



KINETIC STUDIES IN OXIDATIVE DEAMINATION AND DECARBOXYLATION OF GLYCINE BY ACIDIC PERMANGANATE

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Abstract:

A kinetic investigation of oxidative cleavage of glycine by acidic solution of permanganate has been carried out by using permanganate titration. The rate shows a first order dependence on each oxidant and substrate. The reaction is studied at two different temperatures to evaluate activation energy and Arrhenius frequency factor.

INTRODUCTION

Amino acids make up 75% of human body and are vital to every part of human function.¹ The kinetic investigation of the oxidation of amino acids is 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.

Literature survey reveals that permanganate ions are widely used as oxidizing agent in synthetic and analytical chemistry.¹ It has several advantages as an analytical reagent. It is strong and vividly coloured. In acidic medium it exists in different forms as HMnO_4 , HMnO_4^+ , HMnO_3 , Mn_2O_7 and one depending on the nature of the reductant.

Glycine being a simplest amino acid and mild reductant requires powerful oxidants for studying its kinetic behavior because this permanganate is assigned as oxidant in the present investigation.

MATERIALS AND METHODS

Oxalic acid dihydrate (Sigma Aldrich), ferrous ammonium sulphate (Loba) and glycine (Spectrochem), were used as received with no further purification.

Kinetic experiments were carried out on thermostat. The reaction was initiated by adding requisite amount of Permanganate solution to mixture of substrate glycine and sulphuric acid solution.³ The zero time is noted when about half of the permanganate solution was added. The total volume of the reaction mixture was kept in 100 ml.

All kinetic measurement were carried out under pseudo first order conditions where the amount of amino acid was maintained in large excess over the permanganate ion concentration. For kinetic study 10 ml of the reaction mixture was withdrawn at known intervals of time and the reaction was quenched by adding it to a conical flask cooled in ice-cold water. The titre value due to unreacted KMnO_4 at given time were noted.

The work was performed on the determination of dependence of the rate on substrate, oxidant and acid concentration. The reaction was studied at two different temperatures.

RESULTS AND DISCUSSION

In the present work, the oxidation of glycine was observed in different concentration of oxidant, substrate, acid and temperature.

oxidant variation

the reaction was studied at three concentrations of KMnO_4 (0.02N, 0.03N, 0.04N) where the concentration of glycine and H_2SO_4 was (2M) and (1N) respectively. All the reactions were carried out at 323K. It is confirmed by the Time(min) vs $\log(a-x)$ and Time(min) vs $\log(a/a-x)$ graphs (Fig 1 and 2) of these three reactions which is straight line indicates that the reaction follows first order kinetics with respect to oxidant.

Table 1

Time(min)	10	20	30	40	50	60	75	average
K_1' (10^{-3} /min) KMnO ₄ (0.02N)	7.81	6.67	7.44	7.19	6.43	5.94	5.75	6.75
K_2' (10^{-3} /min) KMnO ₄ (0.03N)	8.88	8.12	8.07	7.69	8.01	7.57	7.97	8.04
K_3' (10^{-3} /min) KMnO ₄ (0.04N)	9.43	9.32	9.59	8.91	9.24	9.08	9.24	9.30

Substrate variation

Similar to oxidant variation, the substrate variation was also studied by using three concentration of glycine (1 M, 1.5 M and 2 M) where the concentration of KMnO₄ and H₂SO₄ was (0.02N) and (1N) respectively. The reactions were carried out at 323K. In all the three reaction, time vs log(a-x) and time vs log(a/a-x) the straight line graph (Fig. 3 and 4) indicates that the reaction follows first order kinetics with respect to glycine.

There is a small but regular increase in the rate constant of the reaction with increase in concentration of glycine. The plot K vs glycine concentration (Fig. 5) found linear which also showing the first order dependence of the rate on glycine concentration in the given range.

