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CHAPTER - I

INTRODUCTION

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INTRODUCTION

The subject of chemical kinetics is mainly concerned with the quantitative study of the rates of chemical reactions and of the factors upon which they depend. Such studies may be of prime importance in connection with technical processes, they may throw light on the general principles of reactivity or may be useful in arriving at a reaction mechanism.

A wide variety of experimental techniques have been used to investigate chemical reactions which are again of many different types. Kinetics and mechanisms of reactions in gas phase, liquid phase and <sup>at</sup> solid-gas interface have been elucidated. Although these reactions have been studied kinetically by conventional techniques such as volumetric, conductometric, spectrophotometric analysis etc. The recent developments in electronic techniques have enabled the scientists to investigate the reactions under drastic conditions such as very high temperatures, hydrostatic pressure and the rapid reactions.

Any kinetic investigation generally comprises of two parts - first to establish the relationship between the rate of the reaction and various factors such as concentrations of reactants, temperature and hydrostatic pressure. (in case of gas phase reactions). To these may

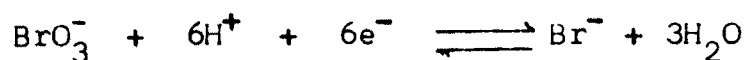
be added some other factors, such as primary and secondary salt effects, dielectric constant of the medium and catalysis. Identification of products of the reaction and detection of free radicals, intermediates etc. are also done. Second part of the investigation is to arrive at a suitable mechanism which can account for the result obtained on velocity measurements.

### 1.1 OXIDATION REACTIONS :

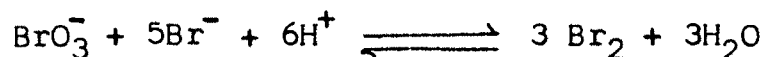
A large volume of kinetic work has been done in liquid phase reactions, because these reactions are of keen interest in the organic and inorganic chemistry. In organic reactions the oxidation reactions are of most important. A variety of oxidizing agents such as nitric acid, chromic acid, potassium permanganate, potassium persulphate, potassium periodate, peroxy disulphate, Chloramine-T, potassium bromate etc. have been used to study the oxidation of variety of organic compounds, like phenols, ketones, aldehydes, esters, alcohols, carboxylic acids, hydroxy acids, anilines etc. The potassium bromate is a strong oxidizing agent. Therefore, it is proposed to take a brief review of the work done on the oxidation of different compounds by potassium bromate.

## 1.2 POTASSIUM BROMATE AS OXIDANT :

Potassium bromate<sup>19</sup> is a powerful oxidising agent having an oxidation potential 1.44 V in an acidic medium, which is reduced smoothly to bromide.



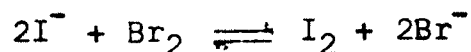
The equivalent is, therefore, 1/6 mole. ( $\text{KBrO}_3/6$ ) or  $167/6$  or 27.833 and a 0.1 N solution contains 2.7833 gms of potassium bromate per  $\text{dm}^3$ . At the end of the titration, free bromine appears



Various substances cannot be oxidized directly with potassium bromate, but react quantitatively with an excess of bromine. Acid solutions of bromine of exactly known concentration are readily obtainable from a standard potassium bromate solution by adding acid and an excess of bromine.

In above reaction one mole of bromate yields six atoms of bromine, hence the equivalent is  $\text{KBrO}_3/6$ , identical<sup>to</sup> that of potassium bromate alone. Bromine is very volatile, and hence such operations should be conducted at as low temperature as possible in conical flasks fitted with round glass stoppers. The excess of bromine may be

determined iodometrically by the addition of excess of potassium iodide and titration of liberated iodine with standard sodium thiosulphate solution.



Potassium bromate is readily available in a high state of purity, the AR product has an assay value of at least 99.9 %. It can be used as primary standard, its only disadvantage is that, the equivalent is comparatively small.

