Kinetics and mechanism of oxidation of glycine by iron(III)–1,10-phenanthroline complex in perchloric acid medium

T V N PARTHA SARATHI,[1] A KALYAN KUMAR,[1] K KRISHNA KISHORE[1] and P VANI[1,*]

Department of Inorganic and Analytical Chemistry, School of Chemistry, Andhra University, Visakhapatnam 530 003, India
e-mail: vani_chem@rediffmail.com

Abstract. Kinetics and mechanism of oxidation of glycine by iron(III)–1,10-phenanthroline complex has been studied in perchloric acid medium. The reaction is first order with respect to iron(III) and glycine. An increase in (phenanthroline) increases the rate, while increase in $[H^+]$ decreases the rate. Hence it can be inferred that the reactive species of the substrate is the zwitterionic form and that of the oxidant is $[Fe(phen)_2(H_2O)_2]^{3+}$. The proposed mechanism leads to the rate law as elucidated.

Keywords. Oxidation of glycine; iron(III)–phenanthroline complex.

1. Introduction

Many kinetics studies have been carried out on the oxidation of glycine, using one-electron oxidants such as Mn(III),[1] ferricyanide,[2] two-electron oxidants like $K_2S_2O_3$[8] and multi-electron oxidants like $KMnO_4$,[4] potassium bromate,[5] aquomanganese(III).[6] The products of oxidation are reported to be formaldehyde, carbon dioxide and ammonia with $K_2S_2O_8$, $KMnO_4$, potassium bromate and aquomanganese(III), while the products obtained with ferricyanide are keto acid and ammonia and with Mn(III) sulphate, formaldehyde, glyoxalic acid, carbon dioxide and ammonia. In an attempt to obtain further insight on the oxidation of glycine, we now report the mechanism of its oxidation using the one-electron oxidant, Fe(III)–1,10-phenanthroline complex, in perchloric acid medium.

2. Experimental

A 1·0 mol dm^{-3} solution of glycine is prepared afresh by dissolving glycine (E-Merck) in water and its strength is determined by the acetuous perchloric acid method. Iron(III) perchlorate solution was prepared (Merck 'pro Analysi' grade) with concentrated perchloric acid. The free acid present in
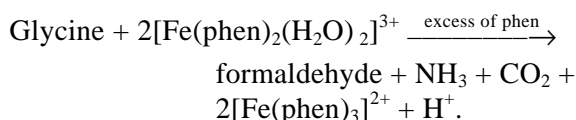
iron(III) stock solution is determined by titrating with NaOH using phenolphthalein as indicator according to the method of Milburn *et al*[7]. A 0·015 mol dm^{-3} solution of 1,10-phenanthroline is prepared afresh by dissolving 1,10-phenanthroline (E. Merck) in distilled water.

Kinetic measurements are carried out at 55 ± 0·1°C in 0·006 mol dm^{-3} perchloric acid medium under the conditions of [glycine] ≫ [Phen] ≫ [iron(III)]. Since glycine and phenanthroline get protonated in acidic medium, $[H^+]$ of the reaction mixture is adjusted to the desired value in a trial run using dilute perchloric acid. The actual runs are then carried out duplicating these conditions in the reaction mixture. The progress of the reaction was followed by measuring the absorbance of tris(phenanthroline) iron(II) formed at 510 nm using Milton Roy 1201 UV–Vis spectrophotometer with 1 cm glass cells. The temperature is kept constant using a Siskin, Julabo V Constant temperature liquid circulatory bath. The rate constants are found to be reproducible within ± 3%.

3. Results and discussion

A known excess (3–6 fold) of iron(III) solution was reacted completely with a known amount of glycine containing excess of phenanthroline at 55°C in 0·06 mol dm^{-3} perchloric acid medium. The stoichiometry corresponds to the reaction,

*For correspondence

329

Glycine + 2[Fe(phen)$_2$(H$_2$O)$_2$]$^{3+}$ $\xrightarrow{\text{excess of phen}}$
$$\text{formaldehyde} + NH_3 + CO_2 + 2[Fe(phen)_3]^{2+} + H^+.$$

Product analysis was carried out by taking the reaction mixture containing 0·3 mol dm^{-3} glycine, 6·0 × 10^{-3} mol dm^{-3} perchloric acid, 6·0 × 10^{-3} mol dm^{-3} phenanthroline and 8·0 × 10^{-5} mol dm^{-3} iron(III) in 50 cm^3 solution and allowing it to stand for 2 h at 55°C. The product formed was identified as formaldehyde by the chromotropic acid test.[8] Iron(III) was found to have no effect on the rate of the reaction.

