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Kinetics and Mechanism of Oxidation of L – Methionine by Potassium Bromate in Aqueous Hydrochloric Acid Medium

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ABSTRACT

The kinetics of the oxidation of L - methionine by bromate ions in aqueous acidic medium at a constant ionic strength, μ , of 0.50 mol dm^{-3} *were investigated spectrophotometrically at temperature of 30.0 ± 1ºC. The reaction shows a stoichiometry of 1:2 (Methionine/ bromate), first order kinetics in [methionine], first order in [bromate] and second order dependence in* $[H^+]$*. An increase in ionic strength and a decrease in dielectric constant of the reaction medium increase the rate of reaction. The reaction is catalysed by anions. Polymerization test conducted suggests the absence of free radicals. The results obtained from this study supports the operation of outer – sphere mechanism. A plausible mechanism is proposed for the reaction.*

Keywords: kinetics, stoichiometry, dependence, catalysis, free radicals.

INTRODUCTION

L–methionine or 2–amino–4(methylthio) butanoic acid, is one of the two sulphur – containing proteinogenic amino acids. The other one being cysteine. It is classified as an essential amino acid for humans and therefore must be supplied in the diet. It participates in a wide range of biochemical reactions and is intermediate in the biosynthesis of cysteine, carnitine, taurine, lecithin, phosphotidyl choline and other phospholipids. It is glycogenic and may participate in the formation of D – glucose and glycogen. It is oxidized by many oxidizing agents [1-4].

Bromate, an oxyanion, is a versatile oxidizing agent [5-8]. It oxidizes reducing agents and can be reduced to bromide and Br_2. Bromate reactions with natural and synthetic gastric juices have been documented [9]

The motivation for carrying out this kinetic investigation is multifold. Firstly, the choice of bromate ion as an oxidant arose from our desire to gain more insight in to the mechanism of its redox reaction which has been reported to be complex [10]. Secondly, it would be of interest to know the mode of activation adopted by methionine in aqueous medium. Thirdly, whether a short lived intermediate of significant stability can be inferred during the course of the reaction.

MATERIALS AND METHODS

Preparation of reagents

All chemicals and reagents used in the work were of analytical grade and were used without further purification. Standard salt solutions were made by dissolving known and accurately weighed amount of each salt in a given volume of distilled water. HCl was used to furnish H^+ to the reaction after it had been standardized titrimetrically; $KBrO_3$ and L-methionine were used as the oxidant and the reductant respectively. NaCl was used to maintain a constant ionic strength for each run.

The rates of reaction were studied by monitoring the increase in absorbance as the reaction progressed using Corning Colorimeter 253 at a wavelength of 420nm. All kinetic measurements were carried out under pseudo-first order conditions with [bromate] in at least 30-fold excess of [methionine] at constant temperature (30 °C), ionic strength of 0.50 mol dm^{-3} and $[H^+] = 5.00 \times 10^{-2}$ mol dm^{-3}. The pseudo-first order plots of log $(A_t - A_\infty)$ against time were made and the slopes of the plots gave the pseudo-first order rate constants, k_1. The second order rate constants, k_2, were determined from k_1 as $k_1/ [BrO_3^-]$. Spectroscopic measurements were carried out to determine whether spectroscopically detectable intermediates were formed during the course of the reaction. Spectra of the reaction mixtures were taken as the reaction progressed. Polymerization test was performed to test for presence of free radicals in the reaction mixture. Product analysis was carried out for some of the suspected products in the reaction mixture.

RESULTS AND DISCUSSION

Stoichiometric studies show that one mole of methionine is consumed by two moles of the bromate, which conforms to the equation equation 1.

$$R^+SCH_3 + 2BrO_3^- + 2H^+ \longrightarrow R^+CH_3S{=}O + Br_2 + H_2O + 2O_2 \text{ …….. (1)}$$

Thiols have three possible sites of attack (at the N, O and S). Sulphur has been established as the most susceptible centre of these three atoms [11]. N-benzoylmethionine sulphoxide, a derivative of methionine sulphoxide was identified as the oxidized product as described elsewhere [12] Literatures have also shown that oxidation of thiols can give rise to sulphenic acid, disulphide, sulphinic acid and sulphonic acid depending on the nature of the oxidant. The yellow colour of the product solution was attributed to the formation of Br_2 which fades with time.

