Article

Kinetics and Mechanism of Oxidation of Glycine and Alanine by Oxone® Catalyzed by Bromide Ion

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A oxidação da glicina e alanina por Oxone®, catalisada por íons brometo foi estudada em meio ácido. A reação é iniciada pela oxidação do brometo ao bromo, que reage com o aminoácido. A formação de bromo é comprovada pelo exame espectrofotométrico da mistura reacional. O intermediário proposto envolve a formação de um complexo entre o bromo e o ânion do aminoácido. A taxa de reação é inibida por um aumento na concentração do íon hidrogênio devido ao equilíbrio de protonação dos aminoácidos. Um mecanismo é proposto e a lei da razão derivada foi verificada graficamente. O efeito da permissividade relativa, força iônica e temperatura também foram acompanhados e esses efeitos também dão suporte ao mecanismo proposto.

Oxidation of glycine and alanine by Oxone® catalysed by bromide ions has been studied in acidic medium. The reaction is initiated by the oxidation of bromide to bromine, which then reacts with the amino acid. The formation of bromine is supported by the spectrophotometric examination of the reaction mixture. The proposed intermediate involves a complex formation between bromine and the anion of the amino acid. The rate of the reaction is inhibited by an increase in the hydrogen ion concentration due to the protonation equilibria of the amino acids. A mechanism is proposed and the derived rate law was verified graphically. Effect of relative permittivity, ionic strength and temperature was also carried out and these effects are also in support of the mechanism proposed.

Keywords: kinetics, Oxone®, bromide, catalysis, amino acids

Introduction

Bromine and its compounds are used as brominating and oxidizing agents in organic chemistry. A moderate redox potential of the $Br_2/2Br^-$ couple of 1.065 V makes it as a selective and mild oxidizing agent[1] in both acidic as well as alkaline solutions. The hazardous nature of bromine limits its uses in environmentally benign protocols. Therefore, attempts have been made to utilise the compounds like tetraalkylammonium salts[2,3] which contains bromine in the form of tribromide anion. These salts, when dissolved in a solvent, produce active bromine species, which effect the desired reaction to occur. Hypobromous acid, HOBr, is another active bromine species, which can be generated *in situ*. Variety of *N*-halo reagents are utilized for the generation of hypohalous acids[4-10] in solution for their application in synthetic organic chemistry, analytical determinations of organic compounds and for the study of mechanistic aspects.

Hypobromous acid (HOBr), a reactive bromine species, is known to be generated[11] during the disinfection process of water using chlorine or ozone containing bromide ion. Bromide ion concentrations[12] in ground water are in the range of 0.01 to 3 mg L^{-1}. This reactive bromine species, HOBr, can also be prepared by the combination of bromide and an oxidizing agent. Such combination of bromide with oxidants, like bromate and Oxone® has been utilized as a green protocol for bromination and oxidation[13] in organic synthesis. Biological production of hypobromous acid is also reported during activation[14] of eosinophils. The release of eosinophil peroxidase due to respiratory burst catalyzes the reaction between hydrogen peroxide and bromide ions to form hypobromous acid. The HOBr, thus, produced kills the invading pathogens,[14] and also plays an important role in damaging the tissues. It was also concluded that proteins are the major biological compounds[15] reacting with the HOBr. Therefore, we investigated kinetically the reaction between amino acids and Oxone® in the presence of bromide in acidic medium in order to understand the probable path of the reduction of the in situ generated bromine species.

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Experimental

Chemicals and solutions

All the chemicals used were of reagent grade and the solutions were prepared in double distilled water. The amino acids glycine and L- alanine were purchased from HiMedia and Oxone® from Spectrochem. The AR grade sulphuric acid (SDFine), potassium bromide (Thomas Baker) and sodium sulphate (SDFine) were used as received. The solutions of all the reactants, catalyst, sulphuric acid and sodium sulphate were prepared in double distilled water. The pH of the solutions was measured by Elico pH meter.

Kinetic measurements

The reaction was initiated by mixing previously thermostated solutions of the reactants at desired temperature. The reaction was followed by determining the unreacted oxidant iodometrically. The pseudo-first-order rate constants were determined from the linear plots of log(oxidant) against time plots and the values were reproducible up to +6%. The UV-Vis spectra of reaction mixtures were measured by using Shimadzu UV-3600.

