

CHAPTER- I

INTRODUCTION:

Kinetics is a part of the science of motion. Kinetics deals with the rate of chemical reaction, with all factors which influence, the rate of reaction and with explanation of the rate in terms of reaction mechanism. Chemical kinetics might very well be called the chemical dynamics.

Chemical dynamics with its dynamic view point may be contrasted with thermo-dynamics, with its static view point. Thermodynamics is only interested in the initial and final state of the system, the mechanism whereby the system is converted from one state to another and the time required are of no importance. Time is not one of the thermodynamic variables. Kinetics is fundamentally concerned with the details of the process where by systems gets from one state to another and with the time required for the transition. A reaction rate cannot be understood on the basis of thermodynamics alone. Therefore a chemical kinetics may be considered a more fundamental science, than thermodynamics. But the theory of chemical kinetics is difficult to apply with accuracy. We find that thermodynamics will tell with precision the extent of the reaction, but only kinetics will tell (perhaps crudely) the rate of the reaction.

The chemists are interested in the fact that kinetics provides the most general method of determining the mechanism of reaction.

Kinetics invariably give a definite answer concerning the individual steps of a chemical reaction. Therefore, 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.

There are wide variety of experimental techniques which have been used to study the chemical reactions. The kinetics and mechanism of reactions in gas phase, liquid phase and solid gas interface have been elucidated. These reactions can also be 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 high temperatures hydrostatic pressure and the rapid reactions..

Any kinetic study involves two parts, one is to establish the relationship between the rate of the reaction and the various factors such as concentrations of reactants, temperature and hydrostatic pressure. (in case of gas phase) reactions. In addition to these some other factors such as primary and secondary salt effects, dielectric constant of the medium and catalysis may be added. Detection of free radicals, intermediates and identification of products etc., are also done. Second part of investigation is to arrive at a suitable mechanism, which can account for the results obtained on velocity measurements.

1.1 Oxidation Reactions :

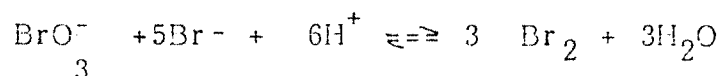
A large volume of kinetic work has been done, in liquid phase reactions, because these reactions are of keen interest in the organic and inorganic chemists. In Organic reactions the oxidation reactions are of most importance. A variety of oxidizing agents such as Nitric Acid, Chromic Acid, Potassium permanganate, Potassium periodate Chloramine-T, Peroxy disulphate, 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 bromate¹⁹ is a powerful oxidising agent having an oxidation potential 1.44 V in an acidic medium, which is reduced smoothly to bromide.

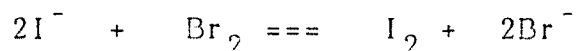


The equivalent is therefore 1/6 mole. (KBrO₃/6) or 167/6 or 27.833 and a 0.1N solution contains 2.7833 gms of potassium bromate per dm³. At the end of the titration free bromine appears.



Various substances can not 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 that of potassium bromate alone. Bromine is very volatile, and hence such operations should be conducted at as to slow a temperature as possible, and in conical flasks fitted with ground 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 per cent. 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 Oxidation with potassium Bromate :

A) 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 in 1980². Order with respect to oxidant was one and fractional with respect to substrate. The order of reacting alcohol is not regular and does not show correlation with Taft plot. Decomposition constants for the alcohol Bromate complexes were calculated and the plot of the log Kd versus Taft σ^* values gave a linear plot with a slope of -0.70 indicating the formation of a transition state with small +ve charge on and carbon atom.

The alcohols are, methanol, ethanol, n-propanol, n-butanol, isobutanol, n-pentanol, isopentanol, n-hexanol, n-heptanol, benzyl alcohol, 2-phenylethyl alcohol, 2-Cl-ethanol.