Plots of log $(A_t - A_\infty)$ versus time obtained under pseudo-first order conditions were linear for almost about 90% extent of the reactions (A_t and A_∞ are the absorbances of the reaction at time, t and at the end of the reaction respectively), suggesting that the reaction is first order with respect to $[BrO_3^-]$. This is confirmed from the gradient of unity obtained from the plot of log k_1 versus log $[BrO_3^-]$ (Fig. 1). This means that the reaction is second order overall and the values of the second order rate constants are presented in Table 1. The rate law can therefore be represented by equation (2).

$$-d[BrO_3^-]/dt = k_2[R^+SCH_3][BrO_3^-] \qquad \text{……….(2)}$$

In the acid range used ($3.0 \times 10^{-2} \leq [H^+] \geq 18.0 \times 10^{-2}$ mol dm^{-3}), rate of reaction increased with increase in $[H^+]$ (Table 1). Plot of log k_1 versus log $[H^+]$ (Figure 2) gives a slope of $1.67 \approx 2$, suggesting that k_1 varies with log $[H^+]^2$. Plot of k_{H+} versus $[H^+]^2$ is linear without an appreciable intercept (Figure 3). The H^+ dependent second order rate constant can thus be presented by equation (3) below

$$k_{H+} = a[H^+]^2 \qquad \text{…………………………………..(3)}$$

The nature of the relationship obtained in equation (3) indicates that equilibrium between protonated and deprotonated forms of a reactant prior to the slow step is rapid and that the equilibrium constant for protonation is small and is not complete at high acidities, only the protonated species is reactive [13]. However, this is at variance with that reported for methionine/chromic system where the reaction proceeds via acid dependent and acid independent pathways. Hence, the observed acid catalysis could be attributed to the nature of the oxidants. In the range of $[H^+]$ used, the overall rate equation is represented by equation (4) below:

$$-d[BrO_3^-]/dt = a[BrO_3^-][R^+SCH_3][H^+]^2 \qquad \text{…………………..(4)}$$

The rate of reaction was found to increase with increase in ionic strength of reaction medium, μ (Table 1). A plot of log k_2 versus √μ gave a positive Bronsted – Debye salt effect with a gradient of 1.15 (Fig. 4). This result is further supported by the increase in the rate of reaction when the dielectric constants, D of the reaction medium were decreased (Table 2). These two observations suggest that reactant ions of like charges are reacting in the activated complex.

Addition of acrylamide to a partially oxidized reaction mixture with addition of excess methanol gave no gel indicative of the absence of free radicals in the reaction mixture.

Based on the above results, the following mechanism is proposed for the reaction.

$$BrO_3\text{-} + 2H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2BrO_3^+ \qquad \text{…………………………..(5)}$$

$$H_2BrO_3^+ + R^+SCH_3 \xrightarrow[\text{Slow}]{k_2} R^+CH_3S{=}O + H_2BrO_2^+ \qquad \text{…………(6)}$$

$$H_2BrO_2^+ + BrO_3^- \overset{K_3}{\rightleftharpoons} Br_2 + H_2O + 2O_2 \qquad \text{……….……..(7)}$$

Equation (6) is the rate determining step.

$\text{Rate} = k_2[H_2BrO_3^+][R^+SCH_3]$ ……………………………….(8)

Applying steady state approximation to the specie $H_2BrO_3^+$, we have equation (9)

$-d[H_2BrO_3^+]/dt = k_1[BrO_3^-][H^+]^2 - k_{-1}[H_2BrO_3^+] = 0$ ……..(9)

$k_1[BrO_3^-][H^+]^2 = k_{-1}[H_2BrO_3^+]$

Therefore, $H_2BrO_3^+ = k_1/k_{-1}[BrO_3^-][H^+]^2$

$= K_1[BrO_3^-][H^+]^2$ ……………………………(10)

Substituting equation (10) into equation (8), we have equation (11),

$\text{Rate} = K_1k_2[BrO_3^-][R^+SCH_3][H^+]^2$ ……… …………………....(11)

Equation (11) conforms to the observed rate law in equation (4), where ‘a’ = K_1k_2.

Thus the proposed mechanism accommodates all the experimental findings.

