Kinetics of the Oxidation of Ethylene Diamine Tetra Acetic Acid by Chloramine-T

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Chloramine-T, kinetics, ethylene diamine tetra acetic acid

The kinetics of the oxidation of ethylene diamine tetra acetic acid (EDTA) by chloramine-T in acidic media has been investigated. The reaction shows first order dependence in chloramine-T and the order in hydrogen ion and substrate is fractional. On the basis of kinetic results a plausible mechanism is suggested. Activation parameters have also been calculated.

Chloramine-T, the sodium salt of \( \rho \)-toluene sulfonamid chloride is a powerful oxidizing agent and has been widely used for the direct and indirect estimation of several organic and inorganic compounds. The literature dealing with the kinetics and mechanism of the oxidations by chloramine-T is, however, scanty. Some work has been carried out on the problem in the last decade.

In the present communication, the chloraminometric oxidations of ethylene diamine tetra acetic acid (EDTA) has been studied in acidic media. The kinetic data show a first order dependence in chloramine-T and fractional order dependence in hydrogen ion and substrate.

Experiments

E. Merck, p. a., sample of chloramine-T was used and the solution was stored in black coated bottle to prevent photochemical decomposition. The strength was determined using iodometric method. Disodium ethylene diamine tetra acetate dehydrate \( \text{(Na}_2\text{H}_2\text{Y} \cdot 2\text{H}_2\text{O}) \) and all others chemicals used were of analytical reagent grade and their solutions were prepared in double distilled water. The reactions were carried out in Jena glass reaction bottles blackened from outside.

Kinetics was followed by estimating unconsumed chloramine-T iodometrically using starch as an indicator.

Stoichiometry

Reaction mixture containing excess of chloramine-T over EDTA was allowed to equilibrate at 50°C at \( \text{pH} = 5.00 \). The results showed that seven moles of chloramine-T were consumed per mole oxidation of EDTA and accordingly the stoichiometry may be represented as follows:

\[
7 \text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{N} \cdot \text{NaCl} + (\text{H}_2\text{Y})^- = 7 \text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NH}_2 + 7 \text{NaCl} + \text{organic products}
\]

Results

Kinetics of the oxidation of EDTA were investigated at several concentration of the reactants at constant pH. The results show first order dependence in chloramine-T and fractional order in EDTA concentration (Table I). The order of the reaction in substrate was found as 0.5 from the slope of the plot of log \( k_1 \) against log (EDTA) (Fig. 1).

![Fig. 1. Plot of log \( k_1 \) versus log [EDTA] at pH = 5.4 and [CAT] = 1 \cdot 10^{-3} \text{ m}].

The reaction was found to show slight dependence on the pH of the reaction mixture. The effect of pH on the reaction rate was followed at constant ionic strength maintained by excess of \( \text{NaClO}_4 \).

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Table I. Dependence of reactants concentrations*.

<table>
<thead>
<tr>
<th>[Chloramine-T] [M]</th>
<th>[EDTA] [M]</th>
<th>$k_1 \cdot 10^4$ [sec$^{-1}$]</th>
<th>$k_1 \cdot 10^3$ [EDTA]$^{1/2}$ [1/sec moles$^{-1/2}$]</th>
</tr>
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<td>-</td>
</tr>
<tr>
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<td>1.58</td>
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</tr>
<tr>
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<tr>
<td>1.0</td>
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<td>2.20</td>
<td>2.01</td>
</tr>
</tbody>
</table>

*pH = 5.4 and temperature = 30°C ± 0.1.

reaction mixture, the order of the reaction with respect to H$^+$ ion was calculated as 0.3 (Fig. 2). Insignificant effect of ionic strength and dielectric constant of the media on the rate of the oxidation was observed.

