MECHANISTIC INVESTIGATION OF OXIDATION OF VITAMIN B6 BY DIPERIODATOARGENTATE(III) IN AQUEOUS ALKALINE MEDIUM

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ABSTRACT
The kinetics of oxidation of vitamin B₆ (Pyridoxine Hydrochloride) by diperiodatoargentate(III) (DPA) in aqueous alkaline medium at a constant ionic strength of 0.50 mol dm⁻³ was studied spectrophotometrically. The main oxidation product was identified as aldehyde (pyridoxinal). The stoichiometry was [Vit B₆]: [DPA] = 1:1. The reaction was first order with respect to [DPA] whereas the order with respect to vitamin B₆ and alkali concentrations changes from first order to zero order as the vitamin B₆ and alkali concentrations are increased. Addition of periodate had no effect on the rate of the reaction. Effect of added products, ionic strength and dielectric constant of the reaction medium has been investigated. Based on experimental results, a mechanism involving complex formation between DPA species and vitamin B₆ was proposed. The reaction constants involved in the mechanism were evaluated. The activation parameters with respect to the slow step of the mechanism were determined and discussed.

KEYWORDS: DPA, Vitamin B₆, oxidation, uncatalysed, mechanism and kinetics.

INTRODUCTION
Vitamin B₆ (vit B₆) is an essential nutrient that must continually replenish as it is water – soluble, that means unused vit B₆ is excreted through the urine and not stored. One of the primary functions of vit B₆ is to metabolise or break down, the protein and fat we consume.[1] It is required for both mental and physical health. The deficiency of vit B₆ leads to many types of illness and diseases.[2] It also finds applications in pharmaceutical industries. Pyridoxinal phosphate is co-enzymes for aminoacid decarboxylase and transaminase.
Diperiodatoargentate(III) (DPA) is a powerful oxidizing agent in alkaline medium with the reduction potential $^{[3]} 1.74$ V. It is widely used as a volumetric reagent for the determination of various organic and inorganic species.$^{[4]}$ Jayaprakash Rao and other researchers have studied DPA as an oxidizing agent for the kinetics of oxidation of some organic substrates.$^{[5]}$ They normally found that order with respect to oxidant was unity and substrate was fraction. The $[$OH$^{-}]$ was found to enhance the rate of reaction. It was also observed that they did not arrive at the possible active species of DPA in alkali, and on the other hand they proposed mechanism by generalizing the DPA as $[Ag(HL)L]^{[3+1]}$. However, Kumar et al.$^{[6,7]}$ put an effort to give an evidence for the reactive form of DPA in large scale of alkaline pH. Ag(III) complex can be stabilized in alkaline medium by periodate or tellurate ions.$^{[8,9]}$ When the silver (III) species are involved, it would be interesting to know which of the species is the active oxidant. Literature survey reveals that oxidation of pyridoxine by different oxidants such as acidic MnO$_2$$^{[10]}$, N-bromamine$^{[11]}$, acidic Mn(III)$^{[12]}$ and N-Chloramine$^{[13]}$ have been studied. In view of pharmaceutical importance of vit B$_6$ and lack of literature on oxidation of vit B$_6$ by DPA, the present investigation was undertaken to know the reactive species for DPA in alkaline medium and to propose a possible mechanism.

**EXPERIMENTAL**

**MATERIALS**

The chemicals used were of reagent grade and double distilled water was used throughout the work. Vit B$_6$ (s.d.fine chem.) was used as received. The stock solution of vit B$_6$ was prepared by dissolving the appropriate amount in water. The required concentration of vit B$_6$ in the reaction was used from its stock solution. The solid DPA complex was prepared by the known method.$^{[14]}$ Aqueous solution of AgNO$_3$ was used to study the product effect, Ag(I). The complex was characterized from its U.V spectrum, exhibited three peaks at 216, 255 and 362 nm. These spectral features were identical to those reported.$^{[14]}$ earlier for DPA. The magnetic moment study revealed that the complex is diamagnetic. The prepared compound was analysed$^{[15]}$ for silver and periodate by acidifying a solution of the material with HCl, recovering and weighing the AgCl for Ag, and titrating the iodine liberated when excess KI was added to the filtrate for IO$_4^{-}$. The aqueous solution of DPA was used for the required concentration in the reaction mixture. Periodate (BDH) solution was prepared in hot water and used after 24 hours. Its concentration was ascertained iodometrically$^{[16]}$ at neutral pH maintained by a phosphate buffer. KOH and KNO$_3$ (BDH, AR) were employed to maintain required alkalinity and ionic strength of the reaction respectively.
Methodology

