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Kinetics and mechanism of oxidation of glycine by permanganate in alkaline medium

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ABSTRACT

Kinetics of oxidation of glycine by permanganate was studied spectrophotometrically in alkaline medium at 526 nm where permanganate has maximum absorbance. It was found that the reaction exhibits first order dependence on [permanganate] and less than unit order on [glycine] and [alkali]. The products of the reaction were found to be formaldehyde, ammonia and carbondioxide. A plausible mechanism involving the formation of intermediate complex has been proposed leading to rate law. The activation parameters of the rate determining step

$$\text{rate} = -\frac{d[\text{Mn}^{\text{VII}}]}{dt} = \frac{kK_1K_2[\text{gly}][\text{OH}^-]}{1+K_1K_2[\text{gly}][\text{OH}^-]}$$

were computed using linear least squares method and the values of E_a and ΔS^\ddagger are found to be $28.49 \pm 0.05 \text{ k J mol}^{-1}$ and $-306.23 \pm 1.6 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively.

Keywords: Glycine, Manganese(VII), Oxidation, Mechanism.

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INTRODUCTION

The kinetic investigations on the oxidation of amino acids are important because of their biological significance and a precise understanding of the mechanism of such biological redox reactions helps in the synthesis of reaction products. Presently large numbers of oxidation studies on α -amino acids are being carried out using various oxidants. Permanganate is one such powerful multi-electron oxidant which can exist in various oxidation states, among which +7 is its highest oxidation state, which occurs in the oxocompounds like MnO_4^- , Mn_2O_7 , MnO_3F . Out of which MnO_4^- is the most commonly used well known oxidant species to carry out kinetic studies in acidic, neutral and alkaline media. Glycine, being one of the simplest amino acid and mild reductant, requires drastic conditions or powerful oxidants for studying its kinetic behavior. The oxidation of glycine has been studied from mechanistic point of view with potassium permanganate in aqueous phosphate buffers by Joaquin et al [1], where the reaction is auto catalyzed by one of the products, colloidal manganese dioxide. Both catalytic and non catalytic paths have been studied by the authors wherein the order with respect to permanganate was found to be one but with glycine, the catalytic path showed unit order and the non catalytic path showed a non integral order of 1.3. Later, uncatalyzed and the surfactant catalyzed oxidation of glycine by acidic permanganate[2] have been studied in which the reaction followed first order dependence in both glycine and permanganate. So, in order to gain further insight into the mechanism of oxidation of glycine, the author has taken up the kinetics and mechanism of its oxidation by permanganate in alkaline medium.

MATERIALS AND METHODS

A 0.01 mol dm^{-3} solution of glycine(E.Merck) was prepared afresh by dissolving in required volume of water and its strength is determined by the acetuous-perchloric acid method [3].

A 0.1 mol dm^{-3} solution of permanganate is prepared by dissolving potassium permanganate in double distilled water. The solution is boiled gently for 15-30 minutes, cooled and filtered through a sintered glass crucible. It is standardized by titrating with sodium oxalate [4].

A $0.025 \text{ mol dm}^{-3}$ solution of manganese(VI) is prepared by heating potassium permanganate in 8.0 mol dm^{-3} sodium hydroxide until a clear green colour is produced and is standardized spectrophotometrically[5] at 610 nm using a molar absorbance value of 1530.

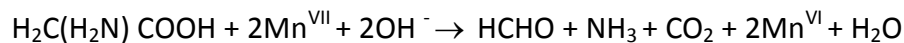
All the chemicals used in this investigation were of analytical grade. Double distilled water is used throughout the investigation.

Kinetic measurements were carried out at $30 \pm 0.1^\circ\text{C}$ in 0.2 mol dm^{-3} sodium hydroxide medium under the conditions $[\text{OH}^-] \gg [\text{glycine}] \gg [\text{Mn}^{\text{VI}}]$. The progress of the reaction was followed by measuring the absorbance of permanganate at 526nm using Milton Roy 1201 UV – VIS Spectrophotometer with 1cm path length glass cells. As no other species except manganese(VII) has any significant absorbance at this wave length under the conditions

employed, the absorbance of the solution is taken as the residual concentration of manganese(VII) at time 't'. The plots of log(absorbance) versus time are found to be linear beyond 75% completion of the reaction and the rate constants were reproducible within $\pm 3\%$.