Potassium bromate is widely used for detection and estimation of various transition metals.

### 1.3 OXIDATIONS WITH POTASSIUM BROMATE :

#### 1.3.1 OXIDATION OF ALCOHOLS :

##### (A) Oxidation of Primary Alcohols :

The kinetics of oxidation of primary alcohols by acid bromate has been studied in acetic acid-water medium in presence of sulphuric acid by Vijaylakshmi and E.V.Sundaram<sup>2</sup> in 1980. Order with respect to oxidant was one and fractional with respect to substrate. The order of reacting alcohols is not regular and does not show correlation with Taft plot. Decomposition constants for the alcohol-bromate complexes were calculated and the plot of  $\log k_d$  versus Taft  $\sigma^*$  values gave a linear plot with a slope of

- 0.70 indicating the formation of a transition state with small positive charge on alpha carbon atom.

The alcohols are methanol, ethanol, n-propanol, n-Butanol, iso-butanol, n-pentanol, iso-pentanol, n-hexanol, n-heptanol, benzyl alcohol, 2-phenyl ethyl alcohol, 2-Cl-ethanol.

Oxidation of primary aliphatic and secondary alcohols<sup>3,20,58,59</sup> by acid bromate has been studied.

(B) Oxidation of Secondary Alcohols :

The oxidation by Br(V) of propan-2 ol, follows the rate law

$$\left( -\frac{d[\text{Br(v)}]}{dt} \right) = k [\text{Alcohol}] [\text{Br(v)}] [\text{H}^+]^2$$

The initial reaction is complicated by the presence of the product bromide ion. The reaction is composed of two second order reactions - the first, a comparatively slow one and the second a faster reaction, which is mainly bromide oxidation. The pure bromate oxidation can be followed by the initial addition of mercuric acetate which prevents the accumulation of bromine in the system under these conditions. The reaction rate does not depend on the nature and structure of the alcohol. A mechanism involving a slow rate determining formation of an alkyl-bromate ester followed by a fast decomposition to the product is in accord with the observed result.

The oxidation of secondary alcohols like propan-2-ol, 1-3-dichloropropan-2ol, 1-Methoxy propan-2-ol, Butan-2-ol, pentan-2-ol, Octan-2-ol,<sup>was</sup> given by R. Natarajan and N. Venkatasubramanian<sup>3</sup> in 1973.

(C) Oxidation of Tertiary Alcohols :

The oxidation of alcohols like Trimethylcarbinol, Dimethylethylcarbinol, Triethylcarbinol, Di-methylphenylcarbinol, Di-methylbenzylcarbinol, 2-3-Dimethylbutane -2-3-diol, 2-methyl-3-phenylbutane-2-3-diol, 2-3-Diphenylbutane-2-3-diol is studied by CH Sanjeeva Reddy and E.V. Sundaram.<sup>1</sup> in 1987.

The oxidation of the above tertiary alcohols by bromate in acid medium is first order in  $[Br(v)]$ . However, the first order rate constants decrease with increase in  $[Bromate]$  and the inverse first order rate constants are linearly related with  $[Br(v)]$ . Increase in  $[substrate]$  increases the rate and the reaction exhibits Michaelis-Mentens type of kinetic behaviour. Ionic strength effect is marginal, but increase in the acidity of the medium enhances the rate. The oxidation rate is also susceptible to changes in dielectric constant of the medium. The results are suggestive of a mechanism which involves fast pre-equilibrium complexation between  $Br(v)$  and the substrate yielding two complexes which differ only by a proton, followed by rate determining carbonyl compound formation and an intermediate which is subsequently oxidised to give products. The retardation effect of bromate may be due to the formation of a bromate dimer, which is inactive towards reduction.