An important point in redox reaction is whether the electron transfer process is activated via the inner or the outersphere mechanistic pathways. Cases of parallel inner- and outersphere mechanisms have been observed [14-15] with the acid dependent pathways occurring via the outersphere mechanism. This issue can be addressed as follows:

(i) Absence of spectrophotometric evidence for precursor complex formation as scanning the reaction mixture did not implicate any shift in wavelength pointing to outersphere pathway.

(ii) Reaction rates were retarded by added anions (SO_4^- and $HCOO^-$) suggesting outersphere mechanistic pathway.

(iii) The above views are further assisted by the fact that Lineweaver Burk modification of Michaelis-Menten plot of $1/k_1$ versus $1/[BrO_3^-]$ was linear without intercept, implying lack of stable intermediate with significant formation constant.

The outersphere mechanism is hereby proposed for the titled reaction.

Table 1: Pseudo – first order and second order rate constants for the reaction of L – methionine and BrO_3^- at $[R^+SCH_3] = 2.0 \times 10^{-3}$ mol dm^{-3}, λ = 420 nm; Temp. 30 ±1.0°C.

10^2 $[BrO_3^-]$ mol dm^{-3}	$10^2[H^+]$ mol dm^{-3}	μ mol dm^{-3}	10^3k_1 s^{-1}	10^2k_2 dm^3 mol^{-1} s^{-1}
8.0	5.0	0.50	5.93	7.41
12.0	5.0	0.50	8.82	7.35
16.0	5.0	0.50	12.16	7.60
20.0	5.0	0.50	15.33	7.67
24.0	5.0	0.50	18.00	7.50
28.0	5.0	0.50	21.05	7.52
8.0	3.0	0.50	2.75	3.44
8.0	5.0	0.50	6.27	7.84
8.0	8.0	0.50	14.45	18.06
8.0	10.0	0.50	18.89	23.61

8.0	13.0	0.50	33.11	41.38
8.0	15.0	0.50	35.22	44.03
8.0	18.0	0.50	45.91	57.39
8.0	5.0	0.20	2.75	3.44
8.0	5.0	0.30	4.00	5.00
8.0	5.0	0.40	4.83	6.04
8.0	5.0	0.50	6.25	7.81
8.0	5.0	0.60	6.50	8.13
8.0	5.0	0.70	8.33	10.41
8.0	5.0	0.80	10.00	12.50

Table 2: Effect of changes in the dielectric constant of the reaction medium on the reaction of L - methionine and BrO_3^- at $[R^+SCH_3] = 2.0 \times 10^{-3}$ mole dm^{-3}; $[BrO_3^-] = 8.0 \times 10^{-2}$ mol dm^{-3}; $[H^+] = 5.0 \times 10^{-2}$ mol dm^{-3}; μ = 0.50 mole dm^{-3} ; λ = 420 nm; T = 30 ± 1 °C

D	10^3k_1 s^{-1}	10^2k_2 dm^3 mol^{-1} s^{-1}
81.00	6.07	7.59
78.00	6.83	8.54
76.20	7.20	9.00
73.80	8.47	10.59
72.60	8.50	10.63
71.40	9.38	11.73
70.00	10.00	12.50
69.00	11.10	13.86

Table 3: Rate data for the effect of added anions (SO_4^{2-} and $HCOO^-$) on the rate of reaction of L - methionine and BrO_3^-. $[R^+SCH_3] = 2.0 \times 10^{-3}$ mol dm^{-3}; $[BrO_3^-] = 8.0 \times 10^{-2}$ mol dm^{-3}; $[H^+] = 5.0 \times 10^{-2}$mol dm^{-3}, μ = 0.50 mol dm¯3; λ = 420nm; Temp. = 30 ± 1°C

Ion	10^3 [Ion], mol dm^{-3}	10^3k_1 s^{-1}	10^2k_2 dm^3 mol^{-1} s^{-1}
SO_4^{2-}	5.0	1.69	2.11
	20.0	1.41	1.76
	60.0	1.00	1.25
	80.0	0.85	1.06
	100.0	0.59	0.74
	120.0	0.46	0.58
$HCOO^-$	1.00	3.00	3.75
	5.00	2.64	3.30
	20.00	1.00	1.25
	60.00	0.21	0.26

