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Kinetics and Mechanism of Oxidation of Glycolic Acid by Hexamethylenetetramine-Bromine in Glacial Acetic Acid Medium

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Abstract

The kinetics of oxidation of glycolic acid by hexamethylenetetramine bromine (HABR) has been studied. The reaction follows second-order kinetics, first-order with respect to each reactant. Glycolic acid is oxidized to give glyoxylic acid. Analysis of the solvent effect indicates that the cat ion solvating power of the solvents plays major role in the reaction rate. The rate of the reaction increases with increasing in concentration of glycolic acid and HABR. Temperature influence is quite marked in all these reactions. And activation parameters have been determined. The effect of temperature was explained by application of Arrhenius equation and transition state theory, a mechanism for the reaction was proposed based on the experimental observation. It involves the formation of a activated complex, which decomposes to give the product.

Keywords: Spectroscopy, Kinetics, Activation Energy

1. Introduction

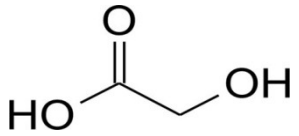
α-hydroxy acids, are a class of chemical compounds that consist of a carboxylic acid substituted with a hydroxy group on the adjacent carbon. They may be either naturally occurring or synthetic. Many well-known α-hydroxy acids are useful building blocks in organic synthesis: the most common and simple are glycolic acid, lactic acid, citric acid, mandelic acid[(1)].

Glycolic acid (Figure.1) is prototype of the series of α-hydroxy carboxylic acids is well known for its important role in dermatology and cosmetics industry, being used as inhibitor of harmful oxidation, biochemical processes. Important research is also presently going on in order to develop new materials based on biodegradable polymers derived from glycolic acid that can be used for reconstruction of biological tissues and in organ transplantation[(2,3)].

Glycolic acid, although apparently present in many plants, has not been associated with any physiological function of the plants. Glycolic acid is 70% solution and is non-flammable and used in various skin-care products. It penetrates the skin, slowly and naturally sloughs away the dead cells that build up on the outer layer of skin leaving the skin looking smoother and healthier and assists in the

exfoliation of the hyper pigmented skin cells resulting from sun damage and also useful in a wide variety of metal cleaning applications, including equipment, stainless steel boilers, heat exchangers and many other industrial surfaces [4,5].

Figure 1: Molecular Structure of Glycolic acid



Glycolic acid is a useful intermediate for organic synthesis, in a range of reactions including: oxidation-reduction, esterification and long chain polymerization. It is used as a monomer in the preparation of polyglycolic acid and other biocompatible copolymers. Among other uses this compound finds employment in the textile industry as a dyeing and tanning agent, in food processing as a flavoring agent and as a preservative. Glycolic acid is often included into emulsion polymers, solvents and additives for ink and paint in order to improve flow properties and impart gloss[6]. So study of kinetics and mechanism of oxidation of glycolic acid helps to understand more about the compound.

2. Materials and Method

2.1. Chemicals

Most chemicals used in the investigation were of AnalaR grade. Chemicals like glycolic acid(96%), hexamine (98%), were used without farther purification and HABR were prepared using standard method. 2,4-dinitrophenylhydrazine (DNP) (97%) used for derivative preparation. Other reagents and solvents used in this investigation were potassium nitrate (99.5%) to investigate the effect of ionic strength. Hydrochloric acid (34.6%) and absolute ethanol (98%), chloroform, water (de-ionized) and glacial acetic acid were used as the solvents throughout the investigation.

2.2. Instruments

UV-Vis spectrophotometer model Jenway 6305 in quartz cell with path length 1cm. Measurements were made at λ_{max} 380 nm. Determinations of the melting point or decomposition temperatures of the products were done with Stuart SMP^3 melting point apparatus. Thermostat water bath was used for temperatures adjustment and other common laboratory equipments were also used during the investigation.

2.3. Experimental

HABR were prepared and characterization of the compound was done using melting point determination. To prepare the hexamethylenetetramine-bromine complex, a solution of bromine (125 mmol) in $CHCl_3$ (100ml) was added drop wise with stirring to a solution of hexamine (60 mmol) in chloroform (100 ml). A yellow solid separated out as the bromine was taken up. The mixture was stirred for an additional 30 min, and then the yellow solid was collected by vacuum filtration.