(D) Oxidation of Benzyl alcohol :

C.H. Sanjeeva Reddy and E.V. Sundaram<sup>4</sup> have shown that the oxidation of benzyl alcohol and substituted benzyl alcohols by bromate in the presence of Mercury(II) ions follows the rate law,

$$-\frac{d[\text{Br}(v)]}{dt} = k [\text{benzyl alcohol}] [\text{Br}(v)]$$

Increasing acidity of the medium enhances the rate and the rate constant correlates well with the acidity function  $H_0$ . From the effect of ionic strength and dielectric constant the reaction has been found to be between a positive ion and a dipole, and the values of  $r^0$  have been evaluated. Benzyl alcohol is oxidised by bromate at a rate 1.6 times faster than  $\alpha$  -  $\alpha$  - dideuteriobenzyl alcohol at 40°C. The order of reactivities among the studied benzyl alcohols is  $p\text{-OCH}_3 > p\text{-CH}_3 > \text{-H} > p\text{-Br} > m\text{-NO}_2 > p\text{-NO}_2$ . Plot of  $\log k_2$  versus Hammett's substituent constant ( $\sigma$ ) is a curve (concave upward), which has been ascribed to the continuous change in the transition state with change in substituent in the substrate from electron-donating to electron withdrawing group. The rate-limiting step involves both the C-H bond breaking and C-O bond formation in a concerted manner. However, the two processes are influenced in two different ways as revealed by the curved Hammett plot, the electron withdrawing groups favouring bond formation while the electron-donating groups facilitating bond breaking.



### 1.3.2 OXIDATION OF AMINO ACIDS :

The oxidation of glycine, L-alanine, L-leucine, L-isoleucine and L-phenylalanine by acidified potassium bromate in aq. acetic acid medium is first order each in  $[\text{Br(v)}]$  and  $[\text{aminoacid}]$  and second order in  $[\text{H}^+]$ , given by S. Anandan, P.S. Subramanian and R. Gopalan<sup>5</sup> in 1985. The product of oxidation have been characterised as the corresponding aldehydes, ammonium ion and carbon dioxide. Electron-releasing substituents on the carbon carrying the amino groups impede the rate of reaction. The results have been rationalised based on inductive effects and Taft's constants. A mechanism involving the interaction between  $\text{H Br O}_3$  and the amino acid molecules has been suggested. The substituent effects suggest that the heterolyses of the C-H and the N-H bonds are important factors in the rate-determining step.

Many reports are available in the recent literature on the kinetics of oxidation of amino acids by variety of metal and nonmetal oxidants.<sup>56-59</sup>

### 1.3.3 OXIDATION OF HYDROXY ACIDS :

(A) According to GY. Rabai, GY. Bazsa and M.T. Beck,<sup>6</sup> the bromide ion concentration exhibits in the bromate ascorbic acid, malonic acid perchloric acid system three extrema as a function of time. To describe this peculiar phenomenon, the kinetics of four component reactions have

been studied separately. The following rate equations were obtained :

1 Bromate-ascorbic acid reaction :

$$-\frac{d[\text{BrO}_3^-]}{dt} = k_1 [\text{BrO}_3^-] [\text{H}_2\text{A}]$$

$$k_1 = 8.3 \times 10^{-3} \text{ M}^{-1} \text{ S}^{-1}.$$

Bromate-bromide ion reaction :

$$-\frac{d[\text{BrO}_3^-]}{dt} = k_2 [\text{BrO}_3^-] [\text{Br}^-] [\text{H}^+]^2$$

$$k_2 = 3.6 \text{ M}^{-3} \text{ S}^{-1}$$

Bromide - ascorbic acid reaction :

$$-\frac{d[\text{Br}_2]}{dt} = k_3 [\text{Br}_2] [\text{H}_2\text{A}]$$

$$k_3 \geq 1.7 \times 10^{+3} \text{ M}^{-1} \text{ S}^{-1}$$

Bromine - malonic acid reaction :

$$-\frac{d[\text{Br}_2]}{dt} = \frac{k_4 k_5 [\text{Br}_2] [\text{H}_2\text{M}]}{(k_4 + k_5 [\text{Br}_2])}$$

$$k_4 = 6 \times 10^{-3} \text{ S}^{-1}$$

$$k_{-4} \geq 1.7 \times 10^{+3} \text{ S}^{-1}$$

$$k_5 > 1 \times 10^{+7} \text{ M}^{-1} \text{ S}^{-1}$$

Taking into account the stoichiometry of the component reactions and using these rate equations, the concentration versus time curves of the composite system were calculated. Although the agreement is not as good as in the case of the component reactions, it is remarkable that this kinetic structure exhibits the three extrema found.

