International Journal of Multidisciplinary Trends

E-ISSN: 2709-9369
P-ISSN: 2709-9350
www.multisubjectjournal.com
IJMT 2025; 7(4): 125-128
Received: xx-01-2025
Accepted: xx-02-2025

Priyanka Patel
Department of Chemistry,
Govt. Model Science College,
Rewa, Madhya Pradesh, India

Corresponding Author:
Priyanka Patel
Department of Chemistry,
Govt. Model Science College,
Rewa, Madhya Pradesh, India

Observation of the Kinetics oxidation of a amino carboxylic acids to Mn(III)

Priyanka Patel

DOI: https://www.doi.org/10.22271/multi.2025.v7.i3a.637

Abstract
The kinetic analysis of Mn(III) oxidizing α-amino carboxylic acid is the focus of this paper. The oxidation was done in a combination of sulfuric acid and water. In both amino acids, glycine and alanine, the rate of reaction was determined to be first order with regard to Mn(III). Regarding [substrate] concentration, the rate of reaction for glycine is first order. Michaelis-Menton-type kinetics are seen in the case of alanine. In both situations, the rate of reaction falls as the concentration of H^+ ions rises. Ag(I) had no effect on the pace of reaction. The activation parameters for the oxidation reaction have been computed, and the reaction rate has been established at various temperatures.

Keywords: Kinetics, oxidation, α amino carboxylic acid, Mn (III), sulphuric acid

Introduction

Mn(III) has multiple oxidation states to which it can be reduced, making its kinetics of oxidation more intriguing (Kumar *et al*. 2013) [9]. Because of its biological significance, Mn(III), which can be produced chemically or electrochemically, is utilized as a mild oxidizing agent for chemical transformations (Kumar *et al.* 2009 and Chandraju *et al.* 1994) [8, 2].

In this paper, glycine and alanine, two amino acids, are oxidized using Mn(III). Important molecules for the production of aldehydes are amino acids. In collagen, glycine is present in every third amino acid (Wang *et al.*, 1998) [12]. The oxidation of glycine has been the subject of numerous kinetic investigations (Joshi *et al.* 2006, Partha *et al.* 2005, Joaquin *et al.* 1987, Gowda *et al.* 2013, Kudesia and Sharma 1981) [5, 10, 4, 3, 7].

Prostate fluid contains alanine, which may help maintain prostate health. Additionally, it provides energy to the brain, central nervous system, and muscle tissues. Thus, scientists are also interested in the kinetics of oxidation studies of these two amino acids (Bailar, 1956, Katre *et al*. 2009, Sen *et al*. 2009) [1, 6, 11].

In this work, we use Mn(III) in a sulfuric acid water media to report the oxidation of these two amino acids.

Experimental

Materials

Every chemical employed in this investigation was of analytical quality. Manganese sulfate and potassium permanganate were added to sulfuric acid to create a Mn(III) solution. Mn(II):MnO_4 has a 20:1 ratio.

$$2H^+ + 3Mn^{2+} + MnO_4^- \rightleftharpoons 3Mn^{3+} + H_2O + MnO_3^{2-}$$

Kinetic measurements

At a steady temperature, the reaction was conducted in a stoppered flask. Kinetic runs with a significant excess of substrate over oxidant were conducted in pseudo-first order circumstances. In a reaction vessel (A), manganese sulphate, sulfuric acid, amino acids, and water were combined and allowed to come to a thermostated temperature.

A potassium permanganate solution was permitted to attain the optimal temperature on its own. The potassium permangnate solution was quickly mixed in reaction vessel (A) to initiate the reaction. For at least 30 minutes, the reaction's progression was tracked by keeping an eye on the drop in (Mn(III)).

Product Study

Kinetic circumstances were used to conduct the quantitative product analysis. After aqueous sodium bicarbonate completely neutralized the oxidized reaction mixture, ether was used to extract it. The 2,4 dinitrophenyl hydrazine solution was used to treat the removed ether layer. The ppt was filtered after the ether was evaporated. Formaldehyde and acetaldehyde are produced by glycine and alanine, respectively. Table 1 shows the product based on its melting point.

Table 1: Study of the Melting point of product formed.

Substrate	Product identified	Melting point of product formed	
		Reported (°C)	Observed (°C)
Glycine	Formaldehyde	166	163
Alanine	Acetaldehyde	168	167

Results and Discussion

Variation of rate with Mn(III)

The logarithm of concentration of [Mn(III)] decreased linearly with time in the oxidation of glycine and alanine by Mn(III), indicating that the rate law of the reaction is first order with Mn(III) concentration.