2.3.1. Product Analysis

Product analyses were carried out under kinetic condition i.e. with an excess of the glycolic acid (0.1M) over HABR (0.01M). The reaction mixture was allowed to stand in dark for 6 h to ensure the completion of the reaction. It was then treated with freshly prepared saturated solution of 2, 4-

dinitrophenylhydrazine (DNP) and 2M HCl and allowed to stand for 24 hour in refrigerator adjusted at 0^oC. The precipitated 2, 4-dinitrophenylhydrazone (DNP) was filtered off, cleaned up using a few drop ethanol and water, dried and its melting point was determined.

2.3.2. Kinetic Experiments

Keeping excess of the glycolic acid (0.1M,0.2M,0.3M,0.4M,0.5M and 0.6M) over HABR (0.01M, 0.02M, 0.03M, 0.04M, 0.05M, and 0.06M) to attain the pseudo first order conditions. The temperature was kept constant to ± 0.1(298K) using adjustable thermostat water bath. The reaction was followed by monitoring the decrease in concentration of HABR spectrophotometrically at λ_{max} 380 nm using a digital UV/ Vis spectrophotometer model 6305.

2.3.3. Stoichiometry

The stoichiometry of the reaction was determined by adding, HABR (0.05 mol) and glycolic acid (0.01 mol) in 100 ml glacial acetic acid. The reaction was allowed to stand for 10 h to ensure the completion of the reaction. The decreases in absorbance of HABR were measured at 380 nm. The number of moles of HABR consumed per mole of glycolic acid was estimated by assuming all the glycolic acid is completely consumed. Their ratio was the stoichiometry of the reaction.

3. Result and Discussion

The qualitative preparation of HABR complex checked using melting point determination it was in the range 170-173 ^oC and the procedure were repeated till three reproducible results were obtained and reproducible results were observed within range of ± 3 ^oC. Since the melting point of the HABR complex is less or grater only by ±2 indicate relatively pure[7].From the product analysis it was found that the melting point of 2,4-DNP derivative of glycolic acid oxidation product were 187-190 ^oC and it is in agreement with literature[8,9]. This indicates that the by-product of oxidation of glycolic acid by HABR under the condition considered is glyoxylic acid.

3.1. Kinetic Experiment

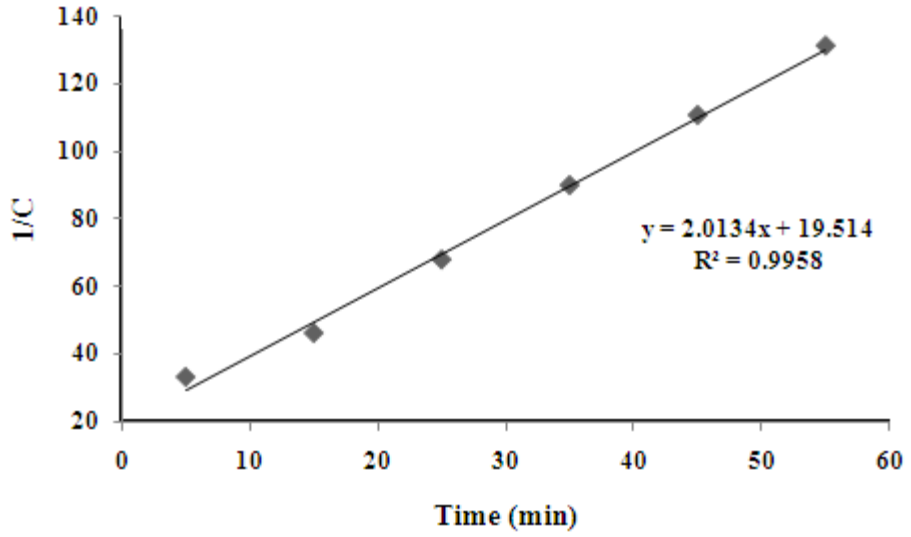
The temperature was maintained constant for all kinetic experiment by making the reaction system immersed in a "constant temperature bath" as much as possible during the course of a given trial. The pseudo constant conditions were attained by keeping a large excess of the glycolic acid over HABR. The decrease in the concentration of HABR was followed spectrophotometrically at 380 nm in glacial acetic acid. Blank was prepared using pure HABR for all trials and all the reactants were thermally equilibrated, thoroughly mixed and quickly transferred to an absorption cell.