(B) The oxidation of  $\alpha$ -hydroxy acids and  $\alpha$ -hydroxy ketones by Br(v), given by R. Natarajan and N. Venkata subramanian<sup>7</sup> in 1976, follows the rate law

$$-\frac{d[\text{Br}(v)]}{dt} = k_2 [\text{Br}(v)] [\text{Substrate}]$$

However, the former reaction exhibits a second-order dependence on hydrogen ion concentration while the latter reaction has a third order dependence. A mechanism involving a slow formation of a bromate ester of the  $\alpha$ -hydroxy acid followed by a fast decomposition is proposed. A rate determining formation of a bromate ester from the conjugate acid of benzoin, followed by a rapid decomposition of the bromate ester, explains the kinetic data for the oxidation of benzoin.

(C) Oxidation of Tartaric Acid :

The bromate oxidation of dextro and meso-tartaric acids has been carried out in aqueous acetic acid medium containing mercuric acetate and sulphuric or perchloric acid in the temperature range 30 - 60°C by C.H. Sanjeeva Reddy and E.V. Sundaram<sup>8</sup> in 1985. The reaction exhibits

first order dependence, each in [Bromate] and [substrate] and shows no stable complex formation between the oxidant and the substrate. The reactions are acid catalysed and the absence of water molecule participation in the mechanism has been indicated and discussed by using Hammett's and Bunnett's criteria. The decrease in dielectric constant of the medium increases the rate. Specific salt effect has been observed. A probable mechanism has been suggested. Related thermodynamic parameters are calculated using  $E_a$ , the sign and magnitude of these parameters being also in accordance with the implications of the proposed mechanism.

#### 1.3.4 OXIDATION OF AROMATIC ALDEHYDES :

The kinetics of oxidation of benzaldehyde by potassium bromate in an acetic acid medium have been studied by K.K. Sen Gupta, Haraprasad Samaddar, Pratik Kumar Sen and Amalendu Banerjee<sup>9</sup> in 1982. The reaction is first order with respect to oxidant concentration whereas the order with respect to substrate is less than one. Hydrogen ion accelerates the rate of reaction. A mechanism involving the formation of an unstable bromate ester which decomposes to the reaction products has been suggested. The activation parameters associated with the rate-determining step and the thermodynamic values associated with the equilibrium stage have been computed. The effect of various functional groups on the ring at the ortho, meta, and para positions of

of benzaldehyde have also been examined.

Oxidation of aromatic Aldehydes<sup>10,11</sup> by acid bromate has been studied.

### 1.3.5 OXIDATION OF PHENOLS :

The oxidation of phenols by acid bromate has been studied in acetic acid-water mixture in the presence of sulphuric acid by Vijaylaxmi and E.V. Sundaram<sup>12</sup> in 1977. The reaction is first order each in the substrate and the oxidant. The rate of the reaction increases with the increase in  $[H_2SO_4]$ . The solvent effect has been studied at  $30^\circ C$  by varying acetic acid content of the medium and keeping the  $[H_2SO_4]$  constant at  $30^\circ C$ . The reaction was found to be of an ion-dipole and the value of  $r$  (distance of closest approach between the ion and the dipole) has been calculated to be 1.3 Å from the Amis plot. The Hammett's reaction constant ( $\rho = -1.74$ ) has been evaluated. The reaction is accelerated by electron-donating substituent and retarded by electron withdrawing groups. The order of reactivity in substituted phenols is

$$m-CH_3 > p-CH_3 > o-CH_3 > H > o-Cl > p-Cl > m-Cl > m-NO_2 > o-NO_2 > p-NO_2.$$

