Kinetics of tween-80 micellar catalysed chloramine-T oxidation of vitamins in HClO$_4$ medium

Varuna Shukla & Santosh K Upadhyay*
Department of Chemistry, H B Technological Institute, Kanpur 208 002, India
Email: upadhyay_s_k@rediffmail.com

Received 16 April 2008; revised 7 November 2008

A catalytic effect of non-ionic (tween-80) micelles on the rate of oxidation of thiaminehydrochloride (vitamin B$_1$) and pyridoxine hydrochloride (vitamin B$_6$) by sodium salt of p-toluene sulphonamide (chloramine-T) in acidic medium has been observed and rate has been found to be proportional to \((k' + k'' [\text{Tween-80}])\), where \(k'\) and \(k''\) are the rate constants in absence and in presence of surfactant, respectively. The rate showed a first order, a fractional order and a zero order dependence on \([\text{Chloramine-T}]_0\), \([\text{Vitamin}]_0\) and \([\text{H}^+\])$_0$, respectively. The association/binding between the oxidant and the surfactant micelle is supported by the spectrophotometric evidence. A mechanism has been proposed and binding parameters have been evaluated.

Keywords: Kinetics of tween-80, Micellar catalyzed, Oxidation of vitamins, Chloramine-T

Due to analogy between enzyme catalyzed and micelles catalyzed reactions, the micellar catalysis has received a considerable attention of investigators. The accelerating/retarding effect of surfactant on the rate of oxidation of amino acids$^{1-3}$, reducing sugars$^{4-6}$, vitamins$^7$, drugs$^{8-11}$ etc by various oxidants is reported. A catalytic action of tween-80 micelles on the rate of oxidation of vitamins B$_1$ and B$_6$ by chloramine-T in perchloric acid medium has been observed. Therefore, the reaction has been studied in detail and results are communicated in the present paper.

Experimental Procedure

Materials and Methods

Stock solution of chloramine-T (Thomas Baker A.R.) was prepared in doubly distilled water. Aqueous solutions of vitamin B$_1$ and vitamin B$_6$ (s.d. fine, A.R.) were prepared just before the experiment. The purity of surfactant tween-80 (Thomas Baker) was checked by determining the critical micelle concentration (CMC) from the surface tension measurement and matching that with reported CMC in literature. Observed CMC was $1.1 \times 10^{-5}$ mol dm$^{-3}$ while that is reported$^{12}$ as $1.2 \times 10^{-5}$ mol dm$^{-3}$. The solution of surfactant was prepared in double distilled water just before the experiment to avoid ageing. Other reagents viz. HClO$_4$, KI, sodium thiosulphate (hypo), starch etc. used were of analytical grade. Double distilled (first time from alkaline KMnO$_4$) deionised water was used throughout.

Kinetic measurements

Appropriate quantities of solutions of vitamin, HClO$_4$ and surfactant were placed in 100 mL jena glass vessel. The requisite amount of doubly distilled water was added so that the total volume of reaction mixture was 50 mL after adding chloramine-T. The reaction mixture was then placed in a thermostat at desired temperature $\pm 0.1^\circ$C. The reaction mixture was allowed to attain the bath temperature and the reaction was then initiated by adding the requisite amount of chloramine-T, placed separately in water bath. The progress of reaction was followed by determining chloramine-T iodometrically in aliquots, withdrawn after regular time intervals. The reaction mixture was homogeneous.

Stoichiometry and product analysis

The stoichiometry of the reaction between vitamins and chloramine-T has been studied. The reaction mixtures containing a known excess of [Chloramine-T] over [Vitamin] were kept in presence of a fixed amounts of HClO$_4$ and surfactant at room temperature for 72 h until the reactions were complete. The unreacted amount of chloramine-T left in the reaction mixture showed a 1:1 stoichiometry ratio between chloramine-T and vitamin.
The reaction may be represented by following stoichiometric equation.

\[
\begin{align*}
\text{RNNaCl} + R'\text{CH}_2\text{OH} & \rightarrow \text{RNH}_2 + R'\text{CHO} + \text{NaCl} \\
\text{R} &= \text{CH}_2\text{O} - \text{SO}_2^- \\
\text{N} &\text{H}_2\text{HCl} \\
\text{R'} &= \text{CH}_2 - \text{N} - \text{C}_2\text{H}_5 \\
\text{HOH}_2\text{C} - \text{OH} & \quad \text{in case of vitamin B}_1 \\
\text{CH}_3 & \quad \text{in case of vitamin B}_6
\end{align*}
\]

Presence of aldehyde group in the oxidation product of vitamin was conformed by forming its derivative with 2, 4-dinitrophenyl hydrazine.

