Chlorination of Toluene & Substituted Toluenes by Trichloroisocyanuric Acid: A Kinetic Investigation

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The kinetics of chlorination of toluene, o-, m- and p-xylenes, m- and p-chlorotoluene and m-nitrotoluene by trichloroisocyanuric acid (TCCA) in aqueous acetic acid in the presence of perchloric acid (HClO4) have been studied. The reaction is first order each in [TCCA] and [substrate]. The reaction is insensitive towards change in [HClO4]. Increase in the percentage of acetic acid in the reaction medium retards the reaction rate. Various thermodynamic parameters have been evaluated. A suitable mechanism is postulated taking the observed kinetic data into consideration.

Table I—Effect of Varying [TCCA] on Reaction Rate

\[
\begin{array}{cccc}
\text{Toluene} & \text{p-Xylene} \\
\text{[TCCA]} & \text{10}^4 \times k_1 \text{ (s}^{-1}) & \text{10}^4 \times k_1 \text{ (s}^{-1}) & \text{10}^4 \times k_1 \text{ (s}^{-1}) \\
0.0005 & 2.61 & 2.84 & 2.49 & 27.68 \\
0.001 & 3.93 & 2.73 & 4.44 & 27.87 \\
0.005 & 4.54 & 2.82 & 8.96 & 27.56 \\
0.01 & 6.05 & 2.73 & 14.29 & 27.87 \\
0.05 & 12.00 & 2.83 & & \\
\end{array}
\]

Results and Discussion

The results of kinetic investigation can be summarised as follows:

(i) The reaction is first order in [TCCA] as is evident from the constancy of the first order rate constants at different initial [TCCA] (Table 1).

(ii) An increase in [substrate] increases the rate of the reaction. The plots of \( \log k_1 \) versus \( \log [S] \) are linear with unit slopes confirming a unit dependence on the substrate (Table 2).

(iii) An increase in [HClO4] has only a marginal effect on the reaction rate indicating the absence of acid catalysis in the rate-determining step (Table 3). The plot of \( \log k_1 \) versus \( \log [H^+] \) is linear with a fractional slope.

(iv) Increasing proportion of acetic acid in the reaction medium retards the reaction rate. For example, employing \([S] = 0.005 \text{ mol dm}^{-3}\), \([\text{TCCA}] = 0.0005 \text{ mol dm}^{-3}\), \([\text{HClO}_4] = 0.01 \text{ mol dm}^{-3}\) at 35°C, the rate constants \(10^4 \times k_1\) respectively in

- Toluene: 2.61, 3.93, 4.54, 6.05, 12.00
- p-Xylene: 2.84, 2.73, 2.82, 2.73, 2.83

<table>
<thead>
<tr>
<th>Substrate</th>
<th>[TCCA] (mol dm(^{-3}))</th>
<th>10^4 \times k_1 (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>0.0005</td>
<td>27.68</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>0.001</td>
<td>27.87</td>
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<td></td>
<td>0.005</td>
<td>27.56</td>
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<td></td>
<td>0.01</td>
<td>27.87</td>
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Products were found to be side chain halides in all the cases except in the case of m-xylene where in addition to side chain halide, 3-methylbenzylchloride the nuclear substituted product, viz. 4-chloro-3-methyltoluene was also formed, the ratio of the two products being 1:3. The products were identified by TLC.
electron releasing groups enhance the reaction rate and electron withdrawing groups retard it. The order of reactivities of different substrates studied is: m-xylene > p-xylene > o-xylene > toluene > m-chlorotoluene > p-chlorotoluene > m-nitrotoluene. The reactivity of m-xylene deserves special mention. We believe that this anomalous behaviour of m-xylene is due to the fact that besides side chain substitution, nuclear substitution also occurs. The product analysis confirms this.

We have not made any attempt to partition the overall rate behaviour of the nuclear and side chain substitution reaction rates because such a partition based on approximate percentage of products may not be accurate.

(vi) The plot of log $k_1$ versus $\sigma^+$ is linear with a $\rho^+$ value of $-3.33$ (Fig. 1). This $\rho^+$ value is in consonance with a mechanism involving the formation of an electron-deficient carbon adjacent to an aromatic ring.

(vii) In order to evaluate the various activation parameters the reaction has been carried out at various temperatures in the range 30-45°C. The plots of log $k_1$ versus $1/T$ are linear. The computed values of various activation parameters are recorded in Table 5.

**Mechanism**

The literature reports chlorination and bromination studies at elevated temperatures in non-aqueous medium and in the presence of large concentration of acid: in all these studies radical initiation is the favoured reaction. Under mild acid conditions, such as in aqueous acetic acid medium presently employed, the formation of positive chlorine rather than the radical would be more plausible. In consonance with this observation no polymerisation of acrylamide occurred in the present study.
Based on the results obtained, a plausible mechanism shown in Scheme 1 is proposed. The reaction involves positive halogen transfer by an electrophilic nuclear pathway to the carbon having the alkyl group. The benzenonium ion thus generated rearranges to give the side chain halogenated product. This mechanism holds good for all substrates except m-xylene, where in addition to side chain halogenation by the above pathway, electrophilic substitution without rearrangement to give nuclear chlorinated product, 4-chloro-3-methyltoluene is also occurring. This peculiarity is due to the double activation of the position-4 in m-xylene. In ortho- and para-xylenes there is no such double activation of any position by both the methyl groups.

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References
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(R = CH₃ or H as the case may be)

(1) Side Chain Halogenation

(2) Nuclear Halogenation

Scheme 1