### 1.3.6 OXIDATION OF PHENYL STYRYL KETONE and ITS DERIVATIVES:

Oxidation of phenyl styryl ketone (chalcone) and some substituted ketones by acid bromate in aqueous acetic acid -  $H_2SO_4$  medium is first order each in  $[Br(v)]$  and  $[chalcone]$  and second order in  $[H^+]$ .  $H_2BrO_3$  has been established as

the reactive oxidant species from the effect of varying ( $H^+$ ) and  $[HOAc]$  on rate. The products of oxidation are benzoic acid and phenylacetaldehyde. Substituents with electron-releasing groups increase the rate and the Hammett's plot is linear with  $\rho = -1.10$ . A possible mechanism involving the attack of oxidant on non-bonded electrons of carbonyl oxygen is proposed, by T. Navaneethrao<sup>13</sup> et al in 1987.

### 1.3.7 OXIDATION OF p-SUBSTITUTED PHENYL METHYL SULPHIDES:

Acid catalysed oxidation of phenyl methyl sulphides and several p-substituted phenyl methyl sulphides by acid bromate ( $HBrO_3$ ) in aq. acetic acid, [ 40 % (v/v) ] was studied by K. Rajasekaran, T. Baskaran and C. Gnanasekaran<sup>14</sup> in 1983.

The dependence of rate on  $[H^+]$  reveals that  $HBrO_3$  is the active oxidizing species. The kinetic results indicate an association equilibrium prior to the rate limiting step followed by break down of the complex into the products in a rate determining step. The Hammett plot ( $r = 0.993$ ) for the decomposition rate constant ( $k_1$ ) excluding electron withdrawing (-K) substituents, such as p- $COCH_3$ , p- $COOH$  and p- $NO_2$  yields a low negative  $\rho$  value (-0.043) at 40°C. The  $k_{overall}$  ( $= k_1^K$ ) has been analysed in terms of Yosioka Kubato equation, Since the -K substituents require  $\sigma_p^-$  value for better correction. A variety of compounds have been used for kinetic study on the oxidation of organic sulphur compounds.

### 1.3.8 OXIDATION OF BENZALDEHYDE AND SUBSTITUTED BENZALDEHYDES :

Ru(III) catalysed oxidation of Benzaldehyde and substituted benzaldehydes given by P.S. Radhakrishnamurti and C.D. Sarangi<sup>15</sup> in 1980.

The title reaction is first order each in [substrate] and [Ru(III)], independent of [acid] and zero order with respect to [Bromate]. The study has been extended to aq. acetic acid medium, where the reaction indicates acceleration in rate with increase in percentage of acetic acid in the reaction medium. A plot of  $\log k$  versus  $1/D$ , is a linear with a +ve slope indicating positive ion dipolar nature of the reactants. The  $\rho - \sigma$  plot is linear with  $\rho$  value - 0.45 indicating a radical pathway. Arrhenius parameters have been computed and a suitable mechanism suggested.

### 1.3.9 Ru(III) CATALYSED OXIDATION OF KETONES :

The kinetics of Ru(III) catalysed oxidation of some cyclic ketones like cyclo-pentanone, cyclohexanone, cycloheptanone and cyclo-octanone and aliphatic ketones like acetone, methyl ethyl ketone, pentan-2 one and isobutyl methyl ketone by acid bromate have been studied by P.S. Radhakrishnamurthi and D.K. Mahapatrao<sup>16</sup> in 1979.