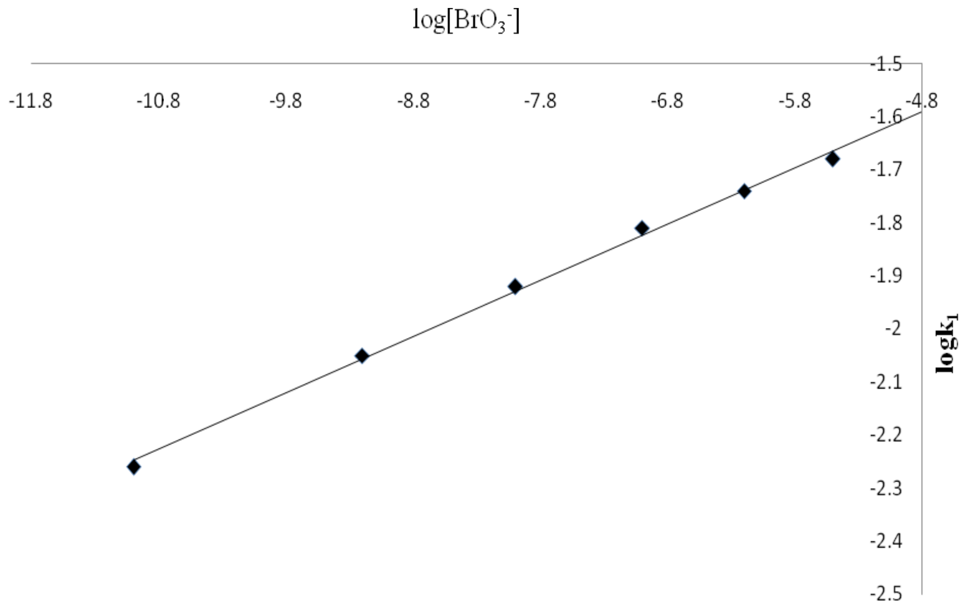

Fig 1: plot of log[BrO$_3^-$] versus logk$_1$

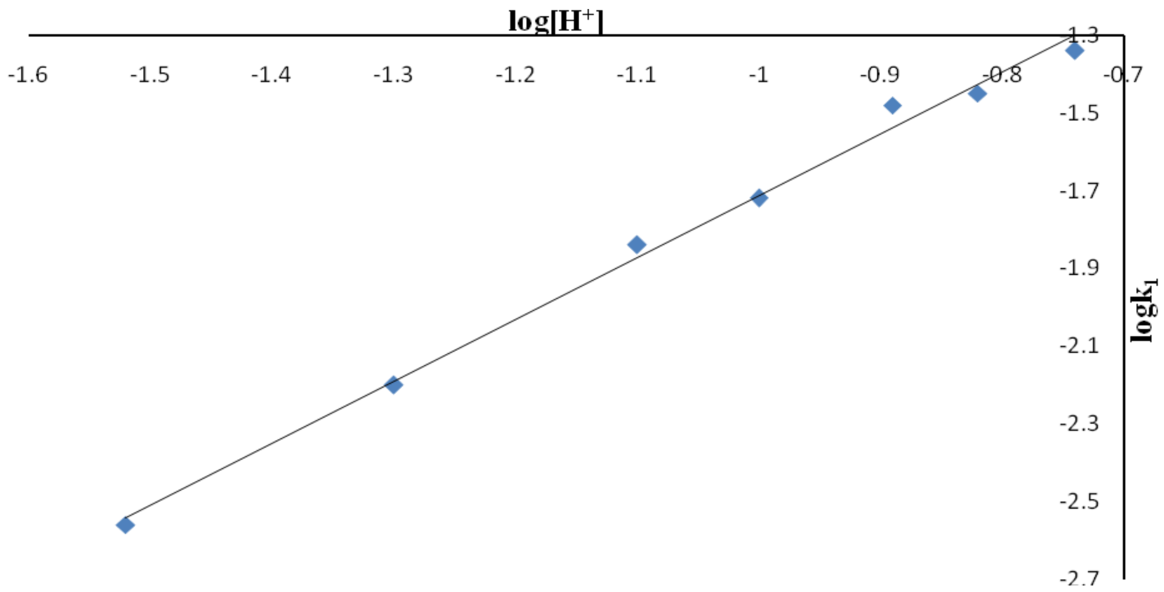

Fig.2 Plot of log[H$^+$] versus logk$_1$

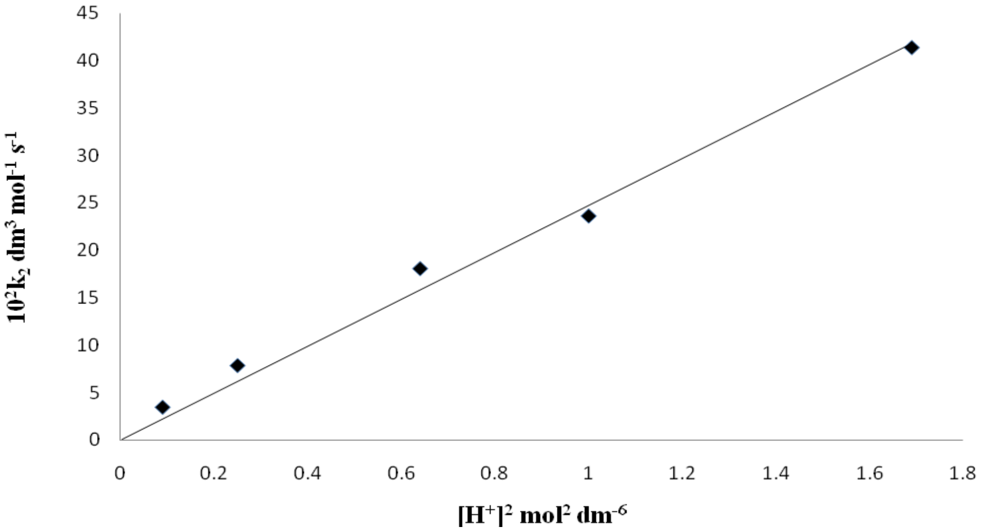