The starting concentrations of Mn(III) and potassium permagnate have no bearing on the first order rate constant. The concentration of potassium permanganate has no effect on the first order rate constant. This indicates that the rate of Mn(III) in two amino acids is first order.

$-d/dt[Mn(III)] = K_1[Mn(III)]$

Table 2: Variation of rate with Mn(III)

$[Oxidant] \times 10^4 mol\ dm^{-3}$	$K_1 \times 10^5 sec^{-1}$	
	Glycine	Alanine
1.25	19.52	1.07
2.50	19.49	1.09
5.00	19.56	1.07
7.50	19.54	1.08
10.00	19.50	1.12

Variation of rate with substrate

In the case of glycine and alanine, the rate of oxidation is first order. There is no kinetic evidence that a compound between the substrate and Mn(III) forms in glycine. Michaelmenten-type kinetics are seen in the case of alanine.

Table 3: Variation of rate with [Amino acids]

$[Oxidant] \times 10^2\ mol\ dm^{-3}$	$K_1 \times 10^5 sec^{-1}$	
	Glycine	Alanine
4.00	16.92	0.91
5.00	19.52	1.09
8.00	31.21	1.64
10.00	39.19	1.82
20.00	76.88	2.75

Variation of rate with sulphuric acid and perchloric acid concentration

A higher $[H^+]$ concentration slows down the rate of reaction. Table 4 summarizes the findings on the impact of sulfuric acid and perchloric acid concentrations.

In order to determine whether Mn(III) oxidized these amino acids, the Zucker-Hammett and Bunnett hypotheses were examined. Log $K_1 + H_o$ against log a_{H2O} and $\log K_1$-log [acid] against log aH_2O are the two Bunnett plots that are displayed in Table-5. The almost linear Zucker-Hammett graphs indicate that the reaction is catalyzed by an acid.

Bunnett's empirical observation states that the water molecule should function as a proton abstracting agent in the rate-determining step based on the values in sulfuric and perchloric acid.

$[H^+]$ in H_2SO_4 was calculated by the formula

$[H^+] = [H_2SO_4] + k_2 /H_2SO_4$

Where $k_2 = 1.2\times10^{-2}$ is second dissociation constant of H_2SO_4. In $H_2SO_4+HClO_4$ medium total $[H^+] = [H^+]$ $H_2SO_4+[H^+]HClO_4$.

The results of the effect of H^+ concentration can be explained in terms of the following equillibria.

$$MnO_3^{2-} + H_2O \rightleftharpoons HMnO_4^{3-} + H^+$$

$$Mn^{3+} + H_2O \rightleftharpoons Mn(OH)^{2+} + H^+$$

[Mn(IV) may exist as MnO_3^{2-}

The effect of $[H^+]$ shows that the reactive species Mn^{3+} and Mn^{4+} are $Mn(OH)^{2+}$ and as $HMnO_4^{3-}$ respectively.

Reactive species concentration will drop with an increase in $[H^+]$, which will lower the reactive rate. One would anticipate that the rate constant will fluctuate as $[H^+]$ from the equillbrium.

Prontonation of the acids is another way to describe the effect of the H^+ ion. As the acidity of the amino acids increases, RCH_2NH_2COOH will exist in prontonated form, or $R.CH_2NH_3^+COOH$.

However, it was anticipated that the reaction would occur with unreacted protonated amino acids and that the protonated form would not be reactive. The rate was predicted to drop as the concentration of H^+ ions increased.

Table 4: Variation of rate with $[H^+]$

$[H_2SO_4]\ mol\ dm^{-3}$	$[H^+]\ mol\ dm^{-3}$	$K_1 \times 10^5 sec^{-1}$	
		Glycine	Alanine
1.00	1.01	30.92	2.10
1.25	1.26	19.51	1.09
1.50	1.51	13.22	0.69
2.00	2.01	8.91	0.34
2.50	2.51	5.72	0.21

Table 5: Correlation of rate with acid concentration

Correlation	Slope	
	Glycine	Alanine
$\log k_1\ vs \log[H^+]$	1.70	1.28
$\log k_1\ vs\ H_0$ Zucker-Hammet plot	0.65	0.58
$\log k_1 +\ H_0\ vs \log a_{H_2O}$ Bunnett plot slope (ω)	3.28	2.94

Effect of rate with Mn(II) ions

In the presence and absence of Mn(II) anions, the impact of Mn(II) on oxidation reactions was investigated (Table 6).