The reaction exhibits first order dependence on [substrate] and [Acid] and zero order dependence on [oxidant] and is independent of [Ru(III)] for all the ketones studied except acetone. Activation parameters have been computed. A mechanism involving enolization of ketones in the rate determining step followed by cleavage of the intermediate enol Ru(III) complex by bromate, successively in fast steps yielding the products has been suggested. In contrast the reaction is first order w.r.t. [Acetone], [Ru(III)] & independent of  $[H^+]$  &  $[BrO_3^-]$  indicating formation of a complex between acetone and Ru(III) in a rate determining step followed by cleavage of the complex to product by  $BrO_3^-$  in a fast step.

### 1.3.10 OXIDATION OF CYCLIC ALCOHOLS :

Vijayalaxmi and E.V. Sundaram<sup>17</sup> in 1978 has given the <sup>mechanism of</sup> oxidation of cyclic alcohols with common rings (five, six and seven membered) by bromate ~~has been studied~~ in binary solvent mixture of acetic acid and water in presence of sulphuric acid. The reaction is first order each in substrate and the oxidant, and second order with respect to sulphuric acid. The rate of reaction increases with increase in sulphuric acid concentration. The reaction was found to follow free radical mechanism, the order of the reactivity of the alcohols is cyclopentanol < cyclohexanol < cycloheptanol, which is in conformity with Bayer strain theory; increasing the acetic acid content of the medium, the rate increases, and the reaction has been described as an ion dipole reaction.



### 1.3.11 OXIDATION OF ORGANIC SULFUR COMPOUNDS :

Oxidation of organic sulphur compounds by  $\text{KBrO}_3$  in either glacial acetic acid or 2N NaOH has been studied by Banerjee Amalendu<sup>18</sup> et. al in 1985.

Oxidation of  $\text{ph-SH}$ ,  $4\text{-RC}_6\text{H}_4\text{S C}_6\text{H}_4\text{R-4}$  ( $\text{R} = \text{H}, \text{NO}_2, \text{AcNH}$ ),  $\text{ph-CH}_2\text{S(O)CH}_2\text{ph}$ ,  $\text{ph.CH}_2\text{SO}_2\text{CH}_2\text{ph}$ , by  $\text{KBrO}_3$  under different experimental conditions gave a variety of partial and complete oxidation product. Thus PhSH was converted into PhS.SPh in 80-94 % yield by treating with  $\text{KBrO}_3$  in either glacial HOAc or 2N NaOH.

### 1.3.12 OXIDATION OF DIOLS :

Oxidation of Diols, <sup>was</sup> studied by C.H. Sanjeeva Reddy and E.V. Sundaram<sup>21</sup> in 1985.

The Michaelis Menten kinetics have been observed for the oxidation of diols, by Bromate in sulphuric acid and perchloric acid solution, of  $1 \text{ mol} \cdot \text{dm}^{-3}$  ionic strength. The reaction has a first order dependence on  $\text{Br(V)}$  concentration. The effect of ionic strength is marginal, but the reaction rate is accelerated with the acidity and the rate constant follows the  $\text{H}_0$  function. Reaction in acetic acid water mixtures indicate that the dielectric constant has an influence on the kinetics. It is observed that increase in acetic acid content of the medium

increases the rate and the linear relationship is observed when the  $\log k_2$  is plotted against  $\frac{1}{D}$  and against  $D-1/2D+1$ . To account the observed rate law, the proposed mechanism assumes an intermediate being formed from the protonated oxidant ( $\text{HBrO}_3$ ,  $k_1 = 0.511 \text{ mol}^{-1} \text{ sec}^{-1}$ ), and  $\text{H}_2\text{Br}^+\text{O}_3$ ,  $k_2 = 0.201 \text{ mol}^{-2}$ ) and a molecule of diol, which decomposes (Both in the normal way as well as incleavage) to yield identifiable products. The observed thermodynamic parameters are also discussed.

