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Permanganate Oxidation of 2-Aminobutyric Acid: Kinetics, Mechanism and Salt Effect

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The permanganate oxidation of 2-aminobutyric acid (2-ABA) has been studied iodometrically in sulphuric acid media. The reaction follows first order kinetics with respect to oxidant and reductant. Zücker-Hammet's and Bunnett's hypotheses were tested and it has been found that the reaction is acid catalysed and water molecules act as a proton abstracting agent in the rate determining step. The effect of various cations and anions on reaction velocity was studied. No primary salt effect was observed. Various activation parameters have been computed.

INTRODUCTION

An increasing number of articles have been published dealing with the oxidation of a variety of organic compounds by potassium permanganate in both acid[1–5] and alkaline medium[6–10]. But there is no kinetic evidence on the oxidation of aminobutyric acids by permanganate. The present report incorporates the results of the kinetics and mechanism of permanganate oxidation of 2-aminobytric acid in moderately high sulphuric acid concentration. The effects of added salts have also been discussed.

EXPERIMENTAL

2-Aminobutyric acid (2-ABA) was procured from Aldrich Chemical Co. All other chemicals used were of either BDH or Merck grade. Double distilled water was used to prepare all the solutions. Solution of 2-ABA was prepared by weighing and then standardised with standard alkali. Potassium permanganate solution was prepared and standardised as given in Vogel[11].

The kinetic experiments were carried out in a glass stoppered dark coloured bottle containing requisite amount of 2-ABA. H_2SO_4 and H_2O were thermostated at 30 ± 0.1°C. To initiate the chemical reaction, measured quantity of potassium permanganate (pre-equilibrated at 30 ± 0.1°C) was added rapidly to the above solution. The run of the reaction was monitored by iodometric determination of the unreacted potassium permanganate present in a measured aliquot of the reaction mixture at different time intervals.

To determine different thermodynamic parameters, the reaction was studied by using the same concentrations of the reactants at different temperatures (30°–50°C).

RESULTS AND DISCUSSION

Order of the reaction: At constant concentrations of 2-ABA and H_2SO_4, first order was invariably found with respect to the permanganate. The process of oxidation undergoes a slow first stage followed by a fast second stage, each being linear. The two-stage process may be due to the gain of optimum concentration of some intermediate or due to the autocatalysis by MnO_2[12].

It was observed that experimental rate constant becomes practically constant as the concentration of permanganate changes. (Table 1). It was also found that experimental first order rate constant values for first and second stages increases as the 2-ABA concentration increases (Table 2). The plot log [2-ABA] vs log K gives a straight line. This confirms that the order of the reaction with respect to 2-ABA is the same in both stages.

TABLE 1
VARIATION OF RATE CONSTANT WITH VARYING CONCENTRATION OF $KMnO_4$ AT 30°C
2-ABA = 0.05 M, H_2SO_4 = 2 M

Conc. of $KMnO_4$ ($\times 10^{-5}$ M)	13.33	10.00	8.00	6.66	5.71
$K \times 10^{-5}\ sec^{-1}$ (1st stage)	3.16	3.44	3.27	3.19	3.52
$K \times 10^{-5}\ sec^{-1}$ (2nd stage)	10.20	10.04	10.11	10.42	9.99

TABLE 2
VARIATION OF RATE CONSTANT WITH VARYING CONCENTRATION OF 2-ABA AT 30°C
H_2SO_4 = 2M, MnO_4^- = 13.33 × 10^{-5} M

Conc. of 2-ABA (M)	0.05	0.10	0.15	0.20	0.25	0.30
$K \times 10^{-5}\ sec^{-1}$ (1st stage)	3.16	8.21	12.82	17.30	21.93	32.22
$K \times 10^{-5}\ sec^{-1}$	10.21	23.11	38.82	48.42	63.39	80.24

Thermodynamic parameters: Rate of reaction was studied at different temperatures (30°–50°C) and activation parameters have been computed

(Table 3). By plotting log K vs 1/T a linear relationship was obtained for both the stages (Fig. 1). This confirms the validity of Arrhenius equation.