Table 1: Rate of oxidation of glycolic acid at constant temperature (298 K).

S. No.	Conc.of glycolic acid (M/L)	Conc. of HABR (M/L)	Change in concentration Average	1/C	Time (min)	Rate constant ($\times 10^{-4}$ M/L.sec^{-1})
1	0.1	0.01	0.0076	131.2	55	1.38
2	0.2	0.02	0.0086	110.7	45	1.91
3	0.3	0.03	0.013	90	35	3.71
4	0.4	0.04	0.015	68	25	6.0
5	0.5	0.05	0.022	46.3	15	14.7
6	0.6	0.06	0.027	33.3	5	54

As shown in Table1, the pseudo rate constant is increasing as the concentration of both reactants increases. This indicate that the rate of the reaction directly proportional to the concentration of both the glycolic acid and HABR.

Figure 2: Graph of 1/C Vs Time (min) at constant temperature 298 K.



From (Figure 2) the pseudo rate constant of the reaction is second order as a whole and the slope of the graph corresponds to rate constant k_{obs} for the reaction. This rate constant is a constant at this particular temperature and independent of concentration. It can also used to calculate the rate for any concentration. The second order rate constants, k_2, were calculated from the relation:

$k_2 = k_{obs}$/ [glycolic acid]

3.2. Determination of Activation Energy

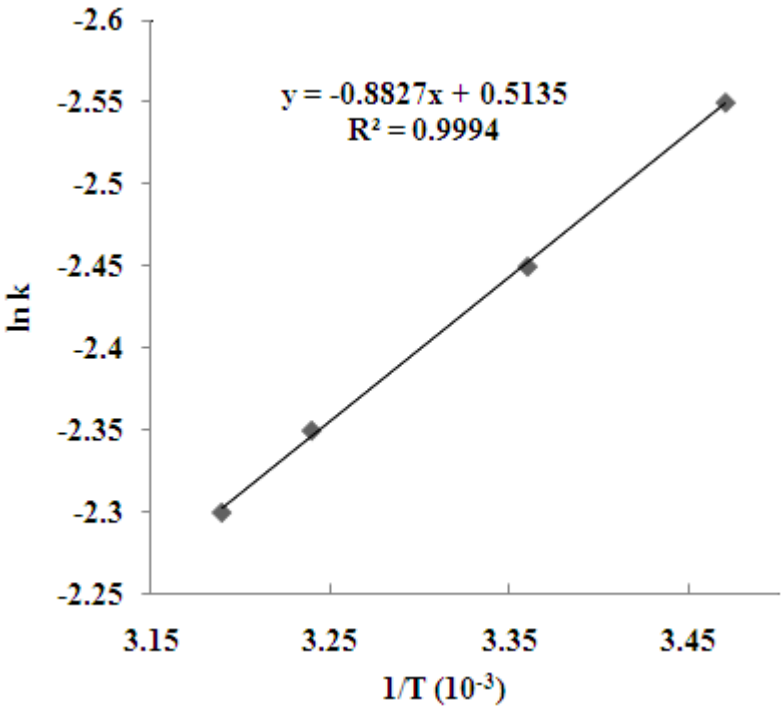
The activation energy (E_a) is the energy difference between the reactants and the transition state where the activated complex is formed. The activated complex is an unstable species which when formed needs no additional energy to proceed to products. The energy difference between the reactants and the products is the change in enthalpy, ΔH, of the reaction, and may be positive (endothermic) or negative (exothermic). The relationship between rates of reaction and temperature is based on the idea that in order to react, reactants must have a certain minimum amount of energy present at the time.

This amount of energy, which is typically furnished by the kinetic energy (energy of motion) of the species present, is called the activation energy, E_a, for the reaction[10]. For this particular case, the reaction were carried out at different temperatures in order to provide information that allows the determination of the activation energy, E_a, by using thermostat water bath at the following temperature 288 K, 298 K, 308 K and 318 K (Table 2). For the lower temperature the thermostat water bath adjustment was done using ice water and wait until equilibration and continuously checked using thermometer.

Table 2: Rate constant of oxidation of glycolic acid at different temperature.