As the acid concentration increases, the rate constant increases.<sup>22,23</sup>

### 1.3.13 OXIDATION OF ANILINE AND SUBSTITUTED ANILINES :

The oxidation of anilines and substituted anilines like Aniline, p-nitro aniline, m-nitro aniline, m-chloro aniline, p-chloro aniline, m-toluidine, and p-toluidine, given by VijayaLakshmi and E.V. Sundaram<sup>24</sup> in 1979.

The oxidation of aniline and substituted anilines by potassium bromate has been studied in acid medium in the presence of mercuric acetate in binary - solvent mixtures of acetic acid and water. The order with respect to the substrate and oxidant is one. First order dependence is observed with respect to hydrogen ions. A decrease in the dielectric constant of the medium increases the rate. The

reaction is of an ion-ion type, the reactive species being anilinium ion and bromate ion. A mechanism involving the decomposition of aniline-bromate complex in the rate-determining step is proposed. The electron withdrawing groups are found to accelerate the reaction and  $\rho$  is found to be +1.74.

#### 1.3.14 Ru(III) CATALYSED OXIDATION OF BENZYLAMINE AND SUBSTITUTED BENZYLAMINES

Kinetics of the title reactions have been investigated in aq. and aq. acetic acid media by P.S. Radhakrishnamurti and L.D. Sarangi<sup>25</sup> in 1982. The reaction is zero order with respect to [Bromate], first order each with respect to [substrate] and [Ru(III)] and inverse fractional order w.r.t. [acid]. The reaction rate increases with the decrease in dielectric constant of the medium and the plot of  $\log k$  vs  $1/D$  is linear with a positive slope indicating the reaction to be of positive ion dipole type. The  $\log k$  plot is linear with a  $\rho$  value of 0.87 indicating a radical pathway. Arrhenius parameters have been computed. A possible mechanism has been proposed and rate law consistent with the mechanism has been derived.

#### 1.3.15 Mn(II) CATALYSED AND UNCATALYSED OXIDATION OF OXALIC ACID

The kinetics of oxidation of oxalic acid by bromate ion in binary solvent mixture of acetic acid-water in the presence of sulphuric acid has been studied in detail by

CH. Sanjeeva Reddy, Vijayalaxmi and E.V. Sundaram<sup>26</sup> in 1980. In the uncatalysed oxidation the reaction is first order each in bromate, sulphuric acid and oxalic acid. There is no stable complex formation between the oxidant and the substrate, where as in Mn(II) catalysed oxidation, the order w.r.t. [bromate] is found to be two. Kinetic evidence for action follows a free radical mechanism. Based on the kinetics data the possible mechanism for uncatalysed and catalysed reaction are suggested.

#### 1.3.16 Mn(II) CATALYSED OXIDATION OF MALONIC ACID :

The kinetics of oxidation of malonic acid by bromate ion catalysed by Mn(II) has been studied in binary solvent mixture of acetic acid and water in presence of  $H_2SO_4$  and mercuric acetate by CH. Sanjeeva Reddy, Vijayalaxmi and E.V. Sundaram<sup>27</sup> in 1980.

The reaction is fractional order in  $KBrO_3$  and Mn(II). But rate of reaction decreases with increasing [Malonic acid], suggesting at least one of the complexes formed between malonic acid and Mn(II) to be inactive. Variation in the ionic strength does not have any effect on the reaction rate. The rate increases with increase in  $[H_2SO_4]$  and plot of  $\log k$  Vs  $H_0$  is linear. Increasing the acetic acid content of the media increases the rate. Thermodynamic parameters like  $\Delta G^\ddagger$ ,  $\Delta S^\ddagger$  and  $E_a$  have been calculated. Based on the kinetic data a possible mechanism has been proposed.