TABLE 3
THERMODYNAMIC PARAMETERS FOR 2-ABA
2-ABA = 0.1 M, H_2SO_4 = 2 M, $KMnO_4$ = 13.33 × 10^{-5} M

Stage	ΔE^* (k cal mol^{-1})	ΔS^* (cal mol^{-1})	PZ (lit mol^{-1})
1st	15.88	–25.94	2.1369 × 10^{-7}
2nd	14.19	–29.46	3.6425 × 10^{-6}

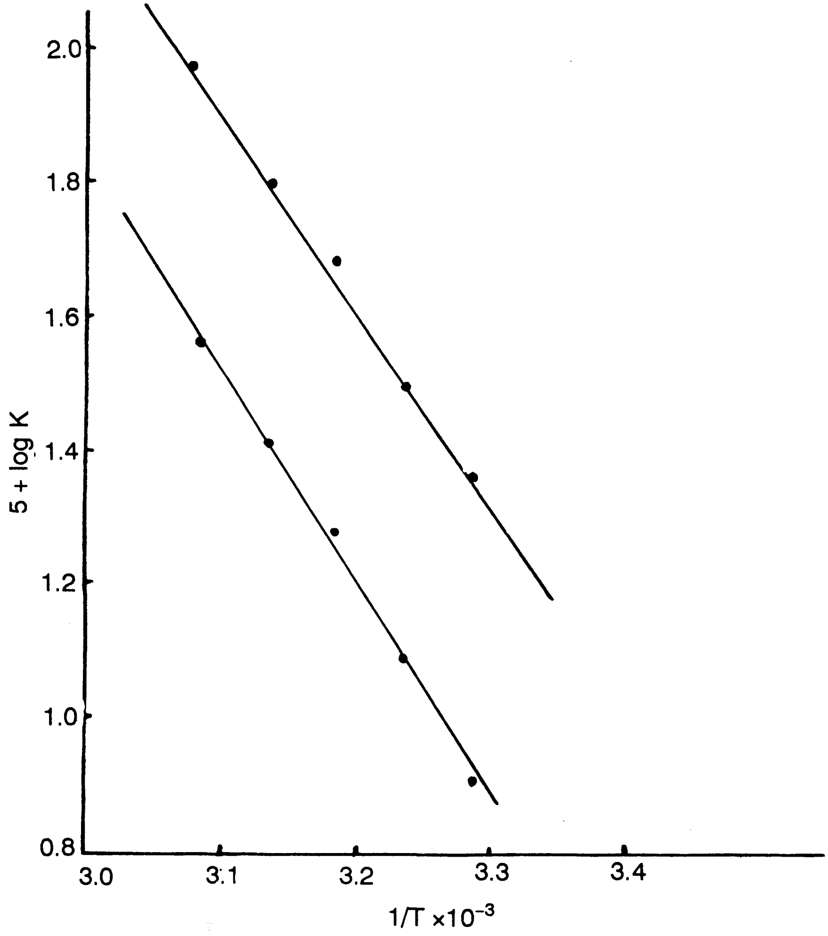
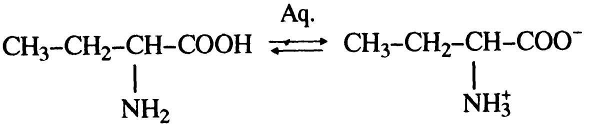
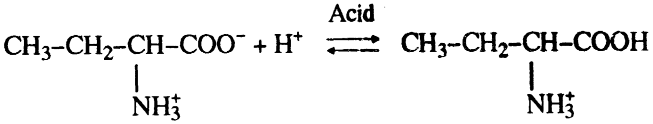