DPA was prepared by oxidizing Ag(I) in presence of KIO4 as described\textsuperscript{[14]}: the mixture of 28 g of KOH and 23 g of KIO4 in 100 cm\textsuperscript{3} of water along with 8.5 g AgNO\textsubscript{3} was heated just to boiling and 20 g of K\textsubscript{2}S\textsubscript{2}O\textsubscript{8} was added in several lots with stirring then allowed to cool. It was filtered through a medium porosity fritted glass filter and 40 g of NaOH was added slowly to the filtrate, whereupon a voluminous orange precipitate agglomerates. The precipitate was filtered as above and washed three to four times with cold water. The pure crystals were dissolved in 50 cm\textsuperscript{3} water and warmed to 80\textdegree C with constant stirring thereby some solid was dissolved to give a red solution. The resulting solution was filtered when it was hot and on cooling at room temperature, the orange crystals separated out and were crystallized from water.

Kinetic studies

The kinetic measurements were performed on a Varian CARY 50 Bio UV-vis spectrophotometer under pseudo first-order conditions where vit B\textsubscript{6} concentration was in excess over DPA(III) concentrations (atleast 10 times) at a constant ionic strength of 0.50 mol dm\textsuperscript{-3} and at constant temperature, (25.0\pm0.1)\textdegree C, unless otherwise specified. The reaction was initiated by adding the DPA to the vit B\textsubscript{6} solution, which also contained the required quantities of periodate, potassium hydroxide and potassium nitrate and the progress of the reaction was followed spectrophotometrically at 360 nm by monitoring the decrease in absorbance due to DPA, where all other species do not absorb significantly at this wavelength. DPA concentration from 0.5 to 5.0x10\textsuperscript{5} mol dm\textsuperscript{-3} in 0.30 mol dm\textsuperscript{-3} alkali obeyed Beer’s law with molar absorbance index, \(\epsilon = 13844 \pm 100\) dm\textsuperscript{3} mol\textsuperscript{-1} cm\textsuperscript{-1} at 360 nm. The first order rate constants \(k_{\text{obs}}\), were obtained by plots of log (absorbance) versus time (Figure 1). Most of the kinetic runs were followed to more than 80% completion of the reaction and the first order plots were linear. The rate constants \(k_{\text{obs}}\) were at least average of four sets and reproducible within \(\pm 5\%\). During the kinetics a constant concentration viz., 1.0x10\textsuperscript{-5} KIO\textsubscript{4} was used throughout the study unless otherwise stated. Thus the possibility of oxidation of vit B\textsubscript{6} by periodate was tested and it was found that there was no significant interference due to KIO\textsubscript{4} under the experimental conditions. The effect of oxygen on the reaction mixture was checked by following the reaction in an atmosphere of nitrogen. No significant difference in the results was observed in presence and absence of nitrogen. However, fresh solutions were always used while performing the experiment.
In view of the modest concentrations of alkali used in the reaction media, attention was also given to the effect of the surface of the reaction vessels on the kinetics. Use of polythene/acrylic equipment and quartz or polyacrylate cell gave the same results as with the glass vessels and cells. Regression coefficient $r$ and the standard deviation $S$, of points from the regression line, were performed with the Microsoft office Excel – 2003 program.

RESULTS

Stoichiometry and product analysis: Different sets of reaction mixtures containing different amounts of DPA and vit B$_6$ at constant ionic strength and alkali were allowed to react for about 2 h at 25±0.1°C in an inert atmosphere and then analysed. DPA (III) was estimated spectrophotometrically at 360 nm. The results indicated that one mole of vit B$_6$ consumes one mole of DPA according to Equation 1.

$$\text{Vit B}_6 + [\text{Ag(H}_2\text{IO}_6)(\text{H}_3\text{IO}_6)]^2\rightarrow \text{Ag(I)} + 2(\text{H}_3\text{IO}_6)^2$$