**Determination of rate constant**

The reaction were initially fast up to 10-15% of reaction, then log (a-x) versus time plots [where (a-x) represents the unreacted amount of chloramine-T at any time t] were linear. Therefore, the pseudo-first order rate constant in chloramine-T have been evaluated from the slopes of linear part of the plots of log (a-x) versus time. The observed rate constants \( k_w \), in absence of tween-80 and \( k_\psi \) in presence of tween-80 were reproducible within \( \pm 5\% \) in replicate kinetic runs.

**Spectrophotometric evidences for the association between chloramine-T and tween-80**

In order to confirm any association or binding between the surfactant and the reactants the spectrum of the surfactant and reactants were taken on a double beam spectrophotometer (Systronics 2203, India). A solution of chloramine-T (2.0 \( \times \) 10\(^{-4}\) mol dm\(^{-3}\)) in presence of HClO\(_4\) (1.0 \( \times \) 10\(^{-3}\) mol dm\(^{-3}\)) gave a peak value at 232 nm. A shift in peak value from 232 to 237 nm was observed when the tween-80 was added in the solution. The absorbance of a series of solution containing a fixed amount of chloramine-T (2.0 \( \times \) 10\(^{-4}\) mol dm\(^{-3}\)) and HClO\(_4\) (1.0 \( \times \) 10\(^{-3}\) mol dm\(^{-3}\)) and a varying amount of tween-80 were measured at 237 nm. The results in the form of (Absorbance) versus [Tween-80] at room temperature. [Chloramine-T] = 2.0 \( \times \) 10\(^{-4}\) mol dm\(^{-3}\) and [HClO\(_4\)] = 1.0 \( \times \) 10\(^{-3}\) mol dm\(^{-3}\).

**Results**

The kinetics was studied at various initial concentrations of the reactants in absence as well as in presence of surfactant. The kinetic results for a variation in [Substrate], [Oxidant] and [HClO\(_4\)] in absence and in presence of surfactant were almost similar. Therefore, the kinetic results in presence of surfactant are reported. The observed pseudo-first order rate constant in chloramine-T (\( k_\psi \)) in presence of tween-80 at various initial concentrations of reactants are reported in Table 1. Nearly same value of \( k_\psi \) at different [Chloramine-T] or [H\(^+\)] suggests a first order dependence of rate with respect to chloramine-T and a zero-order dependence of rate with respect to H\(^+\), respectively.

On increasing the concentrations of vitamin in reaction mixture, an increase in \( k_\psi \) was observed. A double reciprocal plot i.e. plot of log \( k_\psi \) versus log [Vitamin] was linear with a slope nearly \( \pm 0.5 \) in case of each vitamin, suggesting a fractional order dependence of rate with respect to substrate.

The effect of variation of ionic strength (addition of NaClO\(_4\)) in the reaction mixture had a negligible effect on the rate of oxidation, suggesting the involvement of at least one neutral species in the rate.
determining step. The addition of \( p \)-toluene sulphonamide (i.e. RNH₂, reaction product from chloramine-T) had also a negligible effect on the rate of oxidation indicating that chloramine-T (RNNaCl) and \( p \)-toluene sulphonamide (RNH₂) do not involve in reversible step.

The effect of surfactant [Tween-80] on the rate of oxidation has been studied over a wide concentration range of the surfactant and at three different temperatures (35, 40 and 45°C). The rate surfactant profile i.e. the plot of \( k_\psi \) versus [Tween-80] (Fig. 2) was linear with a positive intercept suggesting that the rate is proportional to \( k' + k'' [\text{TWEEN-80}] \), where \( k' \) and \( k'' \) are the rate constants in absence and in presence of the surfactant, respectively. The rate constant in absence of surfactant when [Surfactant]=0, was matching with value of the intercept of the plot of \( k_\psi \) versus [Tween-80] (Fig. 2).