When the kinetic runs were carried out with isolation of iron(III) by taking glycine in excess the plots of log($A\mathbf{a} - A_t$) versus time were bound to be linear up to 70% completion of the reaction, indicating that the order with respect to iron(III) is unity. Furthermore, when [Fe(III)] was varied from 5·0–10·0 × 10^{-5} mol dm^{-3} (Table 1) the pseduo-first order rate constants remained constant, confirming first-order dependence on [Fe(III)].

The order with respect to glycine was determined by varying the [glycine] over the range 1·0–6·0 × 10^{-1} mol dm^{-3}. The pseudo-first order rate constant, k', increases with increase in [glycine] and the plot of k' versus [glycine] is a straight line passing through the origin, confirming first order dependence on [glycine] (table 1).

Ionic strength has negligible effect on the rate of the reaction, but increase in [HClO$_4$] decreases the reaction rate (table 1).

Effect of [phenanthroline] on the pseudo first-order rate constant, k', was studied at 55°C by varying the phenanthroline concentration from 3·0–9·0 × 10^{-3} mol dm^{-3}. The rate constants were found to increase with increase in [phenanthroline]. Further the plot of $1/k'$ vs $1/[\text{phen}]^2$ is linear with a positive intercept on the $1/k'$ axis. This suggests Michaelis–Menten type of behaviour with the formation of a 1 : 2 complex between iron(III) and 1,10-phenanthroline.

Table 1. Effect of [Fe(III)], [Gly], [phen], [H$^+$] and ionic strength, $\mathbf{m}$, on the pseudo first-order rate constants, k', at 55 ± 0.1°C.

[Fe(III)] × 10^5 (mol dm^{-3})	[Gly] × 10 (mol dm^{-3})	[H$^+$] × 10^3 (mol dm^{-3})	$\mathbf{m}$ (mol dm^{-3})	[phen] × 10^3 (mol dm^{-3})	k' (s^{-1})
5·0	3·0	6·0	0·35	6·0	7·34
6·0	3·0	6·0	0·35	6·0	7·36
7·0	3·0	6·0	0·35	6·0	7·25
8·0	3·0	6·0	0·35	6·0	7·25
9·0	3·0	6·0	0·35	6·0	7·30
10·0	3·0	6·0	0·35	6·0	7·30
8·0	1·0	6·0	0·65	6·0	2·40
8·0	2·0	6·0	0·65	6·0	4·53
8·0	3·0	6·0	0·65	6·0	7·22
8·0	4·0	6·0	0·65	6·0	9·43
8·0	5·0	6·0	0·65	6·0	12·07
8·0	6·0	6·0	0·65	6·0	14·47
8·0	3·0	6·0	0·35	3·0	4·57
8·0	3·0	6·0	0·35	4·0	5·81
8·0	3·0	6·0	0·35	5·0	6·69
8·0	3·0	6·0	0·35	6·0	7·30
8·0	3·0	6·0	0·35	8·0	7·94
8·0	3·0	6·0	0·35	9·0	8·26
8·0	3·0	4·0	0·35	6·0	7·30
8·0	3·0	6·0	0·35	6·0	7·14
8·0	3·0	10·0	0·35	6·0	6·82
8·0	3·0	15·0	0·35	6·0	6·18
8·0	3·0	20·0	0·35	6·0	5·44
8·0	3·0	25·0	0·35	6·0	4·80
8·0	3·0	6·0	0·35	6·0	7·19
8·0	3·0	6·0	0·40	6·0	7·30
8·0	3·0	6·0	0·45	6·0	7·25
8·0	3·0	6·0	0·50	6·0	7·15
8·0	3·0	6·0	0·60	6·0	7·25