EXPERIMENTAL

In order to identify the products formed, known amounts of glycine were reacted completely with a known excess of permanganate at 30°C in 0.1 mol dm^{-3} sodium hydroxide and after 24 hours the residual [permanganate] in each case was determined spectrophotometrically at 526nm. The stoichiometry of the reaction was found to correspond to the equation.



The product formaldehyde is identified by chromo tropic acid test[6] in which, a drop of the reaction mixture is mixed with 2ml. of sulphuric acid (72% solution) in a test tube and a little of solid chromo tropic acid is added. The test tube is heated for 10 minutes in a water bath at 30°C . A bright violet colour appeared in the test tube confirming the presence of formaldehyde as the main product along with ammonia and carbon dioxide, which are identified by Nessler's reagent and lime water respectively.

The free radical test has been carried out by taking glycine, sodium hydroxide in a thumberg tube and acrylonitrile and permanganate in the bent tube. After evacuating the system the solutions were mixed by tilting the tube. The reaction mixture was kept aside and after 24 hours a soft precipitate was observed which indicates the formation of free radical.

RESULTS AND DISCUSSION

The dependence of rate on [glycine] was studied by varying the concentrations of glycine in the range of $1.0 - 6.0 \times 10^{-3} \text{ mol dm}^{-3}$ keeping the concentrations of all the other reactants constant at three different temperatures ($25, 30$ & 35°C). The rate increased with increase in [glycine] (Table-1) and the order with respect to [glycine] was found to be fractional. Further, the plots of $1/k'$ vs $1/[\text{glycine}]$ (Fig.1) are linear with positive intercepts on rate axis indicating that the reaction obeys Michelis-Menton behavior.

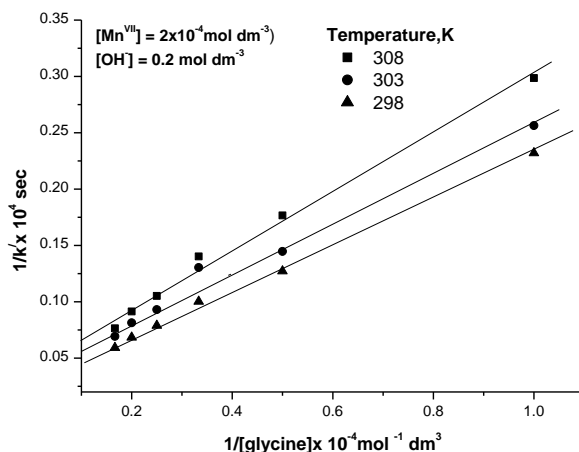


Fig.1

**Table 1. Effect of [Glycine] on the pseudo first order rate constant, k'
 $10^4[Mn^{VII}] = 2.0 \text{ mol dm}^{-3}$; $[OH^-] = 0.2 \text{ mol dm}^{-3}$**

$10^3[\text{glycine}], \text{ mol dm}^{-3}$	$10^4 k'(\text{sec}^{-1})$ Temp, K		
	298	303	308
1.0	3.35	3.91	4.31
2.0	5.66	6.91	7.86
3.0	7.13	7.67	9.97
4.0	9.5	10.75	12.66
5.0	10.94	12.28	14.6
6.0	13.08	14.43	16.88

Table 2. Effect of $[OH^-]$ on the pseudo first order rate constant, k'

$10^3[\text{glycine}] = 3.0 \text{ mol dm}^{-3}$; $10^4[Mn^{VII}] = 2.0 \text{ mol dm}^{-3}$; $t = 30 \pm 0.1^\circ\text{C}$						
$10[OH^-], \text{ mol dm}^{-3}$	1.0	2.0	3.0	4.0	5.0	6.0
$10^4 k'(\text{sec}^{-1})$	6.14	7.68	9.21	10.36	11.13	11.89

The effect of alkali on the rate of the reaction was studied at constant concentrations of glycine and permanganate at 30°C . The rate constants obtained were found to increase with increase in [alkali] (Table-2) and the order with respect to $[OH^-]$ is found to be fractional (0.34).