Stoichiometry and product analysis

The stoichiometry for all the amino acids was determined by analysing the reaction mixtures containing amino acid (1.0×10^{-2} mol dm^{-3}) bromide (5.0×10^{-3} mol dm^{-3}), sulphuric acid (0.03 mol dm^{-3}) and excess of oxidant (0.1 mol dm^{-3}). The reaction mixture containing excess of oxidant, Oxone®, was kept in a thermostat at a required temperature for about a day and the remaining oxidant was iodometrically determined. The stoichiometry was found to be one mole of Oxone® per mole of each amino acid. The products according to the stoichiometry were the corresponding aldehydes.

For product analysis, the reaction mixtures (concentration of each reactant being twenty times that under kinetic condition) were allowed to stand for 24 h and then distilled, the distillate being collected in a closed container. The distillate was treated with 2,4-dinitrophenyl hydrazine (DNP) solution in 4 (N) H$_2$SO$_4$ when a yellow DNP derivative of the product was precipitated. It was filtered off, washed thoroughly, recrystallized from water and dried. The melting point (mp) of the derivatives were found to be 164 °C and 145 °C for glycine and alanine respectively (lit. mp 166 °C and 145 °C, respectively[16]) confirming the formation of formaldehyde and acetaldehyde as the products of the reactions. The presence of ammonia

in the reaction product was tested by Nessler's reagent. The product CO$_2$ was qualitatively detected by bubbling nitrogen gas through the reaction mixture and passing the liberated gas through limewater for all the amino acids. The proton NMR spectra of the DNP derivatives were recorded from Bruker Avence II 300 MHz instrument in CDCl$_3$(S1 and S2). The assignments of the peaks for formaldehyde is ^{1}H NMR (CDCl$_3$, 300 MHz) δ 6.74 (d, 1H, *J* 10.8 Hz), 7.16 (d, 1H, *J* 10.8 Hz), 8.00 (d, 1H, *J* 9.5 Hz), 8.36 (dd, 1H, *J* 2.6 & 2.7 Hz), 9.14 (d, 1H, *J* 2.7 Hz) and for acetaldehyde ^{1}H NMR (CDCl$_3$, 300 MHz) δ 2.15 (d, 3H, *J* 5.4 Hz), 7.58 (q, 1H, *J* 5.3 & 5.5 Hz), 7.94 (d, 1H, *J* 9.5 Hz), 8.30 (dd, 1H, *J* 2.5 Hz), 9.11 (d, 1H, *J* 2.6 Hz). Both spectra confirm the formation of the respective aldehydes.

Results and Discussion

Effect of oxidant and amino acid concentration

The effect of oxidant, Oxone®, was studied by keeping all other concentrations constant at fixed ionic strength and temperature. The concentration of oxidant was varied from 2.0×10^{-3} to 2.0×10^{-2} mol dm^{-3} (Table 1) and the pseudo-first-order rate constants, k$_{obs}$, were found to be constant indicating the first order dependence of the reaction on the oxidant concentration. The pseudo-first-order rate constants were found to increase with increase in concentration of amino acids varied between 0.05 to 0.5 mol dm^{-3} at a constant concentration of oxidant, catalyst, sulphuric acid and at an ionic strength of 0.05 mol dm^{-3}.

Table 1. Effect of concentration of amino acid and Oxone® on the k$_{obs}$ values at 27 °C. [KBr] = 5.0×10^{-3} mol dm^{-3}, [H$_2$SO$_4$] = 3.0×10^{-2} mol dm^{-3}, I = 0.17 mol dm^{-3}

| 10^2[Oxone®] (mol dm^{-3})	10[Amino acid] (mol dm^{-3})	10^3 k$_{obs}$ / s^{-1}	
		Glycine	Alanine
2.0	0.5	0.08	0.63
2.0	0.8	0.15	1.29
2.0	1.0	0.20	1.92
2.0	2.0	0.55	3.49
2.0	3.0	0.77	4.65
2.0	4.0	0.97	5.91
2.0	5.0	1.24	7.29
0.2	2.0	0.55	3.50
0.4	2.0	0.55	3.49
0.6	2.0	0.54	3.48
0.8	2.0	0.55	3.47
1.0	2.0	0.55	3.49
2.0	2.0	0.55	3.49

Table 2. Effect of concentration of sulphuric acid on various amino acid species and on the k_{obs} values at 27 °C. [KBr] = 5.0 × 10^{-3} mol dm^{-3}, [Oxone®] = 2.0 × 10^{-2} mol dm^{-3}, [Amino acid] = 0.2 mol dm^{-3}, I = 0.6 mol dm^{-3}