Equation 1

The main reaction products was identified as aldehyde (pyridoxinal) by spot test\cite{17}. The corresponding aldehyde was confirmed by preparing its 2,4,-DNP derivative. Such products were also obtained by other workers\cite{17b}. The nature of pyridoxinal was confirmed by its IR spectrum which showed a C=O stretching at 1712 cm$^{-1}$. Further, pyridoxinal was subjected to GC- mass spectral analysis. GC-MS data was obtained on a 17 A Shimadzu gas chromatograph with a QP-5050A Shimadzu mass spectrometer using EI ionization technique. The mass spectrum showed a molecular ion peak at 169 amu confirming pyridoxinal (Figure 2). All other peaks observed in GC-MS can be interpreted in accordance with observed structure of the product. The formation of free Ag$^+$ in solution was detected by adding KCl solution to the reaction mixture, which produced white turbidity due to the formation of AgCl. It was observed that the product did not undergo further oxidation under the present kinetic conditions.
Reaction Order
The reaction orders with respect to reactive species were determined from the slopes of log $k_{obs}$ versus log (conc.) plots, or $k_{obs}$ versus [reactant] plots by varying concentrations of the reductant, alkali and periodate, in turn while keeping others constant.

Effect of DPA
The DPA concentration was varied from $0.5 \times 10^{-5}$ to $5.0 \times 10^{-5}$ mol dm$^{-3}$. The linearity and almost parallel plots of log (absorbance) versus time ($r \geq 0.992$, $S \leq 0.0015$), indicates that reaction is first order with respect to DPA. This was also confirmed by varying the concentration of DPA, which did not show any change in pseudo-first order rate constants, $k_{obs}$ (Table 1).

Effect of vit B$_6$
The substrate, vit B$_6$ concentration was varied in the range of $0.5 \times 10^{-3}$ to $5.0 \times 10^{-3}$ mol dm$^{-3}$ at $25^0$C keeping all other reactant concentrations and conditions constant. The $k_{obs}$ values increased with increase in the concentration of vit B$_6$ (Table 1). At lower vit B$_6$ concentration the rate of oxidation shows first order dependence on vit B$_6$ concentration while at intermediate concentrations fractional order dependence was observed and at higher concentrations the oxidation was independent of vit B$_6$ concentrations. Hence the order with respect to vit B$_6$ concentrations changes from first order to zero order as the vit B$_6$ concentration changes from lower concentration to higher concentration.

Effect of Alkali
The effect of alkali concentration on the reaction was studied in the range of 0.05 to 0.50 mol dm$^{-3}$, at constant DPA and vit B$_6$ concentrations and at a constant ionic strength of 0.50 mol dm$^{-3}$ at $25^0$ C. The rate constants increased with increased in the concentration of alkali (Table 1). Similar that of vit B$_6$, the order with respect to alkali concentration also changes from first order to zero order as the alkali concentration changes from lower concentrations to higher concentrations.

Effect of IO$_4^-$
At constant oxidant, reductant and alkali concentration of $5.0 \times 10^{-5}$, $1.0 \times 10^{-3}$ and 0.3 mol dm$^{-3}$ respectively, and at $I=0.50$ mol dm$^{-3}$. IO$_4^-$ was varied between $1.0 \times 10^{-5}$ to $1.0 \times 10^{-4}$ mol dm$^{-3}$ and found that added IO$_4^-$ had no significant effect on the rate of the reaction (Table 1).
Effect of added products
Initially added products, Ag (I) and pyridoxinal, did not have any significant effect on the rate of the reaction.

Effect of dielectric constant and ionic strength
The relative permittivity (D) effect was studied by varying the t-butyl alcohol – water (V/V) content in the reaction mixture with all other conditions being maintained constant. It was found that dielectric constant of the medium had no significant effect on the rate of the reaction. The effect of ionic strength was studied by varying the potassium nitrate concentration. The ionic strength in the reaction medium was varied from 0.05 to 0.5 mol dm$^{-3}$ at constant concentrations of DPA, vit B$_6$ and alkali and it was observed that there was no effect of ionic strength on the rate of reaction.

Test for free radicals (Polymerisation study)
To test for free radicals, the reaction mixture containing acrylonitrile scavenger was kept for 24 h in an inert atmosphere. On diluting the reaction mixture with methanol, no precipitate was observed, indicating that there is no intervention of free radicals in the reaction.