Oxidation of primary aliphatic and secondary alcohols^{3,17,-36,65,66} by acid bromate has been studied.

b) Oxidation of secondary Alcohols :

The oxidation of secondary alcohols like propane-2-ol, 1,3-dichloro propane-2-ol, 1-Methoxy propan-2-ol, butan-2-ol, pentan-2-ol, Octan-2-ol, given by R.Naterajan and N.Venkatasubramanian^{3,17} in 1973.

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

$(-d(\text{Br(V)})/dt) = K [\text{Alcohol}] [\text{Br(V)}] [\text{H}_2^+]$. 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 stage, a faster reaction which is mainly bromine 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 the structure of the alcohol. A mechanism involving a slow rate determining formation of an alkyl bromate ester followed by a fast decomposition to the products is in accord with the observed results.

c) Tertiary Alcohols :

The oxidation of alcohols like Trimethylcarbinol, Dimethyl ethylcarbinol, Triethylcarbinol, Dimethylphenyl carbinol, Dimethyl benzylcarbinol, 2-3 Dimethyl butane 2-3 diol, 2-Methyl-3-phenylbutane-2-3 diol, 2-3 Diphenyl butane 2-3 diol, is studied by C.H. Sanjeeva Raddy and E.V.Sundaram¹ in 1987.

The oxidation of above tertiary alcohols by Bromate in acid medium is first order in $[\text{Br(V)}]$. However, the first order rate constant decreases with increase in $[\text{Bromate}]$ and the inverse first order rate constant linearly related with (Br(V)) . Increase in $[\text{substrate}]$ increases the rate and the reaction exhibits the Michaelis Menten's 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 change in die-



lectric constant of the medium. The results are suggestive of mechanism which involve 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 products. The retardation effect of bromate may be due to the bromate dimer, which is inactive towards reduction.

d) Benzyl Alcohol :

C.H.Sanjeeva Raddy and E.V.Sundaram⁴ in 1984 has given the oxidation of benzyl alcohols and the substituted benzyl alcohols by bromate in presence of Mercury(II) ions. It 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 with the acidity function H_0 . From the effect of ionic strength and the dielectric constant the reaction has found to be between a +ve ion and a dipole and the values of ρ have been evaluated. Benzyl alcohol is oxidized by bromate at rate 1.6 times faster than dideuteriobenzyl alcohol at 40⁰ C. The order of activities among the studied benzyl alcohols is $\text{P.OCH}_3 > \text{P-CH}_3 > \text{-H} > \text{P-Br} > \text{m NO}_2 > \text{p.NO}_2$. Plot of $\log k_2$ versus Hammett's substituent Constant (σ) 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 re-verted by the curved Hammett plot. The electron withdrawing group

favouring bond formation, while the electron donating groups facilitating bond breaking.

B) Oxidation of Amino Acids:

The oxidation of glycine, L-alanine, L-leucine, L-isoleucine and L-Phenyl alanine, by acidified potassium Bromate in acetic Acid medium is first order each in $[\text{Br(V)}]$ and $[\text{Amino acid}]$ and second order in $[\text{H}^+]$ given by S.Anandan, A.S.Subramanian and R.Gopalan⁵ 1985.

The product of oxidation is characterised as the corresponding aldehydes, ammonium ion and CO_2 . Electron releasing substituents on the carbon carrying the amino groups impede the rate of reaction. The results have been rationalized based on inductive effects and Taft's constants. A mechanism involving the interaction between H_2BrO_3 and the amino acid molecules has been suggested. The substituent effect suggests that the Heterolysis of the C-H bond and 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 non metal oxidants⁵⁵⁻⁵⁸

C) Oxidation of Hydroxy Acids :

a) According to G.Y.Rabai, G.Y.Bazsa and M.T.Beck⁶ experiments

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 phenomena the kinetics of four component reactions have been studied separately. The following rate equations were obtained.