10^2[H$_2$SO$_4$] (mol dm^{-3})	pH	10^3[H$^+$] (mol dm^{-3})	[RCOOH] (mol dm^{-3})	[RCOO$^-$] (mol dm^{-3})	10^3 k_{obs} s^{-1} Glycine	Alanine
0.7	3.38	0.417	0.015	0.185	0.96	5.87
0.9	3.27	0.537	0.019	0.181	0.94	5.53
1.5	3.07	0.851	0.029	0.171	0.78	5.26
3.0	2.78	1.66	0.050	0.150	0.55	3.45
5.0	2.52	3.02	0.75	0.125	0.29	2.92
7.0	2.3	5.01	0.101	0.099	0.20	2.38

The plot of k_{obs} against [amino acid] were also found to be linear (R^2 > 0.9916), indicating the first order dependence of the reaction on the [amino acid].

Effect of bromide ion and hydrogen ion concentration

The concentration of bromide ion varied between 1.0 × 10^{-3} to 1.0 × 10^{-2} mol dm^{-3} at constant concentration of all other constituents and at a constant temperature. The pseudo-first-order rate constants increase linearly as the bromide ion (Figure 1) concentration increases, showing a first-order dependence of the reaction on its concentration. The pseudo-first-order rate constants were found to decrease as the hydrogen ion concentration increases from 1.07 × 10^{-2} to 7.92 × 10^{-2} mol dm^{-3} keeping all other concentrations constant. The values of k_{obs} decreases with increase in hydrogen ion concentration (Table 2) and the orders in hydrogen ion concentration were found to be around −0.53 indicating inverse first-order dependence on the hydrogen ion concentration. The hydrogen ion concentration in the reaction mixture was calculated using known equilibrium constants of sulphuric acid and orders in hydrogen ion concentration were determined from log[H$^+$] against log k_{obs} plots.

### Effect of relative permittivity, ionic strength and temperature

The effect of relative permittivity and ionic strength was studied by keeping concentrations of oxidant (0.02 mol dm^{-3}), amino acid (0.2 mol dm^{-3}), potassium bromide (0.005 mol dm^{-3}) and sulphuric acid (0.03 mol dm^{-3}) constant at 27 °C. The ionic strength varied between 0.08 to 0.17 mol dm^{-3} by adding potassium nitrate while that of relative permittivity by adding acetic acid between 0 to 40 % v/v. The pseudo-first-order rate constants of the reaction were found to increase moderately as the ionic strength increases and decrease as the acetic acid content increases. The plot of log k_{obs} against 1/D (where the relative permittivity of the reaction mixture) was found to be linear with negative slope. The effect of temperature was studied between 15 to 45 °C by keeping all the concentrations constant (Table 3.) The activation parameters calculated from the effect of temperature are given in Table 3. The plots of log k_{obs} and log (k_{obs} /T) against T were given in supplementary data (S3 and S4).

Table 3. Effect of temperature on oxidation of amino acids by Oxone® in the presence of KBr. [KBr] = 5.0 × 10^{-3} mol dm^{-3}, [Oxone®] = 2.0 × 10^{-2} mol dm^{-3}, [amino acid] = 0.2 mol dm^{-3}, [H$_2$SO$_4$] = 3.0 × 10^{-2} mol dm^{-3}, I = 0.6 mol dm^{-3}

Temperature / K	$10^3 k_{obs}$ / s^{-1} Glycine	Alanine
288	0.12	1.99
300	0.55	3.52
308	0.73	7.74
318	1.35	14.0
Activation parameters		
E_a / (kJ mol^{-1})	43.6 ± 0.4	35.2 ± 0.5
$\Delta H^{\#}$ / (kJ mol^{-1})	42.2 ± 0.4	33.5 ± 0.5
$\Delta G^{\#}$ / (kJ mol^{-1})	97.6 ± 0.4	90.2 ± 0.5
$-\Delta S^{\#}$ / (JK^{-1}mol^{-1})	184 ± 6	189 ± 8

Figure 1. Effect of concentration of bromide ion on the k_{obs} values at 27 °C. [Oxone®] = 2.0 × 10^{-2} mol dm^{-3}, [Amino acid] = 0.2 mol dm^{-3}, [H$_2$SO$_4$] = 3.0 × 10^{-2} mol dm^{-3}, I = 0.17 mol dm^{-3}. (◆ Glycine, ■ Alanine).

