

NOTE

Induced Oxidation of Glycine by Fe(II)

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The present paper deals with induced oxidation of glycine by Fe(II). The probable mechanism suggests the involvement of Mn(III) as an intermediate species. Presence of salts like potassium nitrate or lanthanum(III) nitrate decreases the induction factor of the reaction.

Key Words: Induced, Oxidation, Glycine, Fe(II).

The kinetic investigation of the oxidations of α -amino acid by a variety of oxidants have been carried out under different experimental conditions. It was reported that amino acids under go oxidative decarboxylation. In the present paper, we report the induced oxidation of glycine under acidic medium using potassium permagnate. We have already reported^{1,2} the induced oxidation of formic acid by Fe^{2+} and As^{3+} .

All the solution and the reagents required for the present study were prepared and standardized using suitable methods. All solutions were prepared in doubly distilled water.

A large number of conical flasks were initially washed with chromic acid and finally with distilled water to check the presence of any trace impurity. Each flask was having different concentration of induction 5 cm^3 of acceptor was added to each flask. 10 cm^3 of $2 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ was added into each reaction flask.

The resultat solutions were titrated against pre-standardized solution of potassium permanganate. Similarly variation of acceptor was carried out keeping inductor concentration constant.

When glycine is treated with acidic potassium permanganate in presence of Fe(II), the induction factor was observed to be 0.44. This suggests the involvement of Mn^{3+} ion for the oxidation of glycine. The permanganate oxidation product of amino acids depends upon reagent used and on the acidic on alkaline media of the reaction system.

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VARIATION OF ACCEPTOR

Inductor: Fe (5×10^{-3} M); Temp.: 45°C;
 Actor: KMnO_4 (0.002 M)

10^3 [Glycine]	M moles of Fe	M moles of glycine	IF
1.0	112	30.00	0.27
2.0	112	37.50	0.33
3.0	112	37.50	0.33
4.0	112	45.00	0.40
5.0	112	45.00	0.40
6.0	112	60.00	0.54
7.0	112	60.00	0.54
8.0	112	60.00	0.54
9.0	112	60.00	0.54
10.0	112	60.00	0.54

Mean induction factor = 0.44

VARIATION OF INDUCTOR

Acceptor: Glycine (0.01 M); Temp.: $27 \pm 0.2^\circ\text{C}$;
 Actor: KMnO_4 (0.0025 M)

10^3 [Fe]	M moles of Fe	M moles of glycine	IF
1.0	22.4	86.13	3.85
2.0	44.8	61.52	1.37
3.0	67.2	73.82	1.10
4.0	89.6	61.52	0.69
5.0	112.0	49.22	0.44
6.0	134.4	49.22	0.37
7.0	179.2	86.13	0.48
8.0	224.0	135.35	0.60

Mean induction factor = 0.72

EFFECT OF POTASSIUM NITRATE AND LANTHANUM(III) NITRATE

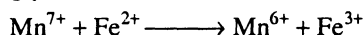
Inductor: FAS (5×10^{-3} M); Actor: KMnO_4 (0.0025 M)

10^3 [KNO_3]]	M moles of Fe	M moles of glycine	IF	10^3 [$\text{La}(\text{NO}_3)_3$]	M moles of Fe	M moles of glycine	IF
1.0	112	30.00	0.27	1.0	112	22.50	0.20
2.0	112	30.00	0.27	2.0	112	22.50	0.20
3.0	112	30.00	0.27	3.0	112	22.50	0.20
4.0	112	30.00	0.27	4.0	112	22.50	0.20
5.0	112	30.00	0.27	5.0	112	22.50	0.20

Mean induction factor = 0.27

Mean induction factor = 0.20

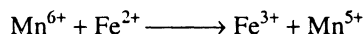
Comparing theoretical value of induction factor with experimental value of induction factor, a probable mechanism can be suggested in which Mn^{3+} may be involved to oxidize the glycine.



The deep green manganate ion (Mn^{6+}) is stable only in basic solutions. Waters³, Symon⁴, Duke⁵ and others have investigated the stability and oxidizing action of manganate. In acid, neutral or only lightly basic solutions it readily disproportionate according to following equation⁶



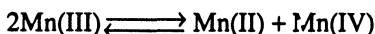
Since no precipitation was observed during experiment it is clear that, as soon as $\text{Mn}(\text{VI})$ is formed it reacts with Fe^{2+} to produce $\text{Mn}(\text{V})$.



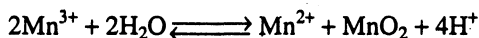
The $\text{Mn}(\text{V})$ was first prepared by Lux⁷ as blue salt. The life time of $\text{Mn}(\text{V})$ is very short therefore the affective intermediate could be Mn^{3+} .



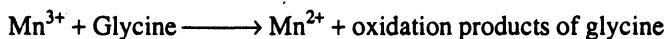
Trivalent manganese exists as the red manganic ion in concentrated acid solutions. However it undergoes disproportionation⁸ in lower acid concentrations such as



In aqueous solutions, it is quite unstable being easily reduced to Mn(II) and even in the absence of reducing agents, Mn(III) aqua-ion is subject to disproportionation according to the following equilibrium⁹



We have experimentally observed that, the solution after titration neither becomes colloidal nor shows any yellow-orange colour precipitation. This indicates that as soon as Mn^{3+} is formed it reacts with glycine.



The induction factor decreases with the addition of salts like potassium nitrate and lanthanide nitrate under similar conditions. This may be due to the formation of complex, which is less reactive than Mn^{3+} .

Various workers suggested different oxidation product of amino acids using various oxidants. Cysteine gives acetaldehyde when oxidized by bromine¹⁰, Vivekanandan and Nambi¹¹ reported aldehyde, CO_2 and NH_3 as oxidation products when amino acids are oxidized by N-chloronicotinamide in aqueous acetic acid medium. When oxidized by Fremy's radical, α -amino acid gives α -ketoacids. These amino-acids give aldehyde when oxidized by pyridinium hydrobromide, per bromide¹³. Stadman and Berlett¹⁴ showed that amino acids after oxidation with H_2O_2 and Fe^{2+} , i.e., Fenton's reagent gives ammonium ion, α -keto-acids, carbon dioxide, amines and aldehydes or carboxylic acids.

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