Table 2

Time(min)	10	20	30	40	50	60	75	average
K'' (10^{-3} /min) Glycine(1M)	5.13	3.90	3.51	4.06	3.84	3.72	3.84	3.99
K'' (10^{-3} /min) Glycine(1.5M)	5.13	5.27	5.41	4.81	5.09	4.79	5.24	5.10
K'' (10^{-3} /min) Glycine(2M)	7.81	6.67	7.44	7.19	6.43	5.94	5.75	6.74

Overall order of reaction

By using Ostwald isolation method we can also calculate the total order of the reaction



$$dx/dt = k [\text{glycine}]^n [\text{KMnO}_4]^m$$

As the amount of glycine is very high, its concentration can be considered unchanged during the reaction.

$$dx/dt = K' [\text{KMnO}_4]^m \quad \text{where } K' = k[\text{glycine}]^n$$

It behaves like pseudo-first order reaction and depends only on the concentration of KMnO₄. The previous tables and related graphs are with in agreement of this. Hence in above equation $m = 1$.

For two different reactions, which differ only by concentration of glycine (2M and 1.5M)

$$K'_{2M}/K'_{1.5M} = [\text{glycine}(2M)]^n / [\text{glycine}(1.5M)]^n$$

$$6.74 \times 10^{-3} / 5.10 \times 10^{-3} = [2/1.5]^n$$

$$\text{Or } \log(1.32) = n \log(1.33)$$

$$n = 0.9733$$

This calculated data also confirms that the overall order of reaction is $1 + 0.9733 = 1.9733$ which is very close to the 2.

variation of temperature

The kinetics was observed at 323K and 373K where the concentration of KMnO₄, glycine and H₂SO₄ was (0.02N), (1M) and (1N) respectively.

However, in both the cases the time(min) vs log(a/a-x) plot is straight line with positive slope (Fig. 6) but the rate constant of the reaction at 373K is increased by more than 10 times of the rate constant of the reaction at 323K. (Fig. 7 and 8)

Table 3

Time(min)	10	20	30	40	50	60	75	Average
K_1' (10^{-3} /min) 323K	5.12	3.90	3.51	4.06	3.84	3.72	3.83	3.99
K_2' (10^{-3} /min) 373K	47.0	45.8	46.2	47.4	46.0	43.1	-----	45.9

The study of temperature variation helps in the determination of various thermodynamic parameters. The activation energy and frequency factor can be calculated by comparing the rate constant observed at two different temperatures.

calculation of activation energy

$$dx/dt = k [\text{glycine}]^n [\text{KMnO}_4]^m$$

At very high concentration of glycine

$$dx/dt = K' [\text{KMnO}_4]^m \quad \text{where } K' = k[\text{glycine}]^n$$

$$n = 1$$

$$K' = k[\text{glycine}]$$

$$[\text{glycine}] = 1 \text{ M}$$

$$K' = k$$

$$k = A e^{-\Delta E_a/RT}$$

$$K_{323}/k_{373} = e^{-\Delta E_a/323R}/e^{-\Delta E_a/373R}$$

$$\text{or } \ln(k_{323}/k_{373}) = \Delta E_a(1/373R - 1/323R)$$

$$\Delta E_a = 48.943 \text{ KJ/mole}$$

Calculation of Arrhenius frequency factor

$$\ln k = \ln A - \Delta E_a/RT$$

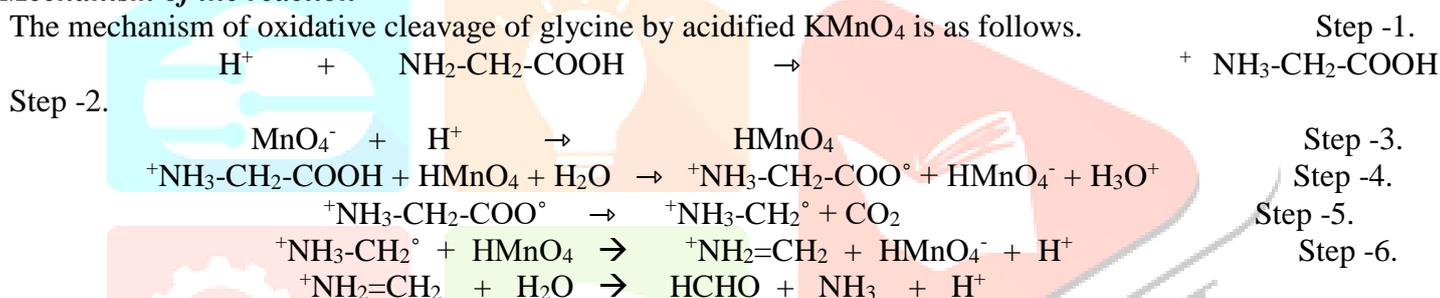
For $[\text{glycine}] = 1 \text{ M}$ at 323K