### 1.3.17 CO-OXIDATION OF ETHYLENE GLYCOL AND PROPAN-2-OL :

Acid bromate oxidation of a mixture of ethylene glycol and propan-2-ol proceeds much faster than that either of the two substrate taken alone has been studied by P. Narasimha Char., S. Sondu, B. Sethuram and T. Navaneeth Rao<sup>28</sup> in 1988. The products of oxidation are acetone and formic acid. The order in  $[\text{BrO}_3^-]$  is unity and in  $[\text{ethylene glycol}]$  and  $[\text{propan-2-ol}]$ , it is fractional. The rate increases with increase in  $[\text{H}^+]$  and percentage of acetic acid in the reaction medium. The amount of acetone formed from propan-2-ol during a particular time period in the presence of ethylene glycol is nearly twice that formed in its absence. A mechanism involving formation of a termolecular complex involving ethylene glycol, propan-2-ol and bromate and decomposition of this complex in the rate determining step is proposed. The nature of the complex formed has not been ascertained.

### 1.3.18 OXIDATION OF GLYCINE :

Oxidation of glycine by bromate was studied in aq. Acetic acid medium, in presence of  $\text{H}_2\text{SO}_4$  by Ramalingam V., Srinivasan S., and Subramanian P.S.<sup>29</sup> in 1980.

The reaction is first order in the oxidant and the substrate and is acid catalysed, and the order with respect to  $[\text{H}^+]$  is unity. Increasing the acetic acid content of the medium increases the rate of reaction.

### 1.3.19 OXIDATION OF RIBOSE BY POTASSIUM BROMATE IN ACID MEDIUM :

The kinetics of oxidation of ribose by  $\text{KBrO}_3$  in acid medium, were studied at constant ionic strength of 0.52 by Shukla S.N. and Bajpayee C.D.<sup>30</sup> in 1986.

The order with respect to each reactant was determined. The effect of temperature on the reaction rate at  $308^\circ\text{K}$ ,  $313^\circ\text{K}$ ,  $318^\circ\text{K}$ , and  $323^\circ\text{K}$  gave the value of energy of activation, temperature coefficient and entropy of activation by use of the appropriate equation. The effect of dielectric constant obtained by using different acetic acid-water mixture gave direct relationship between  $\log k$  Vs  $1/D$ . Thus suggesting the reaction to be between a cation and a dipole. The high acidity, produced by the addition of  $\text{H}_2\text{SO}_4$  in various concentrations, also revealed a linear relationship between  $\log k$  and  $\log [\text{H}^+]$ . which indicates the presence of a solvent mole in the transition state. The product of the reaction were identified using the TLC technique as well as color reaction. Based on the above conclusions, the kinetics and mechanism are discussed.

### 1.4 OXIDATION OF ANILINES BY VARIOUS OXIDANTS :

It is observed by the survey of literature that the field of oxidation of Amines by various oxidant has been neglected. Though the oxidation process of amines by some

oxidants as permanganate, cobaltic perchlorate, chlorine dioxide, alkaline  $K_3Fe(CN)_6$ , N-chlorobenzamide etc. -31-55 was studied. But the oxidation of amines by potassium bromate seems to be totally neglected.

#### 1.5 SCOPE OF THIS WORK :

The potassium bromate is a strong oxidizing agent. The above survey of the work done clearly shows that not much work has been done on potassium bromate. The kinetics and mechanism of oxidation of carboxylic acids, esters, ketones and anilines by potassium bromate seems to be neglected. Hence, it is proposed here to study the kinetics of oxidation of aromatic Amines namely o-Toluidine, m-Toluidine, p-Toluidine by potassium bromate. These investigations will help us, whether the oxidation of above Amines undergo via the same mechanism or not, if not, then to give a possible explanation for the difference. The investigation proposed will include the study of the following factors :

1. Determination of order of reaction with respect to the substrate and oxidant.
2. Effect of sulphuric acid concentration on the reaction rate.
3. Effect of added salt on the reaction rate.
4. Determination of temperature coefficient of the reaction and evaluation of thermodynamic parameters.

5. End product analysis and free radical test.
6. Stoichiometry.

The results on the above investigation will be utilized to suggest a probable mechanism for the reaction, and the results will be interpreted on that basis.