The activation parameters in absence as well as in presence of tween-80 have been evaluated (Table 2). A decrease in energy of activation (\( \Delta E_a^b \)) in presence of tween-80 is in favour of catalysis by Tween-80. A more negative value of \( \Delta S^a \) (entropy of activation) indicates the more compactness of transition state in presence of the surfactant. Nearly same value of \( \Delta G^a \), in absence as well as in presence of surfactant has been observed, which indicate the similar mechanism in aqueous and micellar medium.

**Table 1 — Effect of reactants concentration on the rate constants in presence of tween-80 at 35°C.**

<table>
<thead>
<tr>
<th>[CAT]×10³ (mol dm⁻³)</th>
<th>[HClO₄]×10³ (mol dm⁻³)</th>
<th>[Vitamin] x 10² (mol dm⁻³)</th>
<th>( k_\psi \times 10^4 ) (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vitamin B₁</td>
<td>Vitamin B₆</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>2.0</td>
<td>2.0</td>
<td>1.60</td>
</tr>
<tr>
<td>1.5</td>
<td>2.0</td>
<td>2.0</td>
<td>1.55</td>
</tr>
<tr>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>1.53</td>
</tr>
<tr>
<td>2.5</td>
<td>2.0</td>
<td>2.0</td>
<td>1.53</td>
</tr>
<tr>
<td>3.0</td>
<td>2.0</td>
<td>2.0</td>
<td>1.50</td>
</tr>
<tr>
<td>2.0</td>
<td>1.0</td>
<td>2.0</td>
<td>1.53</td>
</tr>
<tr>
<td>2.0</td>
<td>3.0</td>
<td>2.0</td>
<td>1.50</td>
</tr>
<tr>
<td>2.0</td>
<td>4.0</td>
<td>2.0</td>
<td>1.50</td>
</tr>
<tr>
<td>2.0</td>
<td>6.0</td>
<td>2.0</td>
<td>1.50</td>
</tr>
<tr>
<td>2.0</td>
<td>8.0</td>
<td>2.0</td>
<td>1.50</td>
</tr>
<tr>
<td>2.0</td>
<td>2.0</td>
<td>0.5</td>
<td>0.38</td>
</tr>
<tr>
<td>2.0</td>
<td>2.0</td>
<td>1.0</td>
<td>0.76</td>
</tr>
<tr>
<td>2.0</td>
<td>2.0</td>
<td>1.5</td>
<td>1.15</td>
</tr>
<tr>
<td>2.0</td>
<td>2.0</td>
<td>3.0</td>
<td>2.30</td>
</tr>
<tr>
<td>2.0</td>
<td>2.0</td>
<td>4.0</td>
<td>3.07</td>
</tr>
</tbody>
</table>

[Tween-80]=2.0×10⁻⁴ mol dm⁻³ for vitamin B₁ and 2.66 × 10⁻⁴ mol dm⁻³ for vitamin B₆. CMC of tween-80 – 1.2 × 10⁻⁵ mol dm⁻³.

**Discussion**

Chloramine-T behaves as a strong electrolyte\(^{15,16}\) in aqueous solutions and ionises as given in equilibrium (i)

\[
\text{RNCl}^– + \text{H}^+ \rightleftharpoons \text{RNH}_2 \text{Cl}\]

(\( K_a = 3.8 \times 10^4 \) at 25°C  \( \text{and } [\text{HClO}_4] = 2.0 \times 10^{-3} \text{ mol dm}^{-3} \))

The anion \( \text{RNCl}^– \) gets protonated\(^{15,16}\) in acidic solutions to give \( N \)-chlorotoluene \( p \)-sulphonamide (RNH₂Cl) as

\[
\text{RNCl}^– + \text{H}^+ \rightleftharpoons \text{RNH}_2^+ \text{Cl} \quad \text{Keq} = 103 \text{ mol}^{-1} \text{ dm}^3 \text{ at 25°C} \quad \text{(iii)}
\]

It has also been observed by Rao and coworkers\(^{17,18}\) that at higher acid strength RNHCl is further protonated according to Eq (iii)
Thus in acidic medium RNHCl, RNH₂+Cl and chloramine-T itself, are possible oxidising species of chloramine-T.