$$\ln(3.99 \times 10^{-3}) = \ln A - [48943 / (8.314 \times 323)]$$

$$A = 3.27 \times 10^5$$

Mechanism of the reaction

The mechanism of oxidative cleavage of glycine by acidified KMnO_4 is as follows.



This mechanism⁴ is also supported by kinetic data. The three body collision with proper orientation and energy is difficult than that of two body collision. Hence no doubt the step three is slowest step and rate determining step. This also explains the low reactivity of glycine with acidified KMnO_4 at room temperature even though the activation energy is only 48.943 kJ/mole. The involvement of one molecule of glycine and one molecule of KMnO_4 in rate determining step is also in agreement with second order kinetics of the reaction.

Conclusion

The order of the reaction has been confirmed by different methods. The total order of reaction was found two, one with respect to glycine and one with respect to KMnO_4 . Due to the low value of Arrhenius frequency factor the reaction is categorized under slow reaction at room temperature.

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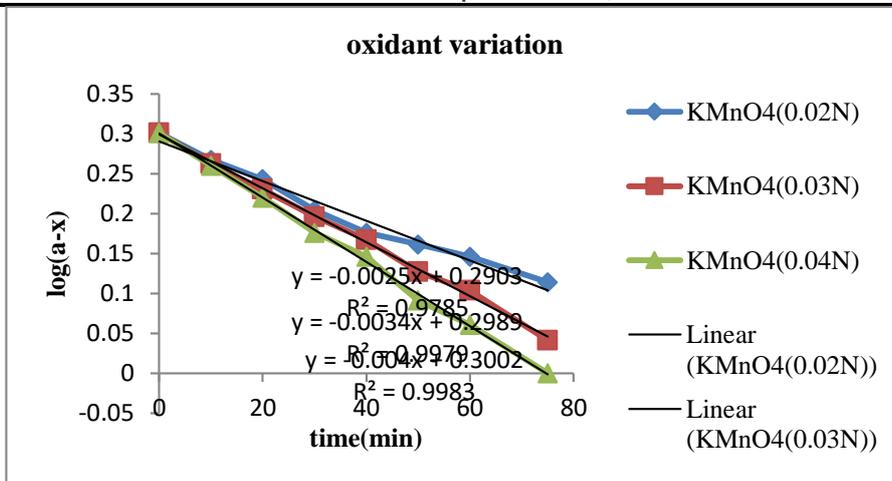