Temperature (K)	Concentration (Average)	Time(min) (Average)	Rate constant×10^{-3} $mol^{-1}dm^3.min^{-1}$	1/T x 10^{-3} K^{-1}	Log *k*
288	0.047	15	3.16	3.47	-2.5
298	0.047	14	3.43	3.36	-2.45
308	0.045	11	4.03	3.24	-2.35
313	0.038	8	4.75	3.19	-2.30

Figure 3: Graph of log *k* vs. 1/T with slope –Ea/R



For particular reaction, the magnitudes of the activation energy determine the degree to which the rate of reaction increase when the temperature is increased under similar concentration conditions. If the concentration conditions are kept the same then it is only necessary to consider changes in the temperature. Influence of temperature can be seen from Table 2, the rate of oxidation of glycolic acids increase as the temperature increase as shown in figure 3. To see the effect of other variables on reaction rate we control the temperature accurate to ±0.01 ^{o}C or preferably better. The reactants must be very rapidly brought to the experimental temperature at zero time so that reaction does not occur during this time.

Activation enthalpies and entropies were determined using plots of In (k/T) vs. 1/T (Table 3). For determination of $\Delta H^{\#}$ and $\Delta S^{\#}$ a plot of ln(k/T) Vs 1/T (Figure 4) gives a slope = $-\Delta H^{\#}/R$ and intercept = (R/Nh) + $\Delta S^{\#}$ /R. Since (R/Nh) is known, $\Delta S^{\#}$ can be calculated from intercept.

$$k = \left[\frac{RT}{Nh}\right] \exp\left\{-\left(\frac{\Delta H\#}{RT}\right)+\left(\frac{\Delta S\#}{R}\right)\right\}$$

Where;

$\Delta H^{\#}$, = Enthalpy of activation

$\Delta S^{\#}$ = Entropy of activation

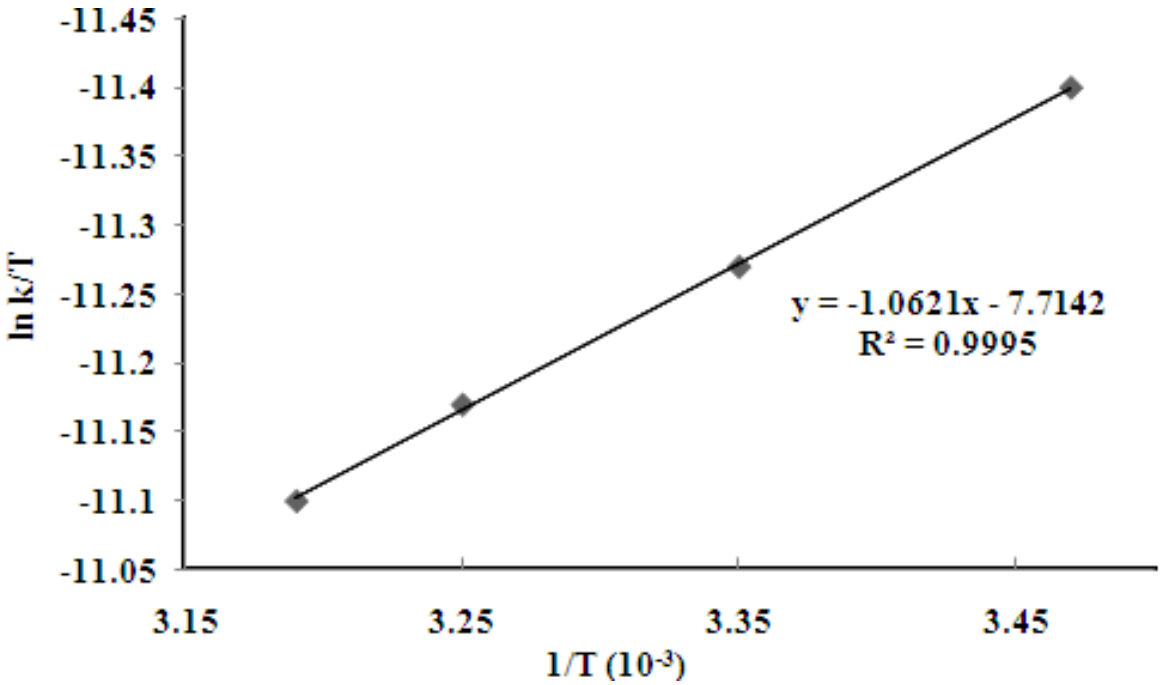
N = Avogadro's number (6.022×10^{23} molecule.mol^{-1})

h = Planks constant (6.626×10^{-34}J sec.mol)

Table 3: Showing the values of 1/T and *ln k*/T

Temperature	1/T	ln *k*/T
288	3.35	-11.4
298	3.43	-11.3
308	4.03	-11.2
313	4.75	-11.09

Figure 4: Plot of ln *k*/T vs 1/T. with slope = - $\Delta H^{\#}$/R.