Bromate ascorbic Acid reaction :

$$-d(\text{BrO}_3^-)/dt = K_1(\text{BrO}_3^-)(\text{H}_2\text{A}) \quad K_1 = 8.3 \times 10^{-3} \text{ M}^{-1} \text{ S}^{-1}$$

Bromate Bromide ion reaction :

$$-d(\text{BrO}_3^-)/dt = K_2(\text{BrO}_3^-)(\text{Br}^-)(\text{H}^+)^2 \quad K_2 = 3.6 \times 10^{-3} \text{ M}^{-1} \text{ S}^{-1}$$

Bromide Ascorbic Acid reaction:

$$-d(\text{Br}_2)/dt = K_3(\text{Br}_2)(\text{H}_2\text{A}) \quad K_3 \geq 1.7 \times 10^{-3} \text{ M}^{-1} \text{ S}^{-1}$$

Bromine Malonic Acid Reaction

$$-d(\text{Br}_2)/dt = \frac{K_4 K_5 (\text{Br}_2) (\text{H}_2\text{M})}{(K_4 + K_5 \text{Br}_2)} \quad K_4 = 6 \times 10^{-3} \text{ M}^{-1} \text{ S}^{-1}$$

$$K_5 \geq 1.0 \times 10^{-7} \text{ M}^{-1} \text{ S}^{-1}$$

Taking into account the stoichiometry of the component reactions and using their 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 α -Hydroxy acids and α -Hydroxy ketones by Br(V) given by R.Natarajan and N.Venkatasubramanian⁷ in 1976 follows the rate law.

$$-d[\text{Br(V)}] / dt = K_2 [\text{Br(V)}] [\text{substrate}]$$

However the former reaction exhibits a second order dependence on hydrogen ion concentration, while the later reaction has third order dependence. A mechanism involving a slow formation of a bromate ester of the hydroxy acid followed by its 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) The bromate oxidation of dextro and mesotartaric Acid has been carried out in aq. acetic Acid medium containing mercuric acetate and sulphuric or perchloric acid in temperature range 30^o To 60^o C by C.H.Sanjeeva Reddy and E.V.Sundaram⁸ in 1985. The reaction exhibits first order dependence each in [bromate] and [substrate] and shows

no stable complex formation between the oxidant and substrate. The reactions are acid catalysed and the absence of water molecule participation in the mechanism has been indicated and discussed by using Hammetts and Bunnett's criteria. The decrease in dielectric constant of the medium increase the rate specific salt effect has been observed. The 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 proposed mechanism.

D) 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, Pratile Kumar Sen and Anatedn Banerjee⁹ in 1982. The reaction is of 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 equilibrium stage have been computed. The effect of various functional groups on the ring at the ortho, meta, and para positions of benzaldehyde have also been examined.

E) 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 Vijayalaxmi and E.V.Sundaram in 1977. The reaction is first order each in substrate and oxidant. The rate of 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 dipole) has been calculated to be 1.3 Å from the Anis plot. The Hammett's reaction constant ($\rho = 1.74$) has been evaluated. The reaction is accelerated by electron with-drawing groups. The order of reactivity in substituted phenols is $m-CH_3 > p-CH_3 > o-CH_3 > H > o-Cl > p-Cl > m-Cl > m-NO_2 > o-NO_2 > p-NO_2$.

F) Oxidation of Phenyl styryl ketones and its derivatives :

Oxidation of phenyl styryl ketones (Chalcone) and some substituted ketones by acid bromate in aq. acetic acid H_2SO_4 medium is first order each $[Br(V)]$ 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 phenyl-acetaldehyde 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 bounded electrons of carbonyl oxygen is proposed. It is given by P-Narasimhachar, S.Sondu, B Sethuram and T.Navaneethrao¹¹.

a) Oxidation of P-Substituted Phenyl Methyl Sulphides:

Oxidation of phenyl methyl sulphides and several P.substituted phenyl methyl sulphides by acid bromate [HBrO_3] in aq.acetic acid, 40% (v/v) is catalysed by acid. Given by K. Rajashekaram, T. Baskaran and C.Gnanasekaran¹² in 1983.