Mechanism

The accepted structure[17] of the oxidant, Oxone® or peroxomonosulphuric acid, used in the present study contains a sulphur atom surrounded tetrahedrally by perhydroxyl group and a hydroxyl group, as shown in Scheme 1. The proton of the hydroxyl group is equivalent to that of sulphuric acid proton and is highly ionized[18] while that of the perhydroxyl group is weakly ionized. The pK value of the perhydroxyl proton is reported[18] to be 9.4, indicating that in strongly acidic pH, the peroxomonosulphate exists mainly in the form of HSO_5^- ion.

$$
\begin{array}{c}
O \\
\parallel \\
HO\!-\!\!\!-\!S\!-\!\!\!-\!O\!-\!\!\!-\!OH \\
\parallel \\
O
\end{array}
$$
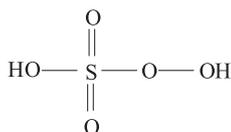
Scheme 1.

Since, the conditions of the present study are carried out in the pH range of 1 to 2, the oxidant is in the form of peroxomonosulphate anion, HSO_5^-. The oxidations of halide ions by peroxomonosulphate ion[19,20] has been studied and an oxygen atom transfer mechanism is proposed. The mechanism involves slow oxidation of bromide ion in acidic medium containing stoichiometrically excess oxidant generating HOBr with a rate constant[19] of 0.7 $dm^3 mol^{-1} s^{-1}$. In acidic medium, hypobromous acid, HOBr, undergoes various equilibrium and redox reactions as given in equations 1-4 with the reported equilibrium and rate constants respectively. The pK value[21] of the hypobromous acid is 8.8, therefore, under the present conditions of the reaction, it exists in the protonated form, HOBr. In acid medium, the first rate determining step of oxidation of bromide ion by peroxomonosulphate, Oxone®, is the formation of hypobromous acid followed by its fast oxidation generating bromine as shown in reaction 2 with a rate constant[21] of the order of $1.6 \times 10^8 dm^6 mol^{-2}$.

$$HOBr \rightleftharpoons OBr^- + H^+ \qquad (1)$$
$$pK = 8.8$$

$$HOBr + H^+ + Br^- \rightleftharpoons Br_2 + H_2O \qquad (2)$$
$$K = 1.6 \times 10^8 dm^6 mol^{-2}$$

$$Br_2 + Br^- \rightleftharpoons Br_3^- \qquad (3)$$
$$K = 16.8 dm^3 mol^{-1}$$

$$2HOBr \longrightarrow BrO_2^- + H^+ + Br^- \qquad (4)$$
$$K = 2.3 \times 10^{-3} dm^3 mol^{-1} s^{-1}$$
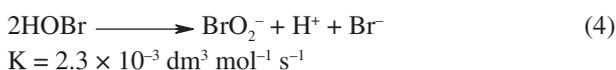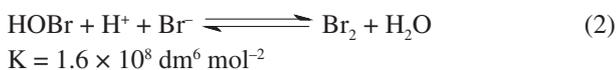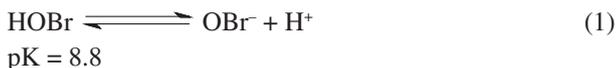
Other possible reactions of bromine are formation of tribromide[21] ion according to reaction 3 and reaction 4. However, it has been predicted that formation of tribromide ion is negligible[19] in solutions containing excess of HSO_5^- than the bromide ion. The rate law for the reaction 4 requires an order of more than unity in bromide ion as it involves two hypobromous acid molecules[21] which is also not observed in the present investigation. Therefore, the oxidation of bromide ion to hypobromous acid in a slow step and bromine in a fast step by the active oxidant species, HSO_5^-, is considered as the probable path of generating the active catalyst species, bromine, in the present reaction. The bromine produced reacts with the amino acid without undergoing any of the reactions 3 and 4. The UV-Vis spectra of various species formed in the reaction between bromide and Oxone® is reported.[19] Therefore, the UV-Vis spectrophotometric examination of the reaction mixture with and without amino acid was carried out to know the probable active species formed in the present study. The UV-Vis examination of a mixture of bromide and Oxone® in the presence of sulphuric acid gave a peak at 394 nm (Figure 2) indicating formation of bromine, the other bromine species HOBr, Br^{3-} and BrO^- absorbs at 262, 266 and 332 nm, respectively. Since, the UV-Vis spectrum of mixture containing bromide and Oxone® shows only one absorption peak at 394 nm corresponding to bromine, the formation of other bromine species is not occurring. Further, in the presence of amino acid (glycine) the absorbance of the peak at 394 nm due to bromine decreases (Figure 2) as a result of reaction between the amino acid and the generated bromine.
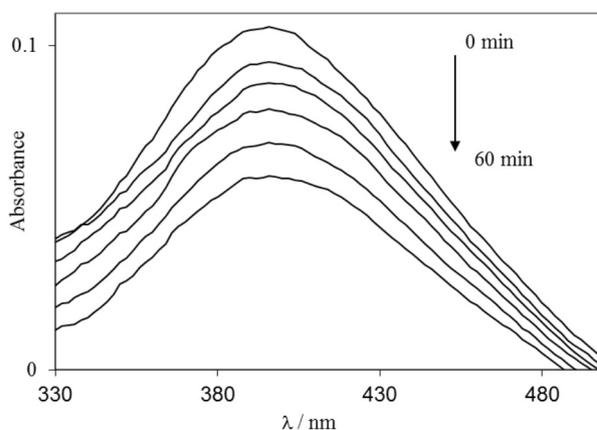
**Figure 2.** UV-Vis spectrum of reaction mixture in presence and in absence of Glycine. 10^4[KBr] = 2.5 mol dm^{-3}, 10^3[Oxone®] = 3.75 mol dm^{-3}, 10^3[Glycine] = 1.0 mol dm^{-3}, 10^3[H$_2$SO$_4$] = 4.6 mol dm^{-3}.