From the above results the experimental rate law are given as follows:
(1) At low vit B$_6$ and Alkali concentrations
$$-\text{d}[\text{DPA}]/\text{dt} = k_{\text{obs}} [\text{DPA}] [\text{Vit B}_6] [\text{OH}^-]$$

(2) At intermediate vit B$_6$ and alkali concentrations
$$-\text{d}[\text{DPA}]/\text{dt} = k_{\text{obs}} [\text{DPA}] [\text{Vit B}_6]^{0.33} [\text{OH}^-]^{0.20}$$

(3) At higher vit B$_6$ and alkali concentrations
$$-\text{d}[\text{DPA}]/\text{dt} = k_{\text{obs}}[\text{DPA}]$$

Effect of temperature.
The rate of reaction was measured at four different temperatures with varying vit B$_6$ concentrations keeping other conditions constant. The rate was found to increase with increase in temperature. The rate constant k, of the slow step of Scheme 1 was obtained from the slopes and intercepts of the plots of $1/k_{\text{obs}}$ versus $1/[\text{Vit B}_6]$ ($r\geq0.988$, $S\leq0.0056$) and $1/k_{\text{obs}}$ versus $1/[\text{OH}^-]$ ($r\geq0.951$, $S\leq0.0027$) at four different temperatures. The energy of activation was calculated from the plot of log k versus 1/T, from which the activation parameters were calculated and are listed in Table 2.
DISCUSSION

The literature survey\textsuperscript{[14]} reveals that the water soluble DPA has a formula $[\text{Ag(IO}_6^2\text{)}_2]^{7-}$ with a square planar structure. When the same molecule is used in alkaline medium it is unlikely to exist as $[\text{Ag(IO}_6^2\text{)}_2]^{7-}$. The periodate is known to be in various protonated forms\textsuperscript{[18]} depending on pH of the solution as given in the following multiple equilibria (2) – (4).

\begin{align*}
\text{H}_3\text{IO}_6 & \rightleftharpoons \text{H}_4\text{IO}_6^- + \text{H}^+ \quad (2) \\
\text{H}_4\text{IO}_6^- & \rightleftharpoons \text{H}_5\text{IO}_6^2- + \text{H}^+ \quad (3) \\
\text{H}_5\text{IO}_6^2- & \rightleftharpoons \text{H}_2\text{IO}_6^3^- + \text{H}^+ \quad (4)
\end{align*}

Periodic acid exists in acid medium as $\text{H}_3\text{IO}_6$ and as $\text{H}_4\text{IO}_6^-$ at pH 7. Thus, under the present alkaline conditions, the main species are expected to be $\text{H}_3\text{IO}_6^2-$ and $\text{H}_2\text{IO}_6^3-$ at higher concentrations, periodate also tend to dimerise\textsuperscript{[19]}. However, formation of this species is negligible under the conditions used in this study. On the contrary, the authors in their recent studies\textsuperscript{[20]} proposed DPA as $[\text{Ag(HL)}_2]^{x-}$, in which L is periodate with uncertain number of protons and HL is a protonated periodate uncertain number of protons. This can be ruled out by considering the alternative form\textsuperscript{[19]} of $\text{IO}_4^-$ at pH greater than 7, which is in the form of $\text{H}_3\text{IO}_6^2-$ or $\text{H}_2\text{IO}_6^3-$. Hence, DPA could be $[\text{Ag(H}_2\text{IO}_6\text{)}_2]^{-}$ or $[\text{Ag(H}_3\text{IO}_6\text{)}_2]^{3-}$ in alkaline medium. Therefore, under the present experimental condition, DPA, may be depicted as $[\text{Ag(H}_3\text{IO}_6\text{)}_2]^{-}$. The similar speciation of periodate in alkali was proposed\textsuperscript{[18]} for diperiodatonicellete (IV). The added products did not have any significant effect on the rate of reaction. Based on these experimental results a mechanism has been proposed in the form of Scheme 1.

\begin{align*}[\text{Ag(H}_3\text{IO}_6\text{)}_2]^{-} + \text{OH}^- & \xrightleftharpoons[K_1]{\text{K}_2}\text{[Ag(H}_3\text{IO}_6\text{)(H}_2\text{IO}_6\text{)]}^{2-} \\
\text{[Ag(H}_3\text{IO}_6\text{)(H}_2\text{IO}_6\text{)]}^{2-} + \text{OH}^- & \xrightarrow[k]{\text{K}_2}\text{[Ag(H}_2\text{IO}_6\text{)(H}_3\text{IO}_6\text{)]}^{2-} \quad \text{Complex (C)} \\
\text{Complex (C)} & \xrightarrow[k]{\text{slow}} \text{[Ag(\text{H}_3\text{IO}_6\text{)(H}_2\text{IO}_6\text{)(H}_3\text{IO}_6\text{)]}^{2-} + \text{Ag(I)} + 2(\text{H}_3\text{IO}_6\text{)}^2- + \text{H}^+} \\
\text{H}^+ + \text{OH}^- & \xrightarrow[\text{fast}]{\text{K}_2}\text{H}_2\text{O}
\end{align*}