Fig.3: plot of k_2 versus [H$^+$]

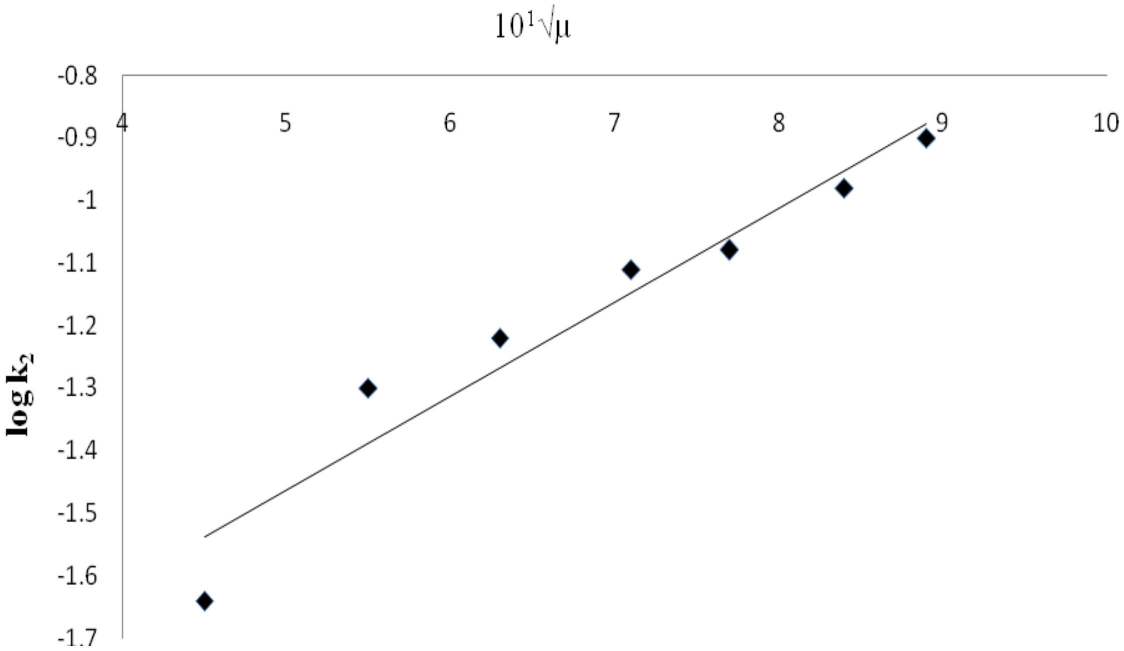

Fig.4: Plot of log k_2 versus $\sqrt{\mu}$

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