Kinetic and thermodynamic study of Os(VIII) catalysed oxidation of glycine by ferrate(VI) in alkaline medium

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Abstract

Kinetc and thermodynamic investigation on Os (VIII) catalysed oxidation of glycine by ferrate(VI) has been done in basic medium and in the temperature range 30–45°C. Rate of oxidation increases with increase in [FeO₄²⁻] and [Os(VI)] and shows first order dependence. Rate of oxidation also increases with the increase in [S] but order is fractional. The rate decreases with an increase in pH. Rate of reaction is independent of [KCl], [KNO₃] and change in ionic strength. The values of rate constant observed at four different temperatures were used to calculate the activation parameters. The energy of activation (ΔE*) of the reaction at pH 11 and temperature 35°C was found to be 49.56 kJmol⁻¹. [OsO₄(H₂O)₂] and [FeO₄²⁻] are proposed to be the reactive species of Os (VIII) and Fe (VI) respectively in the present investigation. Formaldehyde is found to be main product of the reaction along with carbon dioxide and ammonia as by products. On the basis of experimental findings, a suitable mechanism consistent with the observed kinetics is proposed and a rate law has been derived on the basis of obtained data.

Capsule Summary: Kinetic study of Os(VIII) catalysed oxidation of Glycine by ferrate(VI) in alkaline medium and in temperature in the range of 30 °C – 45 °C was done and formaldehyde was found to be the main product. Oxidants, [FeO₄²⁻] and Os(VIII) showed first order kinetics, whereas [Cl⁻] and [NO₃⁻] showed negligible effect.

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INTRODUCTION

Oxidation of α-amino acids are one of the most important biochemical reactions taking place in living beings. These include many important reactions such as oxidative metabolism, oxidative catabolism, oxidative deamination, Krebs Cycle etc. Besides these uncatalyzed oxidation reaction of α-amino acids by range of oxidants are of particular concern in the field of medicine and biotechnology. Moreover, due to the presence of many highly toxic derivatives of amino acids in wastewater such as microcystins (a group of monocyclic heptapeptide heptoxins) produced by numerous freshwater cyanobacteria (Sharma, 2004), oxidation of such derivatives are also important. For treatment of wastewater bodies it is very necessary to remove off or oxidatively degrade the dissolved amino acids in waste water bodies.

In recent years the kinetics and mechanism of amino acids have been studied by some researchers (Devra and Yadav, 2012; Goel et al., 2013; Srivastava et al., 2006, 2007ab; Srivastava and Gupta, 2006; Srivastava et al., 2013). However, the mechanism is different in different
Many transition metals concentrated solutions containing ferrate (VI) are stable but it decomposes with evolution of $O_2$ in neutral water, and especially rapidly in acidic water and are only stable at high pH. The term ferrate is normally used to mean ferrate (VI), although it can refer to other iron-containing anions, many of which are more commonly encountered than salts of [FeO$_4$]$^{2-}$. Aqueous solutions of ferrates are pink when dilute, and deep red or purple at higher concentrations (Wiberg and Wiberg, 2001; Raymond, 1994; Daintith, 2004).

The ferrate ion is a stronger oxidising agent than permanganate (Mackay et al., 2002), and will oxidize chromium(III) to dichromate (Arora, 2005), ammonia to molecular nitrogen (Svanks, 1976). Ferrates are excellent disinfectants, and are capable of removing and destroying viruses (Manahan, 2005). The ferrate (VI) ion has two unpaired electrons, and is thus paramagnetic. It has a tetrahedral molecular geometry, with Fe-O distances of 1.66 Å (Hoppe et al., 1982).

K$_2$FeO$_4$ has attracted interest for applications in "green chemistry" because the side products of its redox reactions are rust-like iron oxides which are environmentally innocuous and K$_2$FeO$_4$ has been described as a "green oxidant." In contrast, some related oxidants such as chromate are considered environmentally hazardous. However, the main difficulty with the use of K$_2$FeO$_4$ is that it is often too reactive, as indicated by the fact that it decomposes in contact with water (Hollema and Wiberg, 2001).

4K$_2$FeO$_4$ + 4 H$_2$O $\rightarrow$ 3O$_2$ + 2Fe$_2$O$_3$ + 8KOH

It has been employed in waste-water treatment as an oxidant for organic contaminants and as a biocide. Conveniently, the resulting reaction product is iron (III) oxihydroxide, an excellent flocculent.