The amino acids glycine and alanine have two protonation sites, the amino group and the carboxylic group. The pK of amino group is more than 9.1 for these amino acids,[22] while

that of the carboxylic group is 2.35 for glycine and alanine.[22] Since the present study is carried out in acidic medium, all the amino groups are protonated and exists as $-NH_3^+$. Due to partial protonation of carboxylic acid group, both protonated, -COOH, and unprotonated, $-COO^-$, species exists together. Assuming an average pK value of carboxylic acid group as 2.3, the concentrations of both protonated and unprotonated species of the amino acids were calculated. It was found that the concentration of protonated species increases while that of unprotonated species decreases as the hydrogen ion concentration increases (Table 2). The values of k_{obs} for the oxidation of amino acids were also found to decrease as the hydrogen ion concentration decreases. The protonation of the oxidant species, HSO_5^-, does not occur under the present conditions and although generation of bromine is hydrogen ion dependent reaction, but it occurs with a high rate constant[19,20] thus making it independent of hydrogen ion. Therefore, the hydrogen ion dependence can be explained satisfactorily by the protonation equilibria of the carboxylic group of the amino acid, which undergo partial protonation.

It can be noticed that the values of k_{obs} and the concentration of unprotonated amino acid decrease as the hydrogen ion concentration in the reaction media increases (Table 2). From the kinetic results and the calculated concentrations of the species of amino acid indicate that its unprotonated species are the reactive ones under the present reaction conditions.