Table 3. Effect of [manganese (VII)] on the pseudo first order rate constant, k'

$10^3[\text{glycine}] = 3.0 \text{ mol dm}^{-3}$; $[OH^-] = 0.2 \text{ mol dm}^{-3}$; $t = 30 \pm 0.1^\circ\text{C}$						
$10^4[Mn^{VII}], \text{ mol dm}^{-3}$	1.0	2.0	3.0	4.0	5.0	6.0
$10^4 k'(\text{sec}^{-1})$	7.67	7.67	7.39	7.67	7.39	7.67

The effect of [permanganate] was studied by varying its concentration in the range of $1.0 - 6.0 \times 10^{-4} \text{ mol dm}^{-3}$ at constant concentration of glycine and alkali. The pseudo-first order rate constants, k' , obtained from the plots of $\log(\text{absorbance})$ versus time are fairly constant (Table-3), indicating first order dependence on [permanganate].

Table 4. Effect of ionic strength on the pseudo first order rate constant, k'

$10^3[\text{glycine}] = 3.0 \text{ mol dm}^{-3}; [\text{OH}^-] = 0.2 \text{ mol dm}^{-3}; 10^4[\text{Mn}^{\text{VII}}] = 2.0 \text{ mol dm}^{-3}; t = 30 \pm 0.1^\circ\text{C}$						
$[\text{NaClO}_4], \text{ mol dm}^{-3}$	0.2	0.3	0.4	0.5	0.6	0.7
$10^4 k' (\text{sec}^{-1})$	7.63	7.67	7.70	7.69	7.69	7.66

The effect of ionic strength on the reaction rate was studied in the range of 0.2-0.7 mol dm^{-3} at constant [glycine], [permanganate] and [alkali]. The rate constants obtained were found to be constant (Table-4) which shows that the ionic strength has negligible effect on the rate of the reaction.

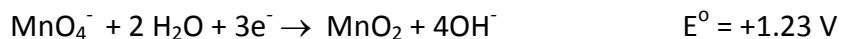
Table 5. Effect of $[\text{Mn}(\text{VI})]$ on the pseudo first order rate constant, k'

$10^3[\text{glycine}] = 3.0 \text{ mol dm}^{-3}; 10^4[\text{Mn}^{\text{VII}}] = 2.0 \text{ mol dm}^{-3}; [\text{OH}^-] = 0.2 \text{ mol dm}^{-3}; t = 30 \pm 0.1^\circ\text{C}$						
$10^4[\text{Mn}(\text{VI})], \text{ mol dm}^{-3}$	1.25	1.50	1.75	2.0	2.25	2.5
$10^4 k' (\text{sec}^{-1})$	7.66	7.64	7.67	7.65	7.67	7.67

The effect of the product, manganese(VI) on the reaction rate, was studied by carrying out kinetic runs keeping the concentrations of all other reactants constant and varying the concentration of manganese(VI) from $1.25 - 2.5 \times 10^{-4}$. The pseudo-first order rate constants thus obtained are found to remain practically constant indicating that manganese(VI), one of the products do not have any significant effect on the rate of the reaction (Table-5).

Glycine, an optically inactive non-essential amino acid exists in the form of zwitter ion $(\text{gly}_2) \text{H}_3\text{N}^+ - \text{CH}_2 - \text{COO}^-$ in neutral medium, in the form of the cationic species $\text{H}_3\text{N}^+ - \text{CH}_2 - \text{COOH}$ in acid medium and in the form of anionic species $(\text{gly}^-) \text{H}_2\text{N} - \text{CH}_2 - \text{COO}^-$ in alkaline medium. The pK values of glycine for carboxylic acid and amino groups are 2.41 and 9.59 respectively which has been determined by pH metric method using computer augmented programs SCPHD and MINQUAD75[7]. Under the experimental conditions employed, in presence of 0.2 mol dm^{-3} alkali, glycine exists predominantly in the anionic form, $\text{H}_2\text{N} - \text{CH}_2 - \text{COO}^- (\text{gly}^-)$.