K$_2$FeO$_4$ has also attracted attention as a potential cathode material in a "super iron battery." It is also used as bleeding stopper for fresh wounds, being also a good disinfectant.

Fe (VI) oxidation with a large number of organic compound has been studied and it has been shown that Fe (VI) is a strong but selective oxidant. It oxidizes selectively primary and secondary alcohols to aldehydes (not acids) and ketones respectively, and primary amines to aldehydes also amino acids generally deaminated and oxidized to carbonyl compound (Audette, 1971, Carr et al., 1985; Lee and Chen, 1998; Read et al., 1998).

Many transition metal ions are employed in the oxidation of α-amino acids. It have been found that most efficient are Os (VIII), Mn (II), Ru (VIII), Ir(III) etc. In the present work we have used Os (VIII) as catalyst and Fe (VI) as an oxidant. Main reason for using Fe(VI) is its homogenous, environment friendly and non-poisonous nature (Sharma et al., 2005).

**MATERIAL AND METHODS**
Chemical and reagents

Potassium ferrate (K$_2$FeO$_4$) of high purity was prepared by the method of Thampson et al. using ferric chloride, potassium hydroxide and sodium hypochlorite. Volumetric titration analysis has been used to determine the ferrate concentration accurately. In addition to this, a visible spectroscopy method has been used to measure the ferrate concentration at a wavelength of 505 nm (Audette et al., 1971).

2FeCl$_3$ + 3NaClO + 10KOH →
2K$_2$FeO$_4$ + 3NaCl + 5H$_2$O + 6KCl

Other chemicals KCl, glycine, KNO$_3$ used in this investigation were of the A.R. grade and solution were prepared dissolving weighed amount of samples in the triple distilled water. KOH (S.D. fine) was used as a source of OH$^-$ ions. A stock solution of OsO$_4$ (Johnson Matthey) was prepared by dissolving the sample in known strength of NaOH. Absorbance of the reaction mixture was recorded on systronics double beam spectrophotometer 2203 at 885 $\lambda_{\text{max}}$ using water as standard.

Table 1: Effect of variation of reactants on the reaction rate

<table>
<thead>
<tr>
<th>[Oxidant] (Pot.ferrate) g/l</th>
<th>[Substrate] $\times 10^2$ M (glycine)</th>
<th>[Os(VIII)] $\times 10^6$ M</th>
<th>$(-\text{dc/dt}) \times 10^5$ ML$^{-1}$s$^{-1}$</th>
</tr>
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<tr>
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<td>23.0</td>
<td>0.62</td>
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<tr>
<td>1.00</td>
<td>1.00</td>
<td>28.20</td>
<td>3.90</td>
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</table>

Solution conditions: [KOH]=1x10$^{-3}$M, [KCl]=1x10$^{-3}$ M, & [KNO$_3$]=1x10$^{-3}$M.

Kinetic procedure

Experimental task has been done by using spectrophotometer at room temperature. Requisite volumes of all reagents, including substrate, were taken in reaction vessel then adding oxidant [K$_2$FeO$_4$] rapidly and transferring it in quartz cuvette having volume capacity 3.5ml & path length 10mm and fitted it in the spectrophotometer for the observation of absorbance of the reaction mixture. Absorbance of the reaction mixture was observed by varying the concentration of one reactant (0.2 g/l to 1.2 g/l oxidant, 0.2x10$^{-2}$ M to 1.2x10$^{-2}$ M substrate, 4.7x10$^{-6}$ M to 28.8x10$^{-6}$ M [Os(VIII)] and 0.4x10$^{-3}$ M to 2.4x10$^{-3}$ M for KCl, KNO$_3$ and KOH) and keeping concentration of other reactants constant.

Stoichiometry

The stoichiometry of the reaction was determined by equilibrating varying ratios of (K$_2$FeO$_4$) to glycine [CH$_2$(NH$_2$)COOH] at room temperature for 24 h under kinetic conditions. Estimation of unconsumed K$_2$FeO$_4$ showed that one mol of glycine is oxidized by one mol of ferrate ion. Result showed 1:1 stoichiometry according to equation,
$$\text{NH}_2\text{-CH}_2\text{-COOH} + \text{FeO}_4^{2-} + 2\text{H}_2\text{O} \underset{\text{Os(VIII)}}{\rightarrow}$$

$$\text{HCHO} + \text{NH}_3 + \text{CO}_2 + \text{Fe(OH)}_3 + 2\text{OH}^-$$

Main oxidation products were identified as aldehyde. It was confirmed by adding 2,4-DNP to the product solution. Aldehyde was precipitated as 2,4-dinitrophenyl hydrazone (yellow coloured) (Scheme 1). The derivatives obtained were checked and identified by TLC.