The reaction of hypohalous acids with amino acids at near neutral pH has been studied and the mechanism involves formation of short lived bromamines or bromamides.[15] These intermediates are formed as a result of an electrophilic attack of hypohalous acid on the lone pair of nitrogen of the amino group. Such a bromamine formation is possible when the lone pair of electron is available on the nitrogen. Since, in acidic solutions, the amino group is in the protonated form therefore, the formation of a bromamine type species is not feasible. Since, in acidic solutions, the amino group is in the protonated form formation of a bromamine is not feasible. Therefore, electrophilic attack of Br_2 on the carboxylate anion[23] of the amino acid would be more probable in acidic medium. The kinetic results also indicate
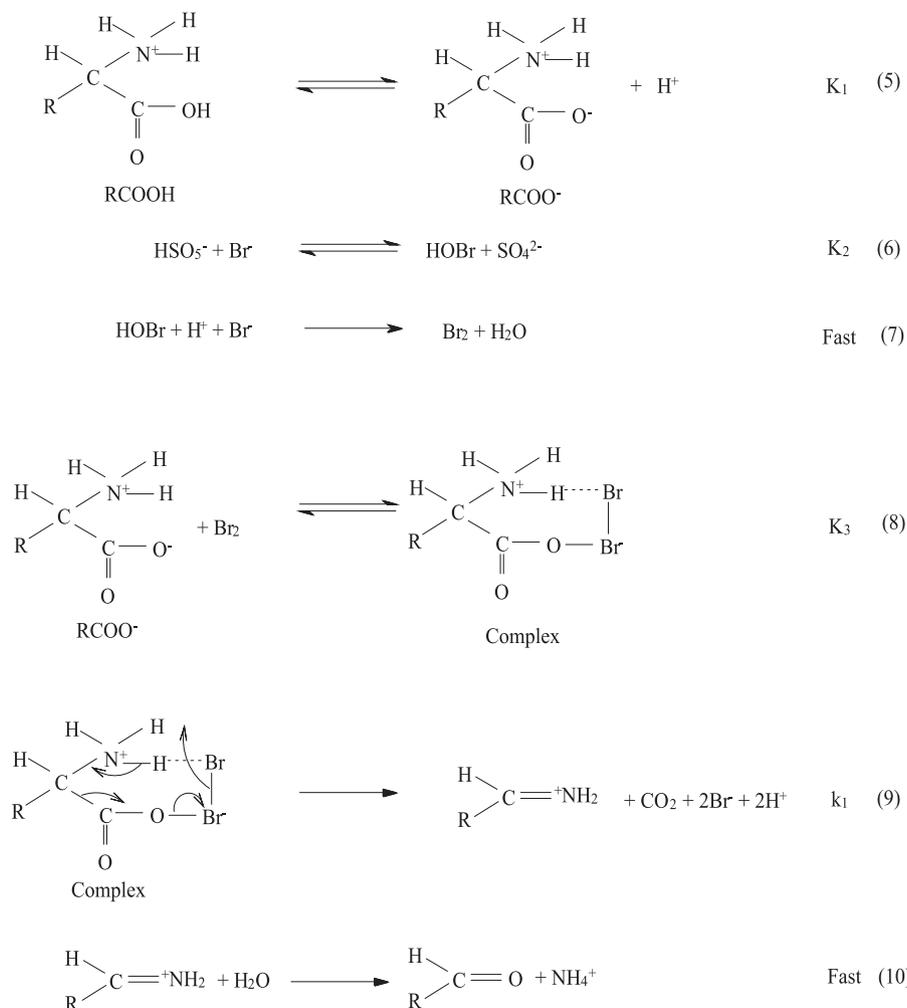
Scheme 2.

that the unprotonated amino acid is the active species. Considering unprotonated amino acid anion as the active species, which reacts with the Br_2 generated as a result of reaction between HSO_5^- and bromide ion, the mechanism can be represented by Scheme 2. The rate law according to Scheme 2 can be derived as follows: the rate of reaction is given by equation 11. The oxidation of bromide ion by Oxone® follows a simple second order rate law with the rate constant[19,20] of 1.0 dm^3 mol^{-1} s^{-1}. Therefore, the $[Br_2]$ as a result of both the steps of Scheme 1 can be represented by equation 13. Substituting the [Complex] in terms of $[Br_2]$ and $[RCOO^-]$ from equation 7 of Scheme 2, we get equation 14. Then from the equilibrium 5 of Scheme 2, the total concentration of amino acid is expressed as in equation 15 where $[RCOOH]_t$, $[RCOOH]_f$ and $[RCOO^-]$ are the concentration of total, free and anion of the amino acid, respectively. Solving for the $[RCOO^-]$, we get equation 16. Substituting for $[RCOO^-]$ in equation 14, we get the final rate law 17 for the reaction. The corresponding expression for the pseudo-first-order rate constant, k_{obs}, is given by equation 18. The expression 18 can be verified by plotting k_{obs} against $[Br^-]$ (Figure 3) and such plots for all the amino acids studied were found to be linear without any intercept in support of the proposed mechanism. Further, inversion of equation 18 results into equation 19, which can also be verified by plotting $(1/k_{obs})$ against $[H^+]$ and such plots for the two amino acids were also found to be linear (Figure 4).

$$Rate = k_1[Complex] \qquad (11)$$

$$Rate = k_1K = [RCOO^-][HOBr] \qquad (12)$$

$$[Br_2] = K_2[HSO_5^-][Br^-] \qquad (13)$$

$$Rate = k_1K_2K_3[RCOO^-][HSO_5^-][Br^-] \qquad (14)$$

$$[RCOOH]_t = [RCOOH]_f + [RCOO^-] = [RCOOH]_f + (K_1[RCOOH]_f / [H^+]) \qquad (15)$$

$$[RCOO^-] = [RCOOH]_t / ([H_+] + K_1) \qquad (16)$$

$$Rate = k_1K_2K_3[RCOOH]_t[HSO_5^-][Br^-] / ([H^+] + K_1) \qquad (17)$$

$$k_{obs} = k_1K_2K_3[RCOOH]_t[Br^-] / ([H^+] + K_1) \qquad (18)$$

$$\frac{1}{k_{obs}} = \frac{([H^+] + K_1])}{k_1K_2K_3[RCOOH]_t[Br^-]} \qquad (19)$$