Permanganate acts as powerful oxidant in acid as well as alkaline media. Its oxidation reactions are very interesting because of the several oxidation states to which it can be reduced. The reduction product of manganese is largely determined by the pH of the medium. In solutions of low alkali and in neutral media, manganese(VII) is reduced to manganese(IV).

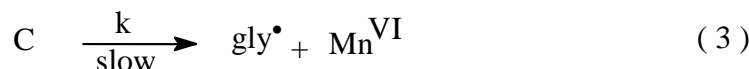
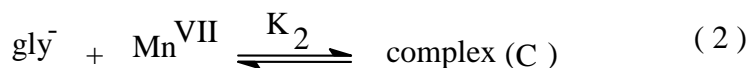
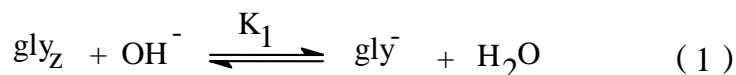


In strongly alkaline medium (pH>12.5) permanganate is usually reduced to manganese(VI).



Most of the oxidations by permanganate in neutral and alkaline media proceed through intermediate complex formation between oxidant and substrate. [8, 9]. In alkaline medium, MnO_4^- is the only active species of permanganate known to exist. Though oxidations by permanganate involve multi electron changes in neutral and acidic media but in strong alkaline media (pH > 12.5) they involve only one electron change, forming manganese(VI). In the present investigation the stoichiometry of the reaction indicates that permanganate is reduced to manganese(VI) state only and no evidence is obtained for further reduction of manganese(VI) by glycine to manganese(IV). Based on these observations the following mechanism has been proposed.

MECHANISM



Where , $\text{gly}_z = \text{H}_3\text{N}^+-\text{CH}_2-\text{COO}^-$ and $\text{gly}^- = \text{H}_2\text{N}-\text{CH}_2-\text{COO}^-$

The above mechanism leads to the rate equation

$$\text{rate} = \quad = k[\text{C}] \quad (5)$$

$$= kK_2[\text{gly}^-][\text{Mn}^{\text{VII}}] \quad (6)$$

Since $[\text{Mn}^{\text{VII}}]_t = [\text{Mn}^{\text{VII}}]_e + [\text{C}]$

$$[\text{Mn}^{\text{VII}}]_e = \quad (7)$$

$$\text{But } [\text{gly}]_t = [\text{gly}_z] + [\text{gly}^-] \quad \text{and} \quad K_1 = \frac{[\text{gly}^-]}{[\text{gly}_z][\text{OH}^-]}$$

$$[\text{gly}^-]_e = \frac{K_1[\text{gly}^-]_t[\text{OH}^-]}{1 + K_1[\text{OH}^-]} \quad (8)$$

$$\therefore \text{rate} = \frac{kK_1K_2[\text{gly}]_t[\text{Mn}^{\text{VII}}][\text{OH}^-]}{1 + K_1K_2[\text{gly}]_t[\text{OH}^-]} \quad (9)$$