Fig. 1 Arrhenius plot
(2-ABA = 0.10 M, $KMnO_4$ = 13.33 × 10^{-5} M H_2SO_4 = 2.0 M)

Acid catalysis: In concentrated acid medium amino acids exist as a protonated species according to the equilibrium[13].



$$CH_3\text{-}CH_2\text{-}\underset{NH_2}{\underset{|}{CH}}\text{-}COOH \overset{Aq.}{\rightleftharpoons} CH_3\text{-}CH_2\text{-}\underset{NH_3^+}{\underset{|}{CH}}\text{-}COO^-$$



$$CH_3\text{-}CH_2\text{-}\underset{NH_3^+}{\underset{|}{CH}}\text{-}COO^- + H^+ \overset{Acid}{\rightleftharpoons} CH_3\text{-}CH_2\text{-}\underset{NH_3^+}{\underset{|}{CH}}\text{-}COOH$$

In permanganate oxidation MnO_4^- is the active oxidising species[14]. It was found that reaction rate increases as the concentration of H_2SO_4 increases (Table 4). It is due to protonation of MnO_4^-, according to the following equation[4, 15].

$$MnO_4^- + H^+ \rightleftharpoons HMnO_4$$

The present study suggests that the effective oxidising species is permanganic acid in sulphuric acid medium. The rate of oxidation is proportional to the [2-ABA], indicating that $HMnO_4$ oxidises 2-ABA directly[16].

The interpretation of the influence of acidity on reaction rate was intially done using the criterion of Zücker-Hammett for the reactions catalysed by acids[17]. A correlation was obtained by plotting log K vs H_0 and log K vs log [acid] which points out that the present reaction is acid catalysed.

Bunnett's criterion was applied to study the role of water in the present oxidation reaction[18]. On plotting $\log(K + H_0)$ against $\log a_{H_2O}$, a straight line was obtained of slope $\omega = 4.00$ (Fig. 2). This value confirms that the water molecule acts as a proton abstracting agent in the rate determining step.

Salt effect: Primary kinetic salt effect was not observed by adding neutral salts within the concentration limits demanded for the application of Bronsted-Bjerrum equation[19]. At higher concentration of added neutral salts, log K varies linearly with the concentration of the salt.[20]

Specific ionic effect: If the activated complex formed in the rate-determining step is charged or dipolar in nature, a specific effect of added cations and anions on the reaction rate is expected[12, 16]. In the present oxidation reaction sodium salts of anions and sulphates of cations were added at identical concentration, to investigate the specific effect of anions and cations on reaction velocity.

The order of effectiveness of anions is

$$PO_4^{3-} > CO_3^{2-} > SO_4^{2-} > NO_3^- > CH_3COO^-$$

and that of cations is

$$K^+ > Zn^{2+} > Mg^{2+} > Na^+ > NH_4^+$$

From the above experiments it is noted that added cations are having more effect than anions in velocity of the reaction. This effect of cations could be