**RESULTS AND DISCUSSION**

The kinetic results were collected at several set of reactant concentrations (Table 1). First order kinetics is observed with respect to the oxidant (K$_2$FeO$_4$) fig.-1; and catalyst Os (VIII) fig.-2. Positive effect is observed with respect to [S] fig.-3; and negative effect is observed with respect to [OH$^-$] fig.-4. Insignificant effect of increase in concentration of KCl and KNO$_3$ was observed, i.e., oxidation of glycine catalysed by Os (VIII) by ferrate is not affected by Cl$^-$ & KNO$_3^-$ radicals (Table 2).

The product formed was identified as formaldehyde by the chromotropic acid test (Feigl, 1954). Similarly, ammonia by Nesseler’s reagent and CO$_2$ was qualitatively detected by bubbling nitrogen gas through the acidified reaction mixture and passing the liberated gas through tube containing lime water. The separated

<p>| Table 2: Effect of KOH, KCl &amp; KNO$_3$ towards d$\text{c}/$d$t$ of the oxidation of glycine |</p>
<table>
<thead>
<tr>
<th>[KOH]$\times 10^{-3}$M</th>
<th>[KCl]$\times 10^{-3}$M</th>
<th>[KNO$_3$]$\times 10^{-3}$M</th>
<th>(-d$c$/dt)$\times 10^5$ML$^{-1}$s$^{-1}$</th>
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<td>2.94</td>
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</table>

Solution Conditions: [FeO$_4^{2-}$] = 1g/l, [S] = 1x10$^{-2}$M and [Os(VIII)] = 23.5x10$^{-6}$M
On the basis of above discussion for the Os(VIII)-catalyzed oxidation glycine by K$_3$FeO$_4$ in alkaline medium, the following reaction steps are suggested.

Considering the negative effect of [OH$^-$] on the rate of reaction, [OsO$_4$(H$_2$O)$_2$] has been earlier reported as the reactive species in alkaline medium (Jiang and Lloyd, 2002; Srivastava et al., 2011; 2012) for Os(VIII) and [FeO$_4$]$^{2-}$ of K$_3$FeO$_4$, the following equilibrium can be assumed to exist.

\[
\begin{align*}
\text{[OsO}_4\text{(H}_2\text{O})_2\text{]} + \text{OH}^- & \rightleftharpoons k_1 \left[ \text{OsO}_4\text{(OH)(H}_2\text{O)}\right]^- + \text{H}_2\text{O} \\
\text{[OsO}_4\text{(H}_2\text{O})_2\text{]} + \{\text{S}\} & \rightleftharpoons k_2 \left[ \text{OsO}_4\text{(H}_2\text{O})\text{...[S]}\right] + \text{H}_2\text{O} \\
\text{[OsO}_4\text{(H}_2\text{O})\text{...[S]}\right] + [\text{FeO}_4]^{2-} & \rightleftharpoons k_3 \text{[FeO}_4\text{...[S]}\text{]}^2 + \text{H}_2\text{O} \\
[\text{FeO}_4\text{...[S]}\text{]}^2 + 4\text{H}_2\text{O} & \text{fast} \\
\text{Fe(OH)}_3 + \text{HCHO} + \text{NH}_3 + \text{CO}_2 + [\text{OsO}_4\text{(H}_2\text{O})_2\text{]} + 20\text{H}^- \\
\text{Rate} = \frac{dc}{dt} = k_3[\text{FeO}_4^2][\{\text{S}\}] \\
\text{Os(VIII)} & \rightarrow \text{[C}_1\text{]} + \text{[C}_2\text{]} + \text{[C}_3\text{]} \\
\frac{dc_1}{dt} = -k_1[\text{C}_1][\text{OH}^-] + k_{-1}[\text{C}_2] - k_2[C_1][\{\text{S}\}] + k_{-2}[\text{C}_3] &= 0 \\
\text{On applying steady state approximation to equation (1) we get,} \\
-k_1[\text{C}_1][\text{OH}^-] + k_{-1}[\text{C}_2] - k_2[C_1][\{\text{S}\}] + k_{-2}[\text{C}_3] &= 0 \\
\text{Similarly we have rate of formation of [C}_2\text{],} \\
\frac{dc_2}{dt} &= k_1[C_1][\text{OH}^-] - k_{-1}[\text{C}_2] \\
\text{On applying s.s.a. to the above equation we get,} \\
k_1[C_1][\text{OH}^-] - k_{-1}[\text{C}_2] &= 0 \\
[C_2] &= \frac{k_1[C_1][\text{OH}^-]}{k_{-1}} \\
\text{From equation (2) and (4) we get,} \\
[C_1] &= \frac{k_{-2}[C_3]}{k_2[S]} \\
\text{Putting the value of [C}_1\text{] in equation (5) we get,} \\
[C_2] &= \frac{k_1k_{-2}[\text{OH}^-][C_3]}{k_{-1}k_2[S]} \\
[C_2] &= \frac{k_1[\text{OH}^-][C_3]}{k_2[S]} \\
\{k_2 \quad k_{-2} & = K_2 \text{ and } \frac{k_1}{k_{-1}} = K_1\}
\]