Addition of Mn(II) anions upto1.5x10^{-3}M increases the rate of reaction, beyond 1.5x10^{-3} M it is observed that addition of Mn(II) retard the rate of reaction.
If these are reactive species, adding a small quantity of Mn(II) should speed up the rate as seen. A small addition of Mn(II) will speed up the creation of Mn(III) and Mn(IV) in solution. However, the interaction of Mn(II) and the active reactive intermediate, Mn(IV), may be the cause of the retardation seen at high concentrations of Mn(II).
Even in Mn(III) pyrophosphate solution, Mn(IV) can exist in considerable proportion.
Therefore, it is quite conceivable that the combination of $KMnO_4$ and Mn(II) also produces Mn(IV) as a reaction intermediate. Compared to Mn(III), Mn(IV) is more reactive. Consequently, the addition of Mn(II) reduces the rate of reaction by destroying the Mn(IV) reactive species.
The reaction-

Mn(IV) + Mn(II) 2Mn(III)

Table 6: Variation of rate with [Mn(II)]

Mn(II) $mol\ dm^{-3}$	$k_1 \times 10^5 sec^{-1}$	
	Glycine	**Alanine**
10.0	17.32	8.71
5.0	19.50	10.88
2.5	22.29	12.72
1.5	25.02	16.63
1.0	21.86	14.14
0.0	8.14	10.72

Effect of sodium pyrophosphate (SPP)
The reactions were studied in absence or presence of pyrophosphate (Table-7)
Pyrophosphate addition has been shown to slow down the rate of reaction. The entire [$P_2O_7^{4-}$] in the reaction mixture may be the cause of the retardation effect when pyrophosphate levels rise because it prevents the development of an intermediate cyclic complex.

Table 7: Variation of rate with [SPP]

SPP $mol\ dm^{-3}$	$k_1 \times 10^5 sec^{-1}$	
	Glycine	**Alanine**
0.0	19.50	10.89
2.5	13.80	7.94
5.0	12.59	5.75
10.0	7.67	4.21
20.0	5.25	2.88

Effect of temperature Rate of reaction increases with temperature Table-8. A plot of log K_2 (K_2 =K_1/substrate) vs.1/T (inverse of absolute temperature) is a straight line. This shows that Arrhenius equation is valid.
The C-H bond is favored by the activation energy, and fission in this oxidation is indicated by the slow reaction's negative entropy value. The activation entropy falls between-11.0 to +0.6 (Table 9). Through a single electron transition, the substrate and Mn(III) or Mn(IV) form a cyclic complex. C-C fission will result from it. Furthermore, the activation energy will be negative since a cyclic intermediate is created from a non-cyclic reactant. Due to energy loss, internal rotation in the reactant transforms into vibration in the activated complex.

Table 8: Variation of rate with Temperature

Temperature °*k*	$k_1 \times 10^5 sec^{-1}$	
	Glycine	**Alanine**
313	19.52	1.11
318	33.81	1.82
323	60.03	2.91
328	98.02	4.82

Table 9: Thermodynamic Parameters for Amino Acids

Thermodynamic parameters	Values	
	Glycine	**Alanine**
Energy of activation ΔEa kJ mol^{-1}	21.71	21.02
Entropy of Activation ΔS JK^{-1}-	-3.84	-8.38

Conclusion
Regarding [Mn(III)] [substrate], the sequence of reaction is one. The reaction with alanine exhibits Michaelis-Menten kinetics and provides proof that a complex between alanin and Mn(III) is undergoing a reaction. It does not, however, imply that no complex of this kind forms. The complex's existence cannot be determined using the kinetic technique if its formation constant is low. The rate of reaction is accelerated by additional Mn(II) addition up to a concentration of 1.5x10-3M. This is because, when Mn(II) is present, $KMnO_4$ rapidly disproportions into Mn(IV) and Mn(III). The addition of Mn(II) will slow down the pace of reaction if Mn(IV) is involved in the oxidation, indicating that both Mn(III) and Mn(IV) are active in the oxidation. The rate of oxidation decreases as the [H^+] concentration rises. Protonated species, which amino acids provide, should be less reactive than unprotonated species. Consequently, a rise in [H^+] lowers the amount of unprotonated amino acids. The activation energy is roughly the same as that which denotes C-C fission in a single electron transfer process via a substrate-oxidant complex.

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