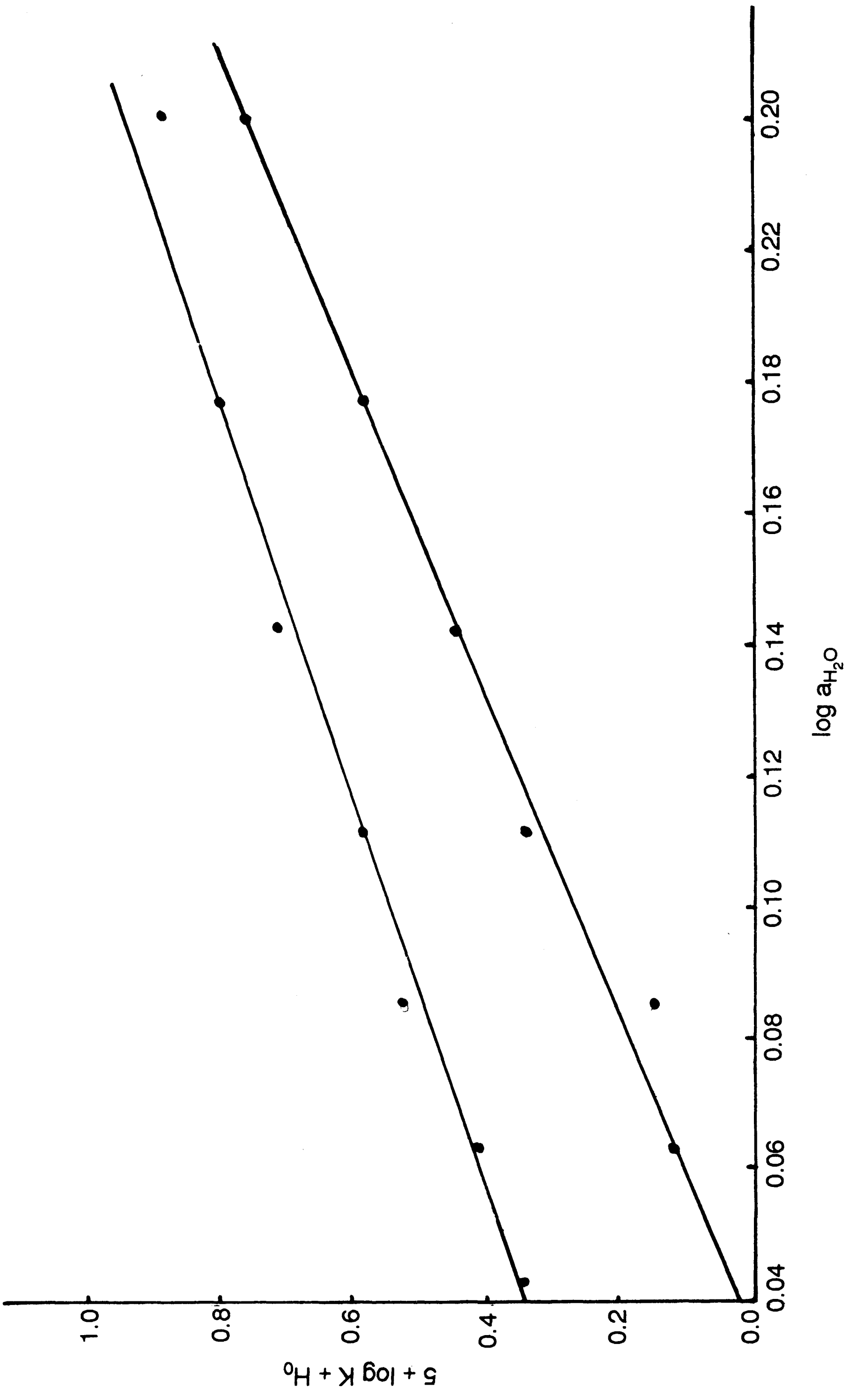


Fig. 2 Bunnett plot at 30°C (2-ABA = 0.05 M, $KMnO_4$ = 13.33 × 10^{-5} M)

