations the rate
of oxidation is independent of [benzoin]. There is thus a break in the order plot, viz. the plot of log \( k \) versus log [benzoin] (Fig. 2). This can be readily seen from the values of \( k_{obs} \) (the pseudo-first order rate constant) for various concentrations of benzoin (Table 1). The rate initially increases with increase in benzoin concentration up to 0.015M, thereafter suddenly drops and then increases with further increase in the concentration of benzoin. Finally, the rate remains constant with further increase in the benzoin concentration. The double reciprocal plots of the \( k_{obs} \) and [benzoin] in the intermediate ranges of benzoin concentration are linear with definite least square y intercepts and the order with respect to benzoin ranges from 0.4 to 0.5. This fact along with the rate independence at higher [benzoin] show the application of Michaelis-Menten kinetics for this reaction, involving the formation of a complex between benzoin and Ce(IV) in a rapid equilibrium step followed by its decomposition in the rate-determining step into the products. The formation constant \( K \), of the benzoin-Ce(IV) complex and its decomposition constant \( k_d \) have been evaluated from the least square slopes and \( y \) intercepts of \( 1/k_{obs} \) versus \( 1/[\text{benzoin}] \) plots and the values are 51.1 litre mol\(^{-1}\) and 14.4 \( \times \) 10\(^{-5}\) sec\(^{-1}\) respectively.

The influence of the acid strength on the rate of oxidation has been studied both at lower concentration of benzoin, viz. 0.015M and at higher concentration of benzoin, viz. 0.04M (Table 2). Interestingly, at [benzoin] = 0.04M increase in [HNO\(_3\)] accelerates the rate while a rate drop is produced with increase in [HNO\(_3\)] at [benzoin] = 0.015M.

Mechanism — In order to account for the above observations it may be presumed that benzoin can react with Ce(IV) ion either through the keto or through the enol form. The reaction can be expressed by Eq. (1).

\[
\text{Benzoin} + \text{Ce}(IV) \rightleftharpoons \text{Complex} \rightarrow \text{Products} \quad \text{(1)}
\]

The rate law can then be expressed by Eq. (2).

\[
\frac{d[\text{Ce}(IV)]}{dt} = \frac{k_1k_d[\text{Benzoin}][\text{Ce}(IV)]}{1 + K[\text{Benzoin}]} \quad \text{(2)}
\]

This demands a first order dependence on benzoin at lower concentrations of benzoin, fractional order dependence at higher concentrations and zero order dependence at very high concentrations. However, the order plot, viz. log \( k_{obs} \) versus log [benzoin] plot should be continuous if a single mechanism operates throughout the entire range of [benzoin]. The break in the order plot (Fig. 2) implies two different rate laws consistent with a dual mechanism — the reaction proceeding via either keto (Scheme 1) or enol form (Scheme 2) of benzoin.

**Table 1 — Dependence of Rate of Oxidation of Benzoin on Its Concentration**

<table>
<thead>
<tr>
<th>[Benzoin] M</th>
<th>( 10^5 k_{obs} ) (sec(^{-1}))</th>
<th>( 10^4 k_{obs} ) litre mol(^{-1}) sec(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.008</td>
<td>6.10</td>
<td>8.02</td>
</tr>
<tr>
<td>0.01</td>
<td>7.95</td>
<td>7.90</td>
</tr>
<tr>
<td>0.015</td>
<td>11.1</td>
<td>7.96</td>
</tr>
<tr>
<td>0.02</td>
<td>7.22</td>
<td>—</td>
</tr>
<tr>
<td>0.04</td>
<td>9.50</td>
<td>—</td>
</tr>
<tr>
<td>0.06</td>
<td>11.2</td>
<td>—</td>
</tr>
</tbody>
</table>

**Table 2 — Effect of Acidity on the Rate of Oxidation of Benzoin**

| [Benzoin] = 0.015M; [NaNO\(_3\)] = 0.25M; temp. = 55\(^\circ\) C; [HNO\(_3\)] = 0.2M; solvent = 80% HOAc-20% H\(_2\)O (v/v) |
|---|---|---|
| [HNO\(_3\)], M | \( 10^5 k_{obs}, \text{sec}^{-1} \) |
| 0.2 | 11.0 (9.5) |
| 0.5 | 10.1 (11.6) |
| 1.0 | 9.53 (20.1) |
| 1.5 | (35.1) |

Values in parentheses obtained at [benzoin] = 0.04M.
The validity of the above analysis is also brought out by a further consideration of the rate law when fractional order dependence on benzoin exists. From the double reciprocal plot of \( k_{\text{obs}} \) and [benzoin] we can evaluate \( k_1 \) and \( K_1 K_2 \) (Eq. 4). In the extreme case where the second term in the denominator is negligible in comparison with \( k_1 \) (i.e., under conditions of low concentrations of benzoin), Eq. (4) reduces itself to Eq. (5).

\[
\frac{d[\text{Ce(IV)}]}{dt} = k_1 K_1 K_2 [\text{Benzoin}] [\text{Ce(IV)}] ...
\]

From Eq. (5) it can be seen that \( k_{\text{obs}} = k_1 K_1 K_2 [\text{Benzoin}] \).

It is interesting to observe that \( k_4 (= k_{\text{obs}}/[\text{Benzoin}]) \), the bimolecular rate constant obtained for the oxidation at low [benzoin] is very nearly identical with the value of the product \( k_1 K_1 K_2 (= 7.4 \times 10^{-8}) \) (Table 1) obtained from the slope of the double-reciprocal plot.

Thus two rate pictures are available for the CAN oxidation of benzoin. The break in the plot of log \( k_{\text{obs}} \) versus log [benzoin] could, therefore, be due to the dual mechanistic pathways either via the keto or the enol form with consequent changes in the dependence of the rate on [benzoin].

References

5. Tse Lok Ho, Synthesis, 10 (1972), 560.