Table 2. Effect of temperature on the pseudo first-order rate constant, k'.
[Fe(III)] = 8.0×10^{-5} mol dm^{-3};   [Gly] = 0.3 mol dm^{-3};
[H$^+$] = 6.0×10^{-3} mol dm^{-3}; $\boldsymbol{m}$ = 0.35 mol dm^{-3} (NaClO$_4$);
[phen] = 6.0×10^{-3} mol dm^{-3}

Temperature	318	323	328	333
$k' \times 10^5$ (s^{-1})	3·23	4·90	7·25	10·99

Activation parameters were determined from the k' values obtained at four different temperatures 45, 50, 55 and 60°C (table 2) keeping the concentrations of all ions constants. The energy of activation E_a, and the entropy of activation $\Delta S^{\#}$, were calculated employing the linear least squares method and were found to be 70.1 ± 11.6 kJ mol^{-1} and 109.6 ± 35.3 JK^{-1} mol^{-1} respectively.

Phenanthroline has a pK value of 4.641 at 55°C and in the [H$^+$] range investigated, phenanthroline exists mainly in the form of Hphen$^+$ ($> 99\%$). Baxendale and Bridge[9] reported that a yellow complex is formed when iron(III) is mixed with 1,10-phenanthroline or 2,2′-bipyridyl and from the photometric study of the complex, concluded that the species has the formula [Fe(phen)$_n$]$^{3+}$, the maximum value of n being 2·5 at very high phenanthroline concentrations. Baxendale[10] carried out a photometric study of the brown complex formed by direct mixing of iron(III) and phenanthroline in aqueous solution and stated that the formula of the complex is probably [Fe(phen)$_2$]$^{3+}$. Subsequently, David and DeMello[11] established the structure of the complex, [Fe(L$_2$(H$_2$O)$_2$)]$^{3+}$, from the interaction of the binuclear species with H$^+$ ions. Hence, from these reports, it may be inferred that the formula of iron(III)–1,10-phenanthroline complex in the present study may be considered to be [Fe(phen)$_2$(H$_2$O)$_2$]$^{3+}$.

Under the present experimental conditions, [H$^+$] (6×10^{-3} mol dm^{-3}), glycine exists in the form of the zwitterionic species, CH$_2$($\overset{+}{N}$H$_3$)COO$^-$(Gly$_z$), to an extent of 63%, the remaining 37% being present in the protonated form, CH$_2$($\overset{+}{N}$H$_3$)COOH (HGly).

On the basis of the above observations, the following mechanism has been proposed.

$$H_3\overset{+}{N}CH_2COO^- + H^+ \underset{}{\overset{k_1}{\rightleftharpoons}} H_3\overset{+}{N}CH_2COOH, \quad (1)$$
$$\text{(Gly}_z\text{)} \qquad\qquad \text{(HGly)}$$

$$Fe(III) + 2Hphen^+ \underset{}{\overset{k_2}{\rightleftharpoons}} Fe(phen)_2^{3+}(C) + 2H^+, \quad (2)$$

$$C + H_3\overset{+}{N}CH_2COO^- \xrightarrow[\text{slow}]{k_1} H_3\overset{+}{N}\overset{\bullet}{C}HCOO^- + Fe(phen)_2^{2+} + H^+, \quad (3)$$

$$C + H_3\overset{+}{N}CH_2COOH \xrightarrow[\text{slow}]{k_2} H_3\overset{+}{N}\overset{\bullet}{C}HCOOH + Fe(phen)_2^{2+} + H^+, \quad (4)$$

$$C + H_3\overset{+}{N}\overset{\bullet}{C}HCOO^- \xrightarrow{\text{fast}} products, \quad (5)$$

$$C + H_3\overset{+}{N}\overset{\bullet}{C}HCOOH \xrightarrow{\text{fast}} products, \quad (6)$$