Dichloramine-T or HOCl has also been considered as the reacting species of chloramine-T which is produced due to disproportionation or hydrolysis, respectively, of RNHCl as follows,

\[ \text{RNHCl} + \text{H}_2\text{O} \rightarrow \text{RNH}_2 + \text{HOCl}; \quad K_h = 4.9 \times 10^{-8} \text{ at 25ºC} \quad \text{(v)} \]

On considering NH₂+Cl is the reactive species of the chloramine-T, a acceleration effect of H⁺ on the rate is expected. Further if, RNCl₂ or HOCl is the reactive species, a second order dependence of rate with respect to chloramine-T and a retarding effect of RNH₂(p-sulphonamide) on the rate is expected. The experimental results (i.e. a first order dependence of rate with respect to chloramine-T, negligible effect of H⁺ or RNH₂ on the rate) are not in favour of RNCl₂, HOCl or RNH₂+Cl as the reactive species of chloramine-T. Since chloramine-T exists as free acid (RNHCl) in acidic medium, RNHCl may be considered as the only reactive species of chloramine-T in present conditions.

Formation of aggregation i.e. micelle of the surfactant and incorporation/association/solubilisation of the substrate with the micelle has been reported. The spectrophotometric evidence also favours the association of chloramine-T with surfactant micelle.

On the basis of experimental results and present spectrophotometric evidence of association for the chloramine-T with surfactant, a common mechanism for the oxidation of vitamins by chloramine - T is proposed (scheme I),

\[
\begin{align*}
\text{RNHCl} + \text{R′CH}_2\text{OH} &\rightarrow k_i \rightarrow \text{R′CH}_2\text{O} - \text{H} - \text{N} - \text{R} \quad \text{(Vitamin)} \quad \text{H} \\
\text{(CAT)} &\rightarrow \text{Cl} \\
\text{RNHCl} + \text{R′CHO} &\rightarrow k_i \rightarrow \text{RNH}_2 + \text{HOCl} \quad \text{(products)} \\
\text{(CAT)} &\rightarrow \text{Cl} \\
\text{RNHCl} + \text{R′CH}_2\text{OH} &\rightarrow k_s \rightarrow \text{R′″CH}_2\text{O} - \text{H} - \text{N} - \text{R} \quad \text{(Vitamin)} \quad \text{H} \\
\text{(CAT)} &\rightarrow \text{Cl} \\
\text{RNHCl} + \text{R′CH}_2\text{OH} + \text{R′CHO} &\rightarrow k_i \rightarrow \text{RNH}_2 + \text{HCl} \quad \text{(products)} \\
\text{(CAT)} &\rightarrow \text{Cl} \\
\end{align*}
\]

Scheme I

According to scheme I, the rate of disappearance of chloramine-T may be given as,

\[
-\frac{\text{d}[\text{CAT}]}{\text{dt}} = k_2[X_T] + k_4[Y_T] [\text{Vitamin}] \quad \ldots(1)
\]

Again,

\[ [X_T] = K_1[\text{CAT}][\text{Vitamin}] \quad \text{from step (a)} \]

and

\[ [Y_T] = K_3[\text{CAT}][\text{Tween-80}] \quad \text{from step (c)} \]

Therefore, the rate law (1) may be written as

\[
-\frac{\text{d}[\text{CAT}]}{\text{dt}} = [\text{Vitamin}] [k_2K_1 + k_4K_3][\text{Tween-80}] \quad \ldots(2)
\]

Now, the total concentration of chloramine - T, at any time may be given as,
\[ [\text{CAT}]_T = [\text{CAT}] + [\text{X}_T] + [\text{Y}_T] \quad \ldots(3) \]

On substituting the values of \([X_T]\) and \([Y_T]\) in Eq. (3) and solving it, the value of \([\text{CAT}]\) in terms of \([\text{CAT}]_T\) may be obtained as,

\[ [\text{CAT}] = \frac{[\text{CAT}]_T}{1 + K_1[\text{Vitamin}] + K_2[\text{Tween-80}]} \quad \ldots(4) \]

Therefore, the rate law (2) becomes as,

\[ \frac{d[\text{CAT}]}{dt} = [\text{CAT}]_w[\text{Vitamin}][k_1 + k_2 K_1[\text{Tween-80}]] \quad \ldots(5) \]

Further, at high concentrations of vitamin or at lower concentrations of surfactant the approximation \((1 + K_1[\text{Vitamin}]) >> K_3[\text{Tween-80}]\) may be taken and, therefore, the rate law (5) reduces to

\[ \frac{d[\text{CAT}]}{dt} = \frac{[\text{CAT}]_w[\text{Vitamin}][k_1 + k_2 K_1[\text{Tween-80}]]}{1 + K_2[\text{Vitamin}] + K_3[\text{Tween-80}]} \quad \ldots(6) \]

The rate laws (5) is in agreement with the experimental results i.e. first order, fractional order and zero order dependence of rate with respect to oxidant, substrate and acid, respectively. The rate is proportional to \(\{k_1 + k_2'[\text{Tween-80}]\}\) which has also been observed experimentally.