The reaction, as shown in Scheme 2 is, initiated by the oxidation of bromide to bromine which oxidizes amino acid in a rate determining step. A moderate increase in the k_{obs}
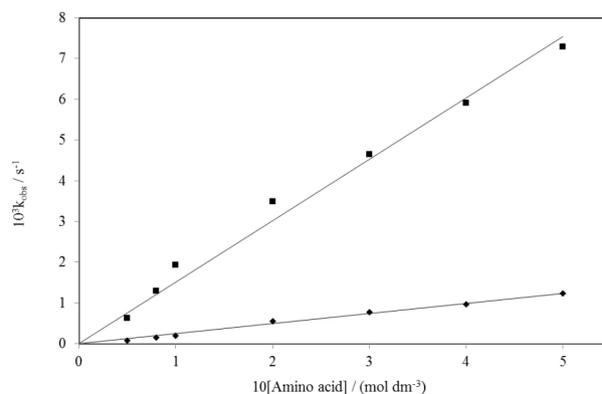
Figure 3. Effect of concentration of amino acid on the k_{obs} values at 27 °C (Conditions as in Table 1) (◆ Glycine, ■ Alanine).
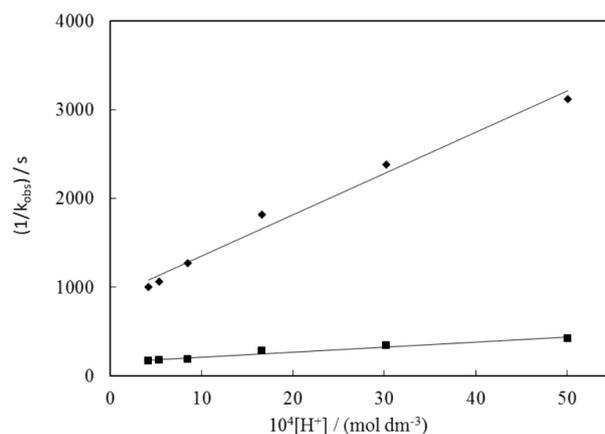
Figure 4. Plot of $(1/k_{obs})$ against $[H^+]$ (Conditions as in Table 2) (◆ Glycine, ■ Alanine).

values as the ionic strength increases indicate the reaction between two negative ions in a prior equilibrium and since the rate determining step involves a neutral Br_2, which is not affected by the change in the ionic strength. The rate of the reaction decreases with decrease in the relative permittivity of the reaction mixture and the plot of log k_{obs} against $(1/D)$ was linear with a negative slope. The transition state formed between Br_2 and the active amino acid species is more polar and it decomposes into ionic species. Further, the decrease in the relative permittivity of the reaction medium also shifts the equilibrium 5 towards the $RCOOH^{24}$ of the amino acid thus diminishing the reactive nucleophile $RCOO^-$. All these effects are reflected in a decrease in the rate of reaction as the relative permittivity decreases. The activation entropy was negative for all the two amino acids. The polar nature of the transition state leads to immobilization of solvent molecules around the charged ends, which results into the loss of entropy as noticed in the present study. The observed enthalpy of activation is of the order glycine > alanine and the enthalpy of formation of these amino acids is of the order[25] alanine > glycine. The enthalpy of activation is the difference in bond energies of the starting compounds[26]

and the transition state including the strain. The amino acid with bulky group will have high ground state energy and the observed decrease in enthalpy of activation energy from glycine to alanine indicate that the transition state has the same energy for the amino acids studied.

Conclusions

Oxidation of glycine and alanine by Oxone® in the presence of bromide ions was found to proceed through formation of bromine. Electrophilic attack of the bromine on the carboxylate anion of the amino acid leads to the formation of an intermediate complex in a fast prior equilibrium. The complex thus formed, decomposes in a slow step. Since, the amino group of the amino acid is in the protonated form, formation a bromamine like intermediate is less feasible. The rate of reaction increase as the ionic strength increases due to the initiation of the reaction between unprotonated Oxone® anion, HSO_5^-, and bromide ions as both are negative ions. The effect of relative permittivity on the rate of the reaction supports the formation of a polar intermediate complex. Similarly, the entropy was negative for the two amino acids, also indicating the polar nature of the transition state leads to immobilization of solvent molecules around the charged ends which results into the loss of entropy as noticed in the present study. The nature of the transition state is the same for all the amino acids studied as noticed by the order of observed enthalpy of activation.