$$Fe(phen)^{2+} \text{ or } Fe(phen)_2^{2+} + phen \xrightarrow{\text{fast}} Fe(phen)_3^{2+}. \quad (7)$$
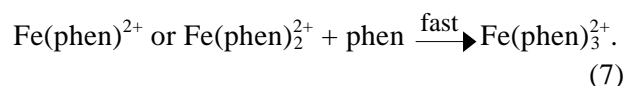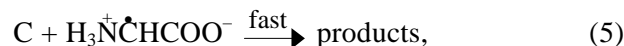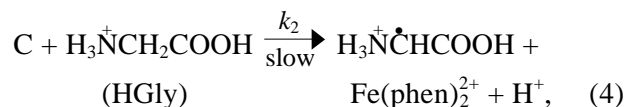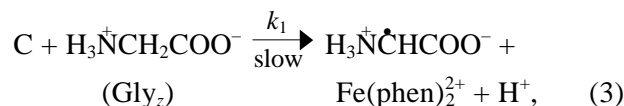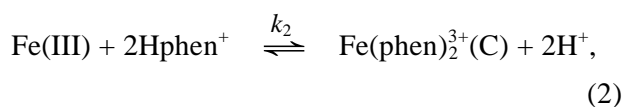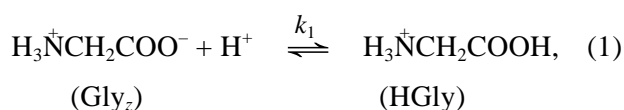
The proposed mechanism leads to the rate law,

$$\text{rate} = \frac{\{(k_1 + k_2 K_1[H^+]_t)K_2[Fe(III)_t[phen]_t^2[Gly]_t}{\{1 + K_1[H^+]_t\}\{[H^+]_t^2 + K_2[phen]_t^2\}}. \quad (8)$$

Ionic strength has negligible effect on the rate of the reaction, but increase in [H$^+$] retards the reaction rate. Since [phen]$_e$ is not significantly altered in the [H$^+$] range studied, retardation by [H$^+$] may be mainly attributed to the conversion of the more reactive neutral species of glycine to the less reactive protonated form. In view of this, k_2 may be presumed to be far less than k_1. Hence, $k_2 K_1[H^+]$ may be neglected in comparison with k_1, in the numerator of (8). Therefore, the rate of equation reduces to

$$\text{rate} = \frac{k_1 K_2[Fe(III)[phen]^2[Gly]}{\{1 + K_1[H^+]\}\{[H^+]^2 + [phen]^2\}}. \quad (9)$$

The rate equation explains the observed first order with respect to iron(III) and glycine, as well as the increase in rate with [phen] and decrease in rate with [H$^+$]. However, our experimental results indicate that the plot of $1/k'$ versus $1/[phen]^2$ is linear with a positive intercept on the rate axis which further supports the proposed mechanism.

4. Conclusion

From our studies, it may be concluded that the oxidation of glycine by iron(III)–1,10-phenanthroline complex proceeds through cleavage of C–H bond in the rate determining step, leading to the formation of

HCHO, CO_2 and NH_3. In the oxidation of glycine by Mn(III) sulphate,[1] $KmNO_4$[4] and aquomanganese(III),[6] the protonated form is the reactive species. However, in the present study, the rate of reaction decreases with increase in [H^+], thereby indicating that the zeitterionic form is far more reactive than the protonated species.

References

1. Beg M A and Kamaluddin 1975 *Indian J. Chem.* **13** 1167
2. Upadhyay S K and Agarwal M C 1977 *Indian J. Chem.* **A15** 416
3. Chandra G and Srivastava S N 1973 *Indian J. Chem.* **11** 773
4. Bharadwaj L M and Nigam P C 1981 *Indian J. Chem.* **A20** 793
5. Anandan S, Subramanian P S and Gopalan R 1985 *Indian J. Chem.* **A25** 308
6. Varadarajan R G and Joseph M 1980 *Indian J. Chem.* **A19** 977
7. Milburn R M and Vosburgh W C 1995 *J. Am. Chem. Soc.* **77** 1352
8. Feigl F 1954 *Spot tests organic applications* 4th edn (Amsterdam: Elsevier) vol. 2, p. 241
9. Baxendale J H and Bridge N K 1955 *J. Phys. Chem.* **59** 783
10. Baxendale J H 1952 *Advances in catalysis and related subjects* (New York: Academic Press) vol. 4, p. 64
11. David P C and DeMello P C 1973 *Inorg. Chem.* **12** 2188