Scheme 1: Detailed mechanism for the oxidation of Vit B\textsubscript{6} by DPA.
In the first equilibrium step of Scheme 1, the [OH] deprotonates the DPA to give a deprotonated DPA. In the second equilibrium step of Scheme 1, DPA combines with a molecule of vit B₆ to give an intermediate complex. The complex decomposes in a slow step to give the products, Pyridoxinal and Ag (I) species by two equivalent changes of Ag(III) in a single step as no intervention of free radicals has been observed. The plot of 1/kobs versus 1/[vit B₆] proved the complex formation between oxidant and reductant. On the basis of square planar structure of DPA, the structure of complex may be proposed as given below.

The oxygen atom of CH₂OH group of the vit B₆ is involved in the formation of intermediate complex. Spectroscopic evidence for the complex formation between oxidant and substrate was obtained from UV-visible spectra of vit B₆ (1.0x10⁻³ mol dm⁻³), DPA (5.0x10⁻⁵ mol dm⁻³), OH⁻ (0.50 mol dm⁻³) and a mixture of both. A bathochromic shift of about 4 nm from 320.9 to 325.0 nm in the spectra of DPA was observed. Scheme 1 leads to the following rate equation.

\[
\text{Rate} = \frac{-d[DPA]}{dt} = \frac{kK_1K_2[DPA][Vit B₆][OH]^{-}}{1+K_1[OH]^{-}+K_1K_2[Vit B₆][OH]^{-}}
\]

Or

\[
\frac{\text{Rate}}{[DPA]} = k_{obs} = \frac{kK_1K_2[DPA][Vit B₆][OH]^{-}}{1+K_1[OH]^{-}+K_1K_2[Vit B₆][OH]^{-}}
\] (5)

The Equation (5) can be rearranged to Equation (6), which is suitable for verification.

\[
\frac{1}{k_{obs}} = \frac{1}{kK_1K_2[Vit B₆][OH]^{-}} + \frac{1}{kK_2[Vit B₆]} + \frac{1}{k}
\] (6)
According to Equation (6), the plots of $1/k_{\text{obs}}$ versus $1/\text{[vit B}_6\text{]}$ and $1/k_{\text{obs}}$ versus $1/\text{[OH}^-\text{]}$ were expected to be linear and found to be so (Figure 3a, b). From the intercepts and slopes of such plots, the reaction constants $K_1$, $K_2$ and $k$ were calculated as $11.1 \text{ dm}^3 \text{ mol}^{-1}$, $1.68 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1}$, $2.97 \times 10^{-3} \text{ s}^{-1}$, respectively, at $25^\circ \text{C}$. Using these values, the rate constants under different experimental conditions were calculated. There was a good agreement between observed and calculated rate constants (Table 1), which supports Scheme 1.

The negligible effect of ionic strength on the rate explains qualitatively the reaction between neutral molecule and charged species, as seen in Scheme 1. The effect of solvent on reaction rate has been described in detail in the literature\textsuperscript{22}. There is no effect on rate with increase in dielectric constant of the medium which supports the involvement of neutral molecule and charged species (Scheme 1).

The thermodynamic quantities for the different equilibrium steps of Scheme 1 can be evaluated as follows. The vit $B_6$ and hydroxide ion concentrations (Table 1) were varied at different temperatures. The plots of $1/k_{\text{obs}}$ versus $1/\text{[vit B}_6\text{]}$ ($r \geq 0.988$, $S \leq 0.0056$) and $1/k_{\text{obs}}$ versus $1/\text{[OH}^-\text{]}$ ($r \geq 0.951$, $S \leq 0.0027$) should be linear as shown in the Fig 3a, b. From the slopes and intercepts, the values of $K_1$ and $K_2$ were calculated for room temperature. A van’t Hoff plot was made for the variation of $K_1$ with temperature [i.e log $K_1$ versus $1/\text{T}$] ($r \geq 0.999$, $S \leq 0.0025$) and the values of enthalpy of reaction ($\Delta H$), entropy of reaction ($\Delta S$) and free energy of reaction ($\Delta G$), were calculated (Table 2). A comparison of the latter values mainly refer to the rate limiting step, supporting the conclusion that the reaction before the rate limiting step, supporting the conclusion that the reaction before the rate determining step is fairly slow and involves a high activation energy.\textsuperscript{21} In the same manner, $K_2$ values were calculated at different temperatures and the corresponding values of thermodynamic quantities are given in Table 2.