To evaluate the binding constants between chloramine-T and surfactant, the kinetic data have been analysed in terms of pseudo-phase kinetic model for micellar catalysis reported by Menger and Portnoy’s\(^{22}\). According to Menger and Portnoy model the solubilisation/incorporation/association of the reactant (chloramine-T) into the micellar phase is given in scheme II.

\[ \begin{align*}
(CAT)_m & \xrightarrow{k_w} \text{products} \\
K_0 & + D_n \\
(CAT)_m & \xrightarrow{k_m} \text{products}
\end{align*} \]

\text{Scheme II}

where, \(k_w\) and \(k_m\) are rate constants in aqueous phase and micellar medium, respectively. \(k_w\) is observed rate constant and \(K_0\) [which is same as \(K_3\) in step (c) of scheme I] is the binding constant for association of chloramine-T with surfactant micelle (\(D_n\)).

According to above scheme and observed rate law, the observed rate constant (\(k_w\)) may be given as,

\[ k_w = \frac{k_1 + k_2 K_1[D_n - \text{CMC}]}{1 + K_2[D_n - \text{CMC}]} \quad \ldots(7) \]

The Eq. (7) may be rearranged in form of Eq. (8) which has been found to hold good for micelle catalysis in various reactions\(^{23-25}\).

\[ \frac{1}{(k_w - k_m)} = \frac{1}{(k_w - k_m)} + \frac{1}{K_0(k_m - k_m)}[\text{[D] - CMC}] \quad \ldots(8) \]

According to Eq. (8), a plot of \(1/(k_w - k_m)\) against \(1/([\text{D}] - \text{CMC})\) should be linear with an intercept. The values of \(k_m\) (rate constant in micellar phase) and \(K_0\) (binding constant) may also be evaluated with the help of intercept and slope of the linear plot.

The kinetic data have been analysed in terms of Menger and Portnoy’s model. The plot of \(1/(k_w - k_m)\) against \(1/([\text{D}] - \text{CMC})\) in case of each vitamin at different temperatures have been found to be linear (Fig. 3). The values of \(K_0\) and \(k_m\) have also been

Fig. 3—Plots of \(1/(k_w - k_m)\) versus \(1/([\text{D}] - \text{CMC})\) at different temperatures. \(\text{[Chloramine - T]} = 2.0 \times 10^{-3}\ \text{mol dm}^{-3}\), \(\text{[Vitamin]} = 2.0 \times 10^{-2}\ \text{mol dm}^{-3}\) and \(\text{[HClO}_4\text{]} = 2.0 \times 10^{-3}\ \text{mol dm}^{-3}\).
Table 3 — Binding constant ($K_0$) and rate constants in micellar phase ($k_m$) evaluated using Menger and Portnay’s model.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Temperature (°C)</th>
<th>$K_0$</th>
<th>$K_m \times 10^4$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vitamin B$_1$</td>
<td>35</td>
<td>275.00</td>
<td>14.09</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>294.11</td>
<td>17.15</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>444.40</td>
<td>21.53</td>
</tr>
<tr>
<td>Vitamin B$_6$</td>
<td>35</td>
<td>199.04</td>
<td>32.76</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>206.36</td>
<td>47.24</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>312.5</td>
<td>66.87</td>
</tr>
</tbody>
</table>

It is observed that the value of $k_m$ or $K_0$ increases on increasing temperature.

Thus it is observed that the oxidation of vitamins by chloramine-T in non-ionic micellar medium proceeds via incorporation/association of chloramine-T with surfactant micelle.

Acknowledgement

Thanks are due to Prof. S K Awasthi, Director, H B T I, Kanpur for his keen interest in the work.

References