

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

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MS received 7 August 2004; revised 3 February 2005

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 $K_2S_2O_8$ ³ 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 Analyti' grade) with concentrated perchloric acid. The free acid present in

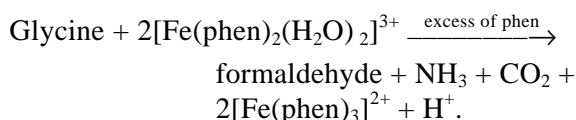
iron(III) stock solution is determined by titrating with NaOH using phenolphthalein as indicator according to the method of Milburn *et al*.⁷ A 0.015 mol dm⁻³ solution of 1,10-phenanthroline is prepared afresh by dissolving 1,10-phenanthroline (E. Merck) in distilled water.

Kinetic measurements are carried out at $55 \pm 0.1^\circ C$ in 0.006 mol dm⁻³ perchloric acid medium under the conditions of $[glycine] \gg [Phen] \gg [iron(III)]$. 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 $\pm 3\%$.

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 $55^\circ C$ in 0.06 mol dm⁻³ perchloric acid medium. The stoichiometry corresponds to the reaction,

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Product analysis was carried out by taking the reaction mixture containing 0.3 mol dm^{-3} glycine, $6.0 \times 10^{-3} \text{ mol dm}^{-3}$ perchloric acid, $6.0 \times 10^{-3} \text{ mol dm}^{-3}$ phenanthroline and $8.0 \times 10^{-5} \text{ mol dm}^{-3}$ 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 $\log(A_\infty - A_t)$ versus time were found to be linear up to 70% completion of the reaction, indicating that the order with respect to iron(III) is unity. Furthermore, when $[\text{Fe}(\text{III})]$ was varied from $5.0\text{--}10.0 \times 10^{-5} \text{ mol dm}^{-3}$ (Table 1) the pseudo-first order rate constants remained constant, confirming first-order dependence on $[\text{Fe}(\text{III})]$.

The order with respect to glycine was determined by varying the $[\text{glycine}]$ over the range $1.0\text{--}6.0 \times 10^{-1} \text{ mol dm}^{-3}$. The pseudo-first order rate constant, k' , increases with increase in $[\text{glycine}]$ and the plot of k' versus $[\text{glycine}]$ is a straight line passing through the origin, confirming first order dependence on $[\text{glycine}]$ (table 1).

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

Effect of $[\text{phenanthroline}]$ on the pseudo first-order rate constant, k' , was studied at 55°C by varying the phenanthroline concentration from $3.0\text{--}9.0 \times 10^{-3} \text{ mol dm}^{-3}$. The rate constants were found to increase with increase in $[\text{phenanthroline}]$. 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 $[\text{Fe}(\text{III})]$, $[\text{Gly}]$, $[\text{phen}]$, $[\text{H}^+]$ and ionic strength, m on the pseudo first-order rate constants, k' , at $55 \pm 0.1^\circ\text{C}$.

$[\text{Fe}(\text{III})] \times 10^5$ (mol dm^{-3})	$[\text{Gly}] \times 10$ (mol dm^{-3})	$[\text{H}^+] \times 10^3$ (mol dm^{-3})	m (mol dm^{-3})	$[\text{phen}] \times 10^3$ (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

HCHO, CO₂ and NH₃. In the oxidation of glycine by Mn(III) sulphate,¹ KmNO₄⁴ 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 zwitterionic form is far more reactive than the protonated species.

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