Fig 1

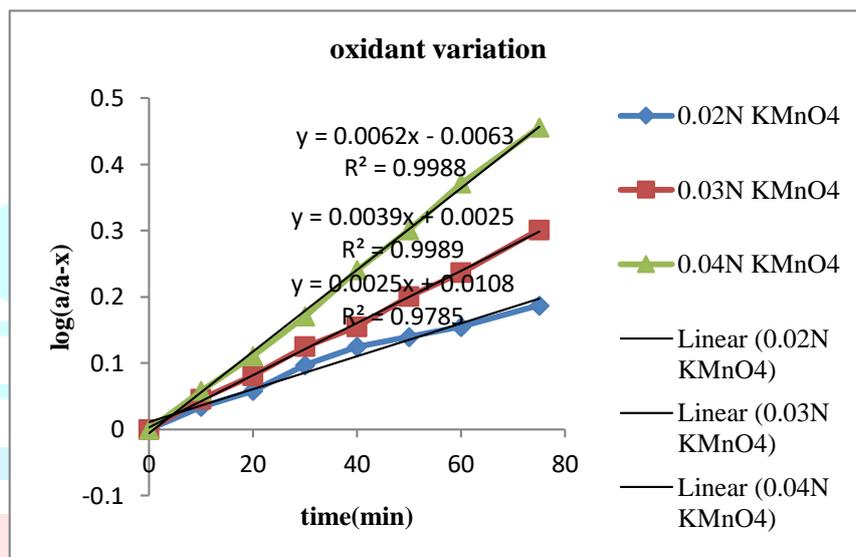


Fig. 2

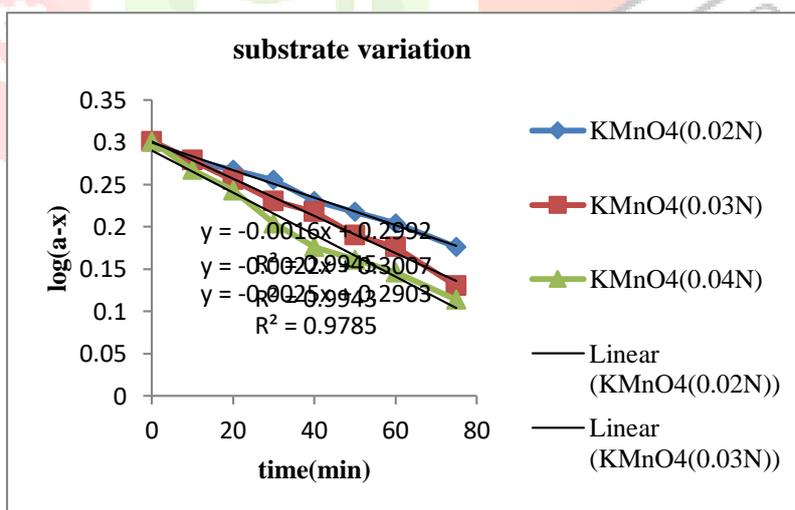


Fig. 3

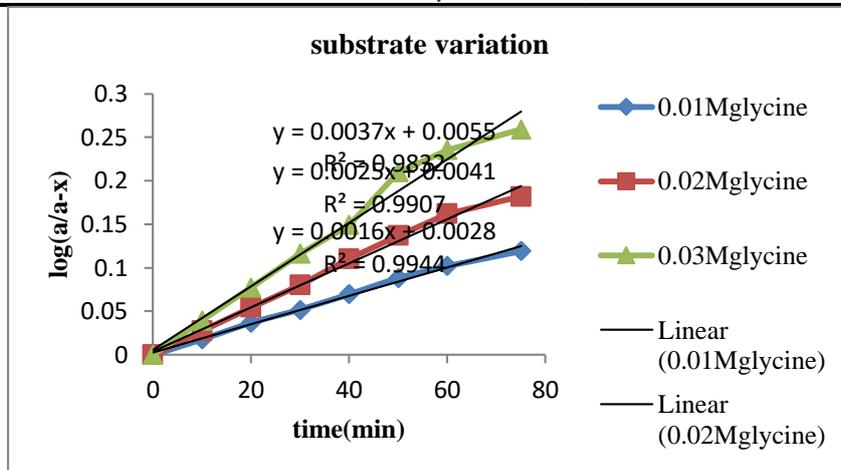


Fig. 4