![Fig. 2. Plot of log $k_1$ versus pH of the reaction mixture at [CAT] = 1 • 10$^{-3}$ M.](image)

Important thermodynamic parameters characterising the reaction were obtained by following the oxidation rates at five temperatures (30 to 50°C). The energy of activation, entropy of activation and frequency factor were computed as 19.2 kcal/mole, −2.50 e.u. and 2.86 • 10$^{12}$ sec$^{-1}$ respectively.

**Discussion**

It is well known that in acidic solution EDTA would exist in the protonated form (H$_4$Y) and formed through the protonation of the anion (H$_2$Y)$^{2-}$ as follows$^{10}$:

$$\text{HOCH}_2\text{C} \rightarrow \text{N CH}_2\text{CH}_2 \rightarrow \text{N CH}_2\text{CH}_2\text{N} \rightarrow \text{CH}_2\text{CO}_2\text{H} + 2 \text{H}^+$$

The protonated form of EDTA (H$_4$Y) is a more reactive species and will predominate in acidic media.

Further, it is well known that chloramine-T in acid solutions hydrolyses$^{11}$ as

$$\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NCl}^- + \text{H}_2\text{O} \rightarrow \text{CAT}^- \rightarrow \text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NHCl} + \text{H}_2\text{O} \ldots \text{(3)}$$

where CAT$^-$ is $p$-toluene sulfochloramide.

During the oxidation of hexacyanoferrate(II)$^6$, $p$-cresol$^2$ and methyl aryl sulphides$^4$ by chloramine-T in acidic media where H$^+$ ions have an accelerating effect, CAT$^-$ has been suggested as the main reacting species. Thus from a consideration of this species present in the solution and from the results presented above following mechanism of this reaction is suggested:

$$\text{(H}_2\text{Y)}^{2-} + 2 \text{H}^+ \rightarrow \frac{k_1}{k_{-1}} \text{H}_4\text{Y} \quad \text{fast} \ldots \text{(2)}$$

$$\text{CAT}^- + \text{H}^+ \rightarrow \frac{k_3}{k_{-2}} \text{CAT}^' \quad \text{fast} \ldots \text{(3)}$$

$$\text{H}_4\text{Y} + \text{CAT}^' \rightarrow \frac{k_3}{k_{4}} \text{X (Intermediate) slow} \ldots \text{(4)}$$

$$\text{X} + 6 \text{CAT}^' \rightarrow \frac{k_{4}}{k_{3}} \text{Products fast} \ldots \text{(5)}$$

Applying steady state conditions with respect to all the intermediates and after making some reasonable approximations, the following rate law equation is obtained:

$$\text{Rate} = \frac{k_1 k_{-1} k_2 [\text{CAT}] [\text{EDTA}] [\text{H}^+]^2}{k_{-2}^2 k_{-3} + k_1 k_{-1} k_3 [\text{EDTA}] [\text{H}^+]^2} \ldots \text{(6)}$$

where (H$_2$Y)$^{2-} = \text{EDTA}$.

The above rate law Equ. (6) successfully predicts the first order dependence in chloramine-T and the fractional order dependence in EDTA and hydrogen ion as under the conditions of study $k_{-2} k_{-3}$ can not be neglected as compared to $k_1 k_{-1} k_3$ [EDTA] [H$^+$]$^2$, and consequently an increase in H$^+$ ion or EDTA concentration (two, three or many fold) will not affect the rate in the same ratio. The change in reaction rate will, therefore, correspond to a very slight increase with the increasing [EDTA] or [H$^+$] concen-
tration and justifies a fractional order dependence \( \text{viz.} \ 0.3 \) and \( 0.5 \) in \([\text{H}^+]\) and \([\text{EDTA}]\) respectively.

The values of energy of activation, entropy of activation, insignificant effect of ionic strength and dielectric constant variation also confirm the rate controlling step (4) in the proposed mechanism.

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8. S. P. Mushran, R. Sanehi, and M. C. Agrawal, ibid. 27b, 1161 [1972].
9. A. Berka and J. Zyka, Ceskoslov. Farmac. 5, 335 [1956].