Kinetics of Oxidation of Benzaldehyde & Substituted Benzaldehydes by Trichloroisocyanuric Acid in Acetic Acid-Perchloric Acid Medium

SUBAS C PATI*, ASHOK KUMAR SAHU & Y SRIRAMULU
Department of Chemistry, Berhampur University, Berhampur 760 007

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The title reaction is first order each in [oxidant] and [substrate]. The dependence on acidity is fractional. Increase in acetic acid content of the solvent medium decreases the rate of reaction. Added chloride ions accelerate the rate. The order of reactivities is p-methoxybenzaldehyde > p-methylbenzaldehyde > p-nitrobenzaldehyde > m-nitrobenzaldehyde > benzaldehyde > p-chlorobenzaldehyde > p-bromobenzaldehyde. Though both electron-releasing and electron-withdrawing substituents enhance the rate, the Hammett plot shows a break in the reactivity order indicating applicability of a dual mechanism. A mechanism in conformity with kinetic data has been proposed.

The kinetics of oxidation of aromatic aldehydes by a number of oxidants except trichloroisocyanuric acid (TCCA), have been extensively investigated in recent times. In view of this and the fact that the kinetics of oxidation of toluenes and ketones by TCCA has earlier been investigated in our laboratory it was considered worthwhile to undertake the title investigation.

The substrates, viz. p-OCH₃, p-CH₃, p-NO₂, m-NO₂, p-Cl and p-bromo-benzaldehydes (all AR reagents) were either redistilled or recrystallised before use. Trichloroisocyanuric acid was of AR (Fluka) grade. Acetic acid (AR) was purified by the standard method. All solutions were prepared in conductivity water.

Solutions (50 ml each) of the oxidant and substrate, preequilibrated separately at the desired temperature (± 0.1°C) were mixed in a vessel painted black from outside. Aliquots (5 ml each) from the reaction mixture were withdrawn at regular time intervals and poured into an aqueous solution of iodate-free potassium iodide and sodium bicarbonate. Sulphuric acid (2 ml, 6 N) was added, the reaction mixture set aside for a few minutes, diluted with water and the liberated iodine titrated against standard thiosulphate to starch end-point.

All the experiments were carried out in duplicate and the rate constants are reproducible within ± 3% error.

Stoichiometric investigations carried out under the conditions: [TCCA] = 0.002 mol dm⁻³, [S] = 0.001 mol dm⁻³, [H⁺] = 0.02 mol dm⁻³, solvent = aq. HOAc (20%, v/v) and temp. = 35°C were largely not meaningful because of the appreciable decomposition of TCCA. However, the product was identified as the corresponding acid.

Oxidation of benzaldehyde and m-NO₂, p-Cl, p-OCH₃, p-CH₃, p-NO₂ and p-bromo-benzaldehydes by TCCA was carried out under identical conditions and the kinetic results can be summarised as follows:

(i) The reaction is first order in [oxidant] as revealed by the constancy of $k_r$ values obtained with different initial [oxidant], and by the linearity of the plot of log [TCCA] versus time. The unit slopes of the linear plots of log $k_r$ versus log [substrate] indicate first order dependence in [substrate].

(ii) Increase in [HClO₄] increase the reaction rate marginally. For example under the conditions [TCCA] = 5.0 x 10⁻⁴ mol dm⁻³, [substrate] = 10.0 x 10⁻³ mol dm⁻³ and temp. = 35°C, 10³ $k_r$ increased from 1.88 to 3.74 min⁻¹ for benzaldehyde, from 2.81 to 5.05 min⁻¹ for m-nitrobenzaldehyde and from 1.15 to 4.02 min⁻¹ for p-chlorobenzaldehyde when [HClO₄] was increased from 0.02 to 0.4 mol dm⁻³.

(iii) Increase in per cent acetic acid of the reaction medium from 10 to 40 (other conditions being same as in (ii) above) decreases the rate constant from 2.61 to 0.94 min⁻¹ for benzaldehyde, from 3.94 to 1.82 min⁻¹ for m-nitrobenzaldehyde and from 1.40 to 0.87 min⁻¹ for p-chlorobenzaldehyde. The retardation in rate may be attributed to the decrease in dielectric constant of the medium.