The rate constant of electron transfer reaction can be explained by considering entropy of activation. If entropy of activation is positive, it corresponds to more probable activated complex and the reaction is likely to be faster than normal.

Table 4: Values of thermodynamic activation parameters.

Thermodynamic activation parameters	Values
Ea	21.6 (KJ/mol)
$\Delta S^{\#}$	-127.54 (J. mol^{-1} K^{-1})
$\Delta H^{\#}$	15.82 (KJ/mol)
$\Delta G^{\#}$	213.1 (KJ/mol)

Gibbs free energy of activation ($\Delta G^{\#}$), determines rate at which a certain reaction will run at a given temperature and as we see the reaction is feasible under the condition considered. The high values of $\Delta G^{\#}$ here suggest that the formation of activated complex is slow. $\Delta H^{\#}$ is a measure for the amount of binding energy that is gained in the transition state relative to the ground state (including solvent effects). $\Delta S^{\#}$ is a measure for the difference in disorder between the transition state and the ground state. For a bimolecular reaction $\Delta S^{\#} << 0$ J/mol. K (since two particles have to come together in the transition state to form one particle, demanding a much greater order).

The large negative value observed for $\Delta S^{\#}$ in this reaction suggests a considerable degree of charge separation in the activated complex. The thermodynamic activation parameters associated with the rate determining step for the oxidation of glycolic acid with HABR are recorded in Table 4. The fairly large and negative $\Delta S^{\#}$ values indicate the formation of a complex in the rate determining step. As the process involves large charge separation in the transition state resulting in an increase in the total number of charges, the two ends become highly solvated. This results in an immobilization of a large number of solvent molecules, reflected in loss of entropy[(11)].

3.3. Order of the Reaction

The order of the reaction with respect to both glycolic acid and HABR was determined using isolation method. The isolation method provides valuable means of investigating the chemical kinetics of reactions that involve two, or more reactants. In essence, it involves isolating in turn the contribution of each reactant by arranging (experimentally) that all of the other reactants are in large excess, such that their contributions remain virtually unchanged during the course of reaction. Normally this means at a ten-fold, excess in concentration compared with the initial concentration of reactant to be isolated[12]. The order with respect to each reactant concentration was calculated by varying the concentration of glycolic acid while keeping the concentration HABR constant and reversing the condition at constant temperature 298 K.

Table 5: Rates of oxidation of glycolic acid by HABR with varying concentration of both reactants at constant temperature (298 K)

S. No.	[Glycolic acid] moles/L	[HABR] moles/L	Initial rate (mol.dm^3.min^{-1})
1	0.1	0.04	1×10^{-3}
2	0.2	0.04	1.9×10^{-3}
3	0.4	0.01	1.5×10^{-3}
4	0.4	0.02	3×10^{-3}

The order of the reaction with respect to glycolic acid HABR was calculated by the following approach. If we take reaction number 1 and 2 (Table5) comparing their initial rate and assuming hypothetically;

Rate = k [glycolic acid] ^{a} [HABR] ^{b}

$$\frac{1x10^{-3}}{1.9x10^{-3}} = \frac{k(0.1)^a(0.04)^b}{k(0.2)^a(0.04)^b}$$

$$0.5 = (0.5)^a$$

Taking the natural logarithm on both side of the equation

ln0.5 = a ln (0.5)

-0.693 = a (-0.693)

a = 1

If we apply the same procedure to reaction number 4 and 5, comparing their rate

$$\frac{1.5x10^{-3}}{3x10^{-3}} = \frac{k(0.4)^a(0.01)^b}{k(0.4)^a(0.02)^b}$$

$$0.5 = (0.5)^b$$

Taking the natural logarithm on both side of the equation

ln0.5 = b ln (0.5)

-0.693 = b (-0.693)

b = 1

The above relation indicate overall order of the reaction is the sum of **a** and **b** which equal to two, so the overall reaction is of second order. From this initial rate method we can see also the relationship between concentrations of each component with rate of reaction.