The negative value of $\Delta S^\#$ suggests that the intermediate complex is more ordered than the reactants.\textsuperscript{23} The observed modest activation energy and sizeable entropy of activation supports a complex transition state in the reaction. The observed modest enthalpy of activation and relative low value of entropy of activation, as well as higher rate constant for the slow step indicates that the oxidation presumably occurs via an inner-sphere mechanism. This conclusion is supported by a literature.\textsuperscript{23}
CONCLUSION
The oxidation of vit B₆ by DPA was studied. The results demonstrate that in carrying out this reaction, the role of pH in the reaction medium is crucial. Rate constant of the slow step and other equilibrium constants involved in the mechanism were evaluated and activation parameters with respect to slow step of reaction computed. The overall mechanistic sequence described here is consistent with product, kinetic and mechanistic studies.

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Figure 1: First order plots for the oxidation of vit B₆ by DPA at 298 K. [vit B₆] = 1x10⁻³; [OH⁻] = 0.30 and I = 0.50 mol dm⁻³ [DPA] x 10⁻⁵ (mol dm⁻³): (1)0.5, (2)1.0, (3)2.0, (4)4.0, (5)5.0.
Figure 2: GC-Mass Spectrum of pyridoxinal
Figure 3: Varification of rate law (Eq. 6)
(a) Plot of $1/k_{obs}$ versus $1/[\text{Vit B}_6]$ (conditions as in Table 1).
(b) Plot of $1/k_{obs}$ versus $1/[\text{OH}^-]$ (conditions as in Table 1).

Table 1. Effect of variation of [DPA], [Vit B$_6$], [OH$^-$] and [IO$_4$$^-$$]$ on the DPA oxidation of vit B$_6$ in alkaline medium at 25$^0$ C, $I = 0.50$ mol dm$^{-3}$

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Table 2. Thermodynamic activation parameters for the oxidation of vit B$_6$ by DPA in aqueous alkaline medium with respect to the slow step of Scheme 1

(A) Effect of temperature

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>k x10$^3$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>2.98</td>
</tr>
<tr>
<td>303</td>
<td>4.98</td>
</tr>
<tr>
<td>308</td>
<td>6.19</td>
</tr>
<tr>
<td>313</td>
<td>8.43</td>
</tr>
</tbody>
</table>

(B) Activation parameters

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_a$ (kJ mol$^{-1}$)</td>
<td>80±4</td>
</tr>
<tr>
<td>$\Delta H^o$ (kJ mol$^{-1}$)</td>
<td>78±4</td>
</tr>
<tr>
<td>$\Delta S^o$ (JK$^{-1}$ mol$^{-1}$)</td>
<td>-33±3</td>
</tr>
<tr>
<td>$\Delta G^o$ (kJ mol$^{-1}$)</td>
<td>88±6</td>
</tr>
<tr>
<td>log A</td>
<td>11±1</td>
</tr>
</tbody>
</table>

(C) Effect of temperature on equilibrium constants of Scheme 1 for the oxidation of vit B$_6$ by DPA in alkaline medium

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$K_1$(dm$^3$ mol$^{-1}$)</th>
<th>$K_2$ x10$^3$(dm$^3$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>11.1</td>
<td>1.68</td>
</tr>
<tr>
<td>303</td>
<td>7.14</td>
<td>1.89</td>
</tr>
<tr>
<td>308</td>
<td>4.36</td>
<td>3.70</td>
</tr>
<tr>
<td>313</td>
<td>2.88</td>
<td>4.32</td>
</tr>
</tbody>
</table>

(D) Thermodynamic quantities using $K_1$ and $K_2$ at 298

<table>
<thead>
<tr>
<th>Thermodynamic quantities</th>
<th>Values from $K_1$</th>
<th>Values from $K_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H$(kJ mol$^{-1}$)</td>
<td>-70±4</td>
<td>244±16</td>
</tr>
<tr>
<td>$\Delta S$(JK$^{-1}$ mol$^{-1}$)</td>
<td>-213±10</td>
<td>54.0±5</td>
</tr>
<tr>
<td>$\Delta G$(kJ mol$^{-1}$)</td>
<td>-5.7±0.3</td>
<td>18.0±1</td>
</tr>
</tbody>
</table>

REFERENCES