Supplementary Information

Supplementary data are available free of charge at http://jbcs.sbq.org.br as PDF file.

References

1. Palou, J. J.; *Chem. Soc. Rev*. **1994**, *23*, 357.

2. Kajigaeshi, S.; Kakinami, T.; Okamoto, T.; Fujisaki, S.; *Bull. Chem. Soc. Jpn*. **1987**, *60*, 1159.

3. Mondal, E.; Bose, G.; Khan, A. T.; *Synlett* **2001**, *6*, 785.

4. Mahadevappa, D. S.; Rangappa, K. S.; Gowda, N. M. M.; Gowda, B. T.; *Int. J. Chem. Kinet*. **1982**, *14*, 1183.

5. Meenakshisundaram, S.; Sockalingam, R. M.; *J. Mol. Catal. A: Chem*. **2000**, *160*, 269.

6. Puttaswamy; Jagadeesh, R. V.; *Cent. Eur. J. Chem.* **2005**, *3(3)*, 482.

7. Kondarasaiah, M. H.; Ananda, S.; Puttaswamy; Gowda, N. M. M.; *Synth. React. Inorg. Met.-Org. Chem.* **2003**, *33(7)*, 1145.

8. Puttaswamy; Jagadeesh, R. V.; *Int. J. Chem. Kinet*. **2005**, *37*, 201.

9. Puttaswamy; Jagadeesh, R. V.; *Ind. Eng. Chem. Res*. **2006**, *45*, 1563.

10. Vinod Kumar, C. H.; Jagadeesh, R. V.; Shivananda, K. N.; Sree Sandhya, Y.; Naga Raju, C.; *Ind. Eng. Chem. Res*. **2010**, *49*, 1550.

11. Beckwith, R. C.; Margerum, D. W.; *Inorg. Chem*. **1997**, *36*, 3754.

12. U.S. Environmental Protection Agency; *Federal Register*; GPO: Washington, DC, 1994; Vol. 59 (July 29), 38721.

13. Adimurthy, S.; Ghosh, S.; Patoliya, P. U.; Gadde, R.; Agrawal, M.; Gandhi, M. R.; Upadhyay, S. C.; Ghosh, P. K.; Ranu, B. C.; *Green Chem*. **2008**, *10*, 232.

14. Weiss, S. J.; Test, S. T.; Eckmann, C. M.; Roos, D.; Recvani, S.; *Science* **1986**, *234*, 200.

15. Hawkins, C. L.; Davies, M. J.; *Free Radical Bio. Med.* **2005**, *39*, 900.

16. Buckingham, J.; *Dictionary of Organic Compounds*, 5th ed., Chapman & Hall: New York, 1982.

17. Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M.; *Advanced Inorganic Chemistry*, 6th ed., John Wiley & Sons: Singapore, 2003.

18. Donald, L. B.; Edwards, J. O.; *J. Chem. Soc*. **1956**, 1125.

19. Lente, G.; Kalmár, J.; Baranyai, Z.; Kun, A.; Kék, I.; Bajusz, D.; Takács, D. M.; Veres, L.; Fábián, I.; *Inorg. Chem*. **2009**, *48*, 1763.

20. Fortnum, D. H.; Battaglia, C. J.; Cohen, S. R.; Edwards, J. O.; *J. Am. Chem. Soc*. **1960**, *82*, 778.

21. Beckwith, R. C.; Margerum, D. W.; *Inorg. Chem*. **1997**, *36*, 3754.

22. *CRC Handbook of Chemistry and Physics*, 67th ed., CRC Press, Inc.: Boca Raton, Florida, 1986-87.

23. Pink, J. M.; Stewart, R.; *Can. J. Chem*. **1971**, *49*, 649.

24. Sen, P. K.; Gani, N.; Midya, J. K.; *Transition Met. Chem*. **2008**, *33*, 229.

25. Sagadeev, E. V.; Gimadeev, A. A.; Barabanov, V. P.; *Russ. J. Phys. Chem. A* **2010**, *84*, 209.

26. Garg, D.; Kothari, S.; *Indian J. Chem*. **2005**, *44 B*, 1909.