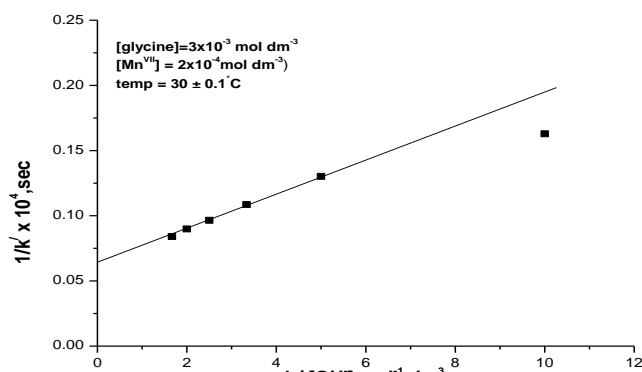


Fig. 2 Plot of $1/k'$ versus $1/[\text{OH}^-]$

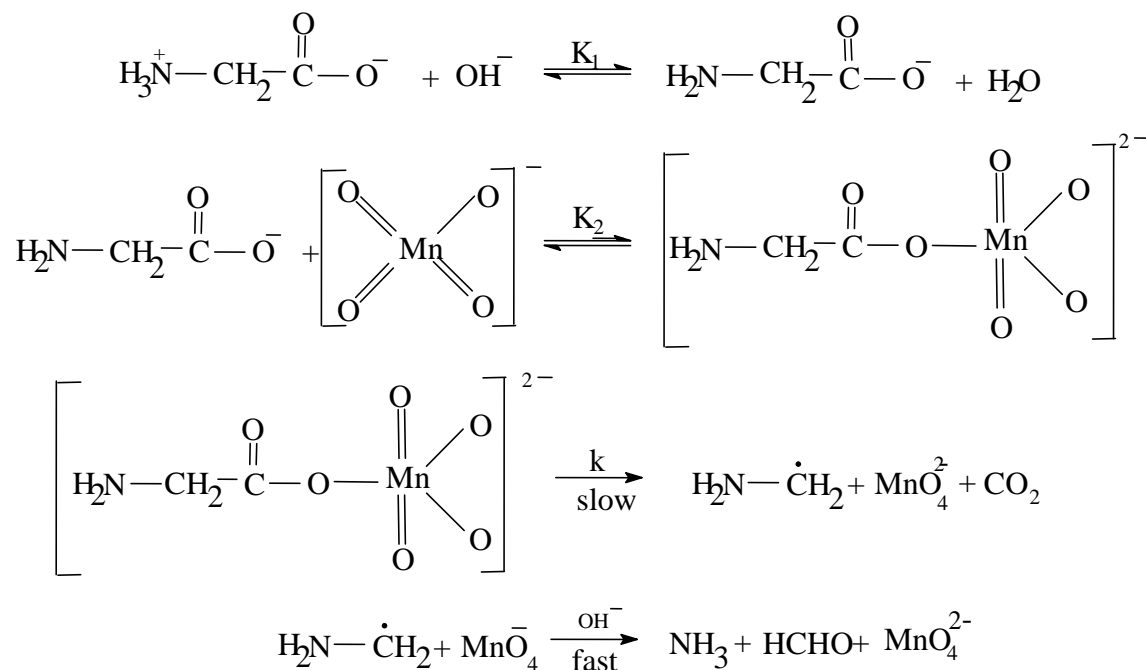
Fig.2

The rate equation explains the observed first order with respect to $[\text{Mn}^{\text{VII}}]$ and fractional order on $[\text{gly}]$ and $[\text{OH}^-]$. Further, equation(9) predicts the plots of $1/k'$ versus $1/[\text{glycine}]$ and $1/k'$ versus $1/[\text{OH}^-]$ (Fig.1,2) should be straight lines with positive intercept on y-axis. Experimentally observed plots are the one similar predicted from the rate equation thus supporting the proposed mechanism. Also the rate constants of the rate determining step, k , are determined from the intercepts of the plots of $1/k'$ versus $1/[\text{glycine}]$ at three different temperatures(25,30 & 35^oC) and the activation parameters E_a and ΔS^\ddagger are computed using linear least square method and were found to $28.49 \pm 0.03 \text{ kJ mol}^{-1}$ and $-306.23 \pm 1.62 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively. A high negative value of entropy indicates that the transition state is rigid in nature.

CONCLUSION

The observations in the present study reveal that anionic form of glycine, $\text{H}_2\text{N}-\text{CH}_2-\text{COO}^-$ (gly^-) and MnO_4^- are the reactive species in alkaline medium and formaldehyde is the product of oxidation.

INTIMATE MECHANISM



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