So it confirms the result under kinetic experiment *i.e.*, the rate of reaction increases as concentration of each component increase. The reactions were found to be first order with respect to HABR and glycolic acid. The reaction rate increases linearly with increase in the concentration of glycolic acid and HABR. The rate expression is

Rate = k[glycolic acid][HABR]

3.4. Stoichiometry of the Reaction

The absorbance of HABR was converted to concentration for each trial using Beer-Lambert law and the average of the concentration left after the reaction subtracted from the original HABR concentration assuming all glycolic acid consumed in the reaction. The ratio of HABR consumed in the reaction to glycolic acid concentration is the stoichiometry by which they react.

Table 6: The decreases in absorbance of HABR measured at 380 nm and at constant temperature (298 K).

[glycolic acid]	[HABR]	Average absorbance	Concentration of HABR left
0.01M	0.05M	0.00069	0.033
0.01M	0.05M	0.00067	0.032
0.01M	0.05M	0.00063	0.030
0.01M	0.05M	0.00060	0.029
		Average	**0.031**

By subtracting the amount of HABR left untreated from the original concentration of HABR after the reaction kept for 10 hour the amount of HABR reacted with glycolic acid is determined.

$(0.05 - 0.031 = 0.019)$

If we divide the amount of HABR left by amount of glycolic acid we can get the ratio.

$$\frac{0.019}{0.01} = 1.9 \approx 2$$

The ratio of glycolic acid to HABR is two to one (2:1). This means that two moles of hydroxy acids are oxidized per mole of HABR.

$2HOCH_2COOH + (CH_2)_6N_4Br_4 \rightarrow 2HCOCOOH + (CH_2)_6N_4 + 4HBr$

3.5. Induced Polymerization Test by Acryl Amide

Acrylonitrile and acrylamide are commonly used to test whether a given reaction pass through free radical or not[13]. To see the presence of free radicals in this reaction, acryl amide solution was added to reaction mixtures containing the substrate and the HABR solution and kept for 24 h, methanol, was then added to the reaction mixture .

No precipitate was observed in the reaction mixture. This clearly indicates that there is no formation of free radicals in the redox reactions under investigation[14]. The failure to induce polymerization with acrylamide indicating absence of involvement of free radicals intermediate. The absence of polymerization and negative entropy of activation indicate the transfer of hydride ion in the rate determining step which also supported by solvent effect on rate constant of reaction which is more facilitated in water. This observation is due to the difference in the ability of the solvent stabilizing the activated complex.

3.6. Effect of Bromide Ion

The rate of oxidation of the glycolic acids by HABR using excess bromine was not observed on the reaction rate at the same concentration of both glycolic acid and HABR and at constant temperature. This observation indicates that following equilibrium is less likely.

$(CH_2)_6N_4Br_4\ 2Br_2 + (CH_2)_6N_4$

This observation farther indicates bromine was not responsible for oxidation instead the HABR complex itself was active oxidizing agent and confirms the absence of the following equilibrium.

3.7. Solvation (Solvent Effects)

The solvent effects usually apply considerable influence on the electron transfer kinetics in solution. A few solvation models have been developed for the description of the interaction between the solute and the solvent molecules. For the convenience of the rate-constant comparison, we assume that the inner reorganization energy and the solvent reorganization can contribute two independent parts to the activation energy of electron transfer reaction[15]. Influence of solvation on the reaction rate of oxidation of glycolic acid and HABR, was investigated and the results are presented in Table 7.

Table 7: Variation of rate constant with solvent composition at the same concentration and temperature (298 K).

Sl. No	[Glycolic acid]M/L	[HABR] M/L	Rate constant $\times 10^{-4}$ $mol^{-1}dm^3.min^{-1}$		
			Water	Ethanol	chloroform
1	0.1	0.01	1.56	1.52	1.15
2	0.2	0.02	14	8.95	7.73
3	0.3	0.03	19	10.9	9.75
4	0.4	0.04	31	24	14.06
5	0.5	0.05	44	38.8	31.0
6	0.6	0.06	68	63.2	53.25

The observations (Table 7) can be explained by considering the entropy changes caused by the solvent reorganization on forming the transition state. When the electron transfer takes place a new charge asymmetry develops. The polar solvent molecules must adopt specific orientations for charge stabilization. This may be considered as a "freezing" of the solvent molecules in the transition state and results in negative activation entropy. In solvents like water and ethanol, the molecules are in a more ordered structure due to hydrogen bonding. Therefore, the entropy change for reaching the transition state will be less than in solvent like chloroform[14].