(iv) Added chloride ions accelerate the rate of reaction probably due to the formation of molecular

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$10^3 k_r$ (min⁻¹)</th>
<th>$E_a$ (kJ mol⁻¹)</th>
<th>$\Delta H^\circ$ (kJ mol⁻¹)</th>
<th>$\Delta S^\circ$ (JK⁻¹ mol⁻¹)</th>
<th>$\log_{10} A$ (mol⁻¹)</th>
<th>$\frac{-\Delta S^\circ}{\Delta H^\circ}$</th>
<th>$\frac{-\Delta S^\circ}{\Delta H^\circ}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzaldehyde</td>
<td>1.88</td>
<td>50.59</td>
<td>47.83</td>
<td>7.82</td>
<td>103.85</td>
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<tr>
<td>m-Nitrobenzaldehyde</td>
<td>2.81</td>
<td>43.08</td>
<td>40.52</td>
<td>6.75</td>
<td>124.24</td>
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<td></td>
</tr>
<tr>
<td>p-Chlorobenzaldehyde</td>
<td>1.15</td>
<td>63.83</td>
<td>61.27</td>
<td>9.88</td>
<td>64.29</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$k_r$ values at 35°C.
chlorine as per the equilibrium: 
\[ \text{H}_2\text{OCl}^+ + \text{Cl}^- \rightleftharpoons \text{Cl}_2 + \text{H}_2\text{O} \] 
(H$_2$OCl$^+$ is the species liberated by the hydrolysis of TCCA).

(v) The plots of log $k_1$ versus $1/T$ are linear in the temperature range of 35-50°C. Activation parameters have been calculated from these and are given in Table 1. The plots of log$_{10} A$ versus $1/\sqrt{E}$ are linear indicating that both activation energy and the frequency factor control the reaction. The Leffler’s plot of $\Delta H^f$ versus $-\Delta S^f$ is also fairly linear.

Based on the above observations the mechanism given in Scheme 1 is proposed.

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Scheme 1

\[ \text{R-CH-CH(OH)} \xrightarrow{\text{K}_1} \text{R-CH-CHO} + \text{HO} \]
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which reduces to Eq. (3) on assuming $1 \gg K_3$ and $1 \gg K_3 [\text{H}^+]$

\[ = K_1 K_3 k_4 [S]_T [\text{TCCA}] + K_1 K_2 K_3 k_3 [S]_T [\text{TCCA}] [\text{H}^+] \] 

This rate law explains the observed unit dependence each on [substrate] and [TCCA] and fractional dependence on [H$^+$].

The order of reactivities of various benzaldehydes (see Table 2) under identical conditions is:

\[ p\text{-OCH}_3 > p\text{-CH}_3 > p\text{-NO}_2 > m\text{-NO}_2 > \text{benzaldehyde} > p\text{-Cl} > p\text{-Br} \]

The plot of log $k_1$ versus $\sigma$ comprises two linear portions converging at a point (Fig. 1). The concave nature of the plot indicates that (i) both electron-releasing and electron-withdrawing groups enhance the reaction rates, and (ii) applicability of a dual mechanism. The $p$-values come out to be $-2.5$ and $+0.41$ for substrates with electron-releasing and electron-withdrawing groups, respectively. Further, the concave curve indicates that the rate of hydrate formation, a process which is facilitated by the pres-
Table 2—The values of $k_1$, $k_4$, and $k_s$ for Various Substrates Studied

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$10^3 k_1$ (min$^{-1}$)</th>
<th>$10^3 k_4$ (min$^{-1}$)</th>
<th>$10^3 k_s$ (min$^{-1}$)</th>
<th>$\sigma$*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzaldehyde</td>
<td>1.88</td>
<td>282.85</td>
<td>8.61</td>
<td>+0.0</td>
</tr>
<tr>
<td>m-Nitrobenzaldehyde</td>
<td>2.81</td>
<td>28.64</td>
<td>0.78</td>
<td>+0.71</td>
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<tr>
<td>p-Chlorobenzaldehyde</td>
<td>1.15</td>
<td>94.28</td>
<td>4.70</td>
<td>+0.28</td>
</tr>
<tr>
<td>p-Methoxybenzaldehyde</td>
<td>10.28</td>
<td>606.25</td>
<td>13.69</td>
<td>-0.27</td>
</tr>
<tr>
<td>p-Methylbenzaldehyde</td>
<td>6.26</td>
<td>-0.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-Nitrobenzaldehyde</td>
<td>3.49</td>
<td>+0.78</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-Bromobenzaldehyde</td>
<td>0.93</td>
<td>+0.23</td>
<td></td>
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</tr>
</tbody>
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*The $\sigma$ values were taken from Jaffe H H, Chem Rev, 53 (1953) 191.

The presence of electron-withdrawing groups is also competing with the rate-determining hydride ion loss from the hydrate (a reaction which is accelerated by the presence of electron-releasing groups). Due to this competition, the Hammett plot shows a break. Such anomalous curves have been reported by Bakore and Shanker\(^7\) in the oxidation of benzyl alcohol by V(V) in acid medium and also by Pati and Mahapatra\(^8\) in the Ru(III)-catalysed oxidation of benzaldehyde by phenyliodosyl acetate. The plots of $k_4$ versus $\sigma$ and $k_s$ versus $\sigma$ are fairly linear confirming the applicability of the Hammett’s treatment.

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References