Therefore total concentration of catalyst,

\[
\text{[C}_1\text{] + [C}_2\text{] + [C}_3\text{]} \
\]

The rate measurements were done at 30-45°C and products (yields 75-85%) were filtered and re-crystallised from alcohol. Iron [III] was found to have no effect on the rate of the reaction.

Specific rate constants were used to draw a plot of logk versus 1/ T, which was linear (fig-5). A thermostat water bath has been used to maintain the desired temperature. The values of activation energy (ΔE*), the Arrhenius factor (A), Entropy of activation (ΔS*), free energy of activation (ΔG*) and enthalpy of activation (ΔH*) were calculated from the rate measurement at 30, 35, 40 and 45°C and these values have been recorded in (Table-3).

Fig. 1: Plot between (−dc/dt) x 10$^5$ M$^{-1}$s$^{-1}$ and [FeO$_4$]$^{2-}$ g/l

Fig. 2: Plot between (−dc/dt) x 10$^5$ M$^{-1}$s$^{-1}$ and [Os(VIII)] x 10$^6$ M

Fig. 3: Plot between (−dc/dt) x 10$^5$ M$^{-1}$s$^{-1}$ and [Glycine] x 10$^2$ M
Os(VIII)$_T$ = $[C_1] + [C_2] + [C_3]$

$$= \frac{[C_3]}{K_2[S]} + \frac{K_1[OH^-][C_3]}{K_2[S]} + [C_3]$$

$$= [C_3] \left( \frac{1 + K_1[OH^-]}{K_2[S]} + \frac{K_1[OH^-]}{K_2[S]} \right)$$

$$[C_3]= \left\{ \frac{K_2[S][Os(VIII)T]}{1 + K_1[OH^-] + K_2[S]} \right\}$$

Therefore,

$$Rate = \left\{ \frac{k_3 K_2[FeO_4^{3-}][Os(VIII)T][S]}{1 + K_1[OH^-] + K_2[S]} \right\}$$

The rate equation is in agreement with all observed kinetics.

**CONCLUSIONS**

From the present spectrokinetic study of [Os(VIII)] catalysed oxidation of glycine by [FeO$_4^{2-}$] following points can be concluded as. Ferrate is a dual-function chemical reagent and has great potential to oxidise amino acids throughout the entire pH range with a reduction potential varying from +2.2 V to +0.7 V in acidic and basic solutions, respectively. [FeO$_4^{2-}$] is found to be reactive species in present study. First order kinetics is observed in respect of ferrate (oxidant) and Os [VIII] (catalyst). [OsO$_4$(H$_2$O)$_2$] is found to be reactive species in the present study. Negative effect is observed with respect to [OH$^-$] and positive effect with respect to [glycine]. Zero order kinetics is observed with respect to ionic species such as [KCl] & [KNO$_3$]. [FeO$_4^{2-}$ ...OsO$_4$(OH) ...[S]]$^{3-}$ is the complex that has been reported to be formed in slow and rate determining step and produces product.

**ACKNOWLEDGEMENT**

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