The dependence of rate on $[\text{H}^+]$ 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 in the products in a rate determining step. The Hammett plot ($r = 0.993$) for the decomposition rate constant K excluding electron withdrawing ($=k$) substituents such as P.COCH_3 , P.COOH and P.NO_2 yields a low negative ρ 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 ρ values for better correction. A variety of compounds have been used for kinetic study on the oxidation of organic sulphur⁵⁹⁻⁶⁴ compounds.

H) Ru (III) Catalysed oxidation of Benzaldehyde and substituted benzaldehydes Given by P.S.Radhakrishnamurti and C.D.Sarang¹³ 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 $p-6$ plot is linear with value -0.45 indicating a radical pathway. Arrhenius parameters have been computed and a suitable mechanism suggested.

I) Ru(III) Catalysed Oxidation of Ketones :

The kinetics of Ru(III) catalysed oxidation of some cyclic ketones like cyclopentanone, Cyclohexanone, Cycloheptanone and Cyclooctanone and aliphatic ketones like acetone, methyl ethyl ketone, pentan-3-one and isobutyl methyl ketone by acid bromate have been studied by P.S.Radhakrishnamurthi and D.K.Mahapatrao¹⁴ in 1979.

The reaction exhibits first order dependence on [substrate] and [Acid] and zero order dependence on [oxidant] and is independent on [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 with respect to [Acetone] and [Ru(III)] and independent of [acid] and [BrO₃⁻] indicating the formation of a complex between acetone and Ru(III) in a rate determining step followed by cleavage of the complex to product by BrO₃⁻ in a fast step.

J) Oxidation of Cyclic Alcohols :

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Vijaylaxmi and E.V.Sundaram¹⁵ 1978 has given the 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 increase 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^t of the medium the rate increases, and the reaction, and the reaction has been described as an ion dipole reaction.

K) The oxidation of alcohols by bromine in the presence of bromate given by L.Farkas and O.Schachter¹⁶ in 1949.

The oxidation of alcohols with bromine in presence of bromate is described. The bromate maintains a nearly constant bromine concentration and pH of about 2.5 under these conditions bromine substitution can be kept low, even in the temperature range between 50 To 80°C.

Up on oxidation primary aliphatic alcohols give esters, secondary alcohols, ketones and benzyl alcohol mainly the aldehyde.

L) Oxidation of Diols, studied by C.H.Sanjeeva Reddy and E.V.Sundaram¹⁸.

The Michaelis Menten kinetics have been observed for the oxidation of diols, by Bromate in sulphuric and perchloric acidsolution, of 1 mol dm⁻³ ionic strength. The reaction has a first order dependence on 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 Ho 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 HBrO_3^- , $K = 0.51 \text{ l mol}^{-2}$ and $\text{H}_2\text{Br}^+\text{O}_3$, $K = 2.20$

1 mol^{-2} and a molecule of diol, which decomposes (Both in the normal way as well as incleaves) to yield identifiable products. The observed thermodynamic parameters are also discussed.

As the acid concentration increases the rate constant increases 25.26

1.4 Oxidation of Anilines by various oxidants 45 to 54

It is observed that by the survey of literature, found that the field of oxidation of Amines by various oxidant has been neglected. Though the oxidation process of amines by some oxidants as permanganate, lead tetraacetate, cobaltic perchlorate chlorine dioxide, alkaline $[\text{K}_3\text{Fe}(\text{CN})_6]$ etc. was studied. But the oxidation of amines by 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 anilines namely aniline ($\text{C}_6\text{H}_5\text{NH}_2$), O-Chloro Aniline

($C_6H_4Cl-NH_2$) and P-Chloro Aniline ($C_6H_4Cl.NH_2$) by potassium bromate. These investigations will help us, whether the oxidation of Anilines 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 w.r.to the substrate and oxidant.
2. Effect of sulphuric acid concentration on the reaction rate.
3. Salt effect.
4. Determination of temperature coefficient of the reaction and evaluation of thermodynamic parameters.
5. End product Analysis and free radical test.
6. Stiochiometry.

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.