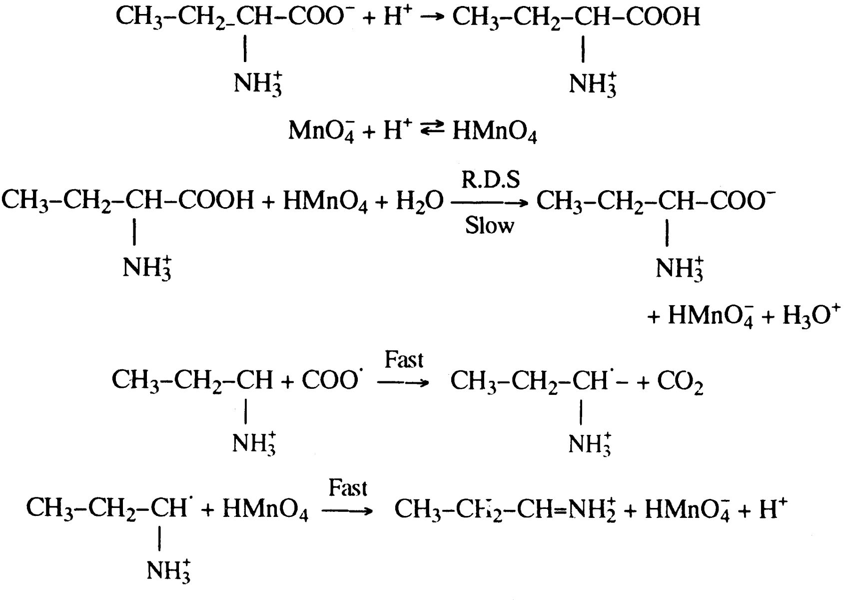
due to the incorporation of cation into the activated complex[21], or may be due to the influence of the cationic atmosphere on the activity coefficients of the reactants and activated complex.[22]

The specific effect of the cations and anions can be interpreted in terms of bridge formation, which facilitates or retards electron transfer in redox systems[23].

The products obtained in the present investigation were ammonia, carbon dioxide and aldehyde. Formation of these products was detected as tests given in Fiegl.[24] Similar products were reported by different workers for the oxidative decarboxylation of amino acids by permanganate[4, 16]

Mechanism

From the above findings and discussions the following mechanism is suggested:



$$CH_3-CH_2-\underset{\underset{NH_3^+}{|}}{CH}-COO^- + H^+ \rightarrow CH_3-CH_2-\underset{\underset{NH_3^+}{|}}{CH}-COOH$$

$$MnO_4^- + H^+ \rightleftharpoons HMnO_4$$

$$CH_3-CH_2-\underset{\underset{NH_3^+}{|}}{CH}-COOH + HMnO_4 + H_2O \xrightarrow[\text{Slow}]{\text{R.D.S}} CH_3-CH_2-\underset{\underset{NH_3^+}{|}}{CH}-COO^{\cdot} + HMnO_4^- + H_3O^+$$

$$CH_3-CH_2-\underset{\underset{NH_3^+}{|}}{CH} + COO^{\cdot} \xrightarrow{\text{Fast}} CH_3-CH_2-\underset{\underset{NH_3^+}{|}}{CH^{\cdot}}- + CO_2$$

$$CH_3-CH_2-\underset{\underset{NH_3^+}{|}}{CH^{\cdot}} + HMnO_4 \xrightarrow{\text{Fast}} CH_3-CH_2-CH=NH_2^+ + HMnO_4^- + H^+$$

$$CH_3-CH_2-CH=NH_2^+ + H_2O \rightarrow CH_3-CH_2-CHO + NH_3 + H^+$$

The formation of free radical in the reaction system is justified by the induced reduction of mercury (II) chloride[25-27]. Finally the formation of iminium ion and its subsequent hydrolysis to give an aldehyde and ammonia have also been proposed in the mechanisms of the permanganate oxidatation of L-leucine[28] and L-valine[29]

The above mechanism leads us to write the following rate expression:

$$-\frac{d}{dt}[MnO_4^-] = K[2\text{-}ABA][MnO_4^-]$$

TABLE 4
VARIATION OF RATE CONSTANT WITH VARYING CONCENTRATION OF H_2SO_4 at 30°C
2-ABA = 0.05 M, $KMnO_4 = 13.33 \times 10^{-5}$ M

Con. of H_2SO_4 (M)	2.00	2.50	3.00	3.50	4.00	4.50	5.00
$K \times 10^{-5}$ sec^{-1} (1st stage)	3.16	5.08	7.06	10.76	13.50	17.85	24.03
$K \times 10^{-5}$ sec^{-1} (2nd stage)	10.21	13.17	17.38	19.59	24.79	29.20	32.03

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