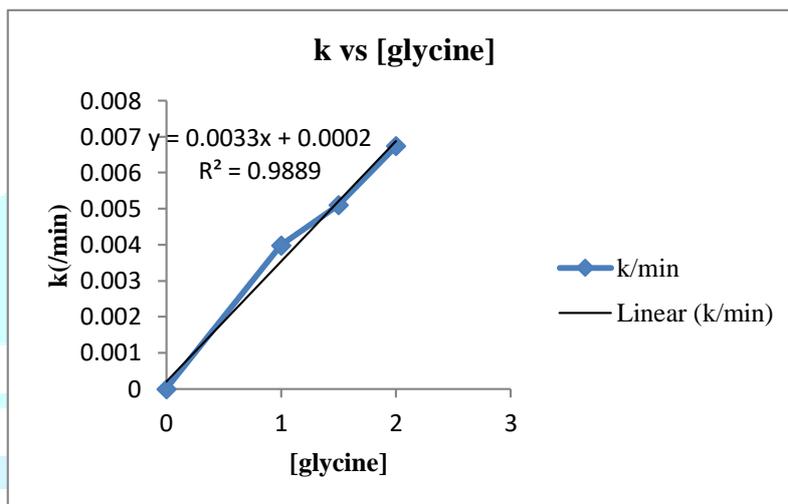


Fig.5

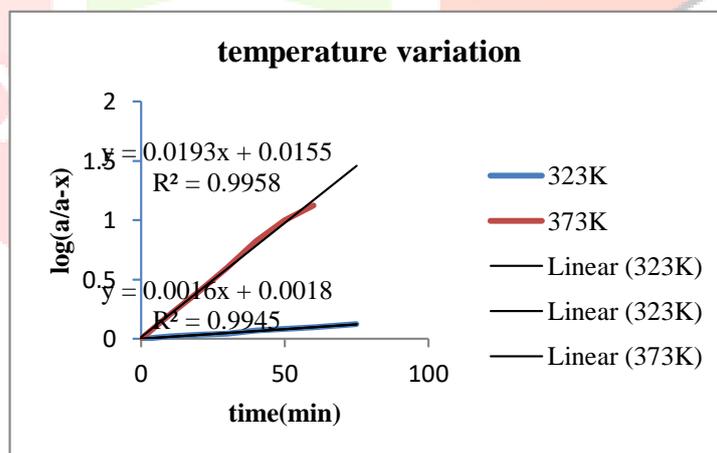


Fig. 6

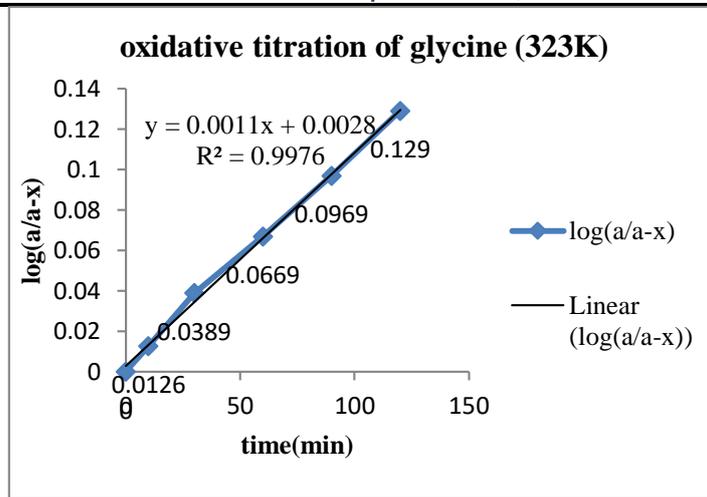


Fig.7

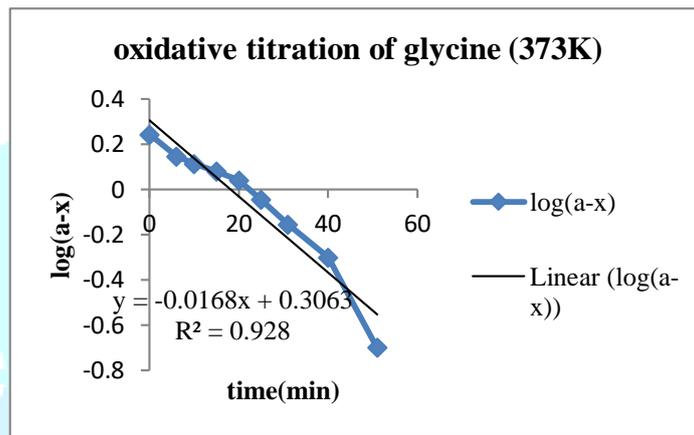


Fig. 8