3.8. Effect of Ionic Strength

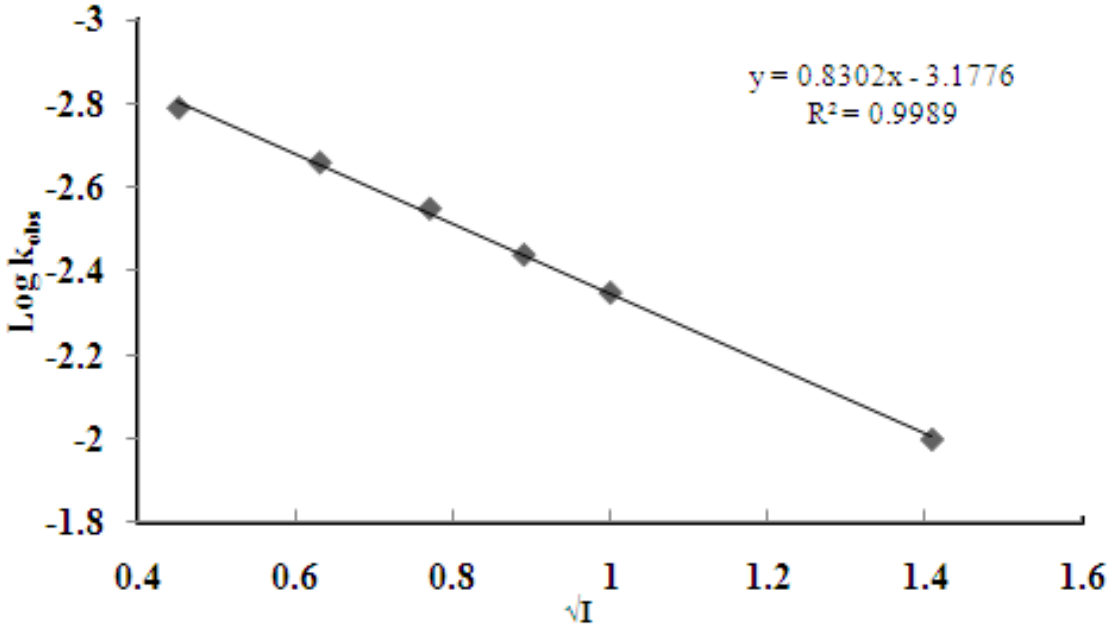
If the charges on the reactants have the same sign, the activated complex will be more highly charged than the reactants. Increasing the ionic strength of the solution will have a greater stabilizing effect upon the complex than on the reactants, and will thus increase the rate constant by lowering the effective activation energy. The reaction was studied at different ionic strengths (Table 8) by the addition of KNO_3 [(0.2–2) mol dm^{-3}] but at constant [HABR], [glycolic acid], and constant temperature pseudo-first-order rate constant increases with increase in salt concentrations as shown in figure 3. The observation is to be expected if the reactions occur between ions[14]. In this particular case, the effect of ionic strength on the reaction was examined by varying the concentration KNO_3 from 0.20 - 2.0 $mol.dm^{-3}$ at constant concentrations of glycolic acid and HABR[16].

Table 8: Effect of ionic strength by varying the concentration of KNO_3 from 0.2 M to 2 M.

S. No.	Concentration of salt in $mol^{-1}dm^3$	Concentration (Average)	Time (min)	Rate10^{-3} $mol^{-1}dm^3.min^{-1}$	Log k_{obs}	I	$\sqrt{I}$
1	0.2	0.092	56	1.6	-2.79	0.2	0.45
2	0.4	0.078	40	2.2	-2.66	0.4	0.63
3	0.6	0.045	17	2.6	-2.55	0.6	0.77
4	0.8	0.037	11	3.4	-2.45	0.8	0.89
5	1	0.036	5	7.2	-2.35	1	1
6	2	0.037	10	9.2	-2.1	2	1.41

As we observe from (Table 8), rate of the reaction increase as the ionic strength of the solution increases that indicates the reaction involves species of positive charge (charge separation) in the transition state.

Figure 5: Plot of log of rate constant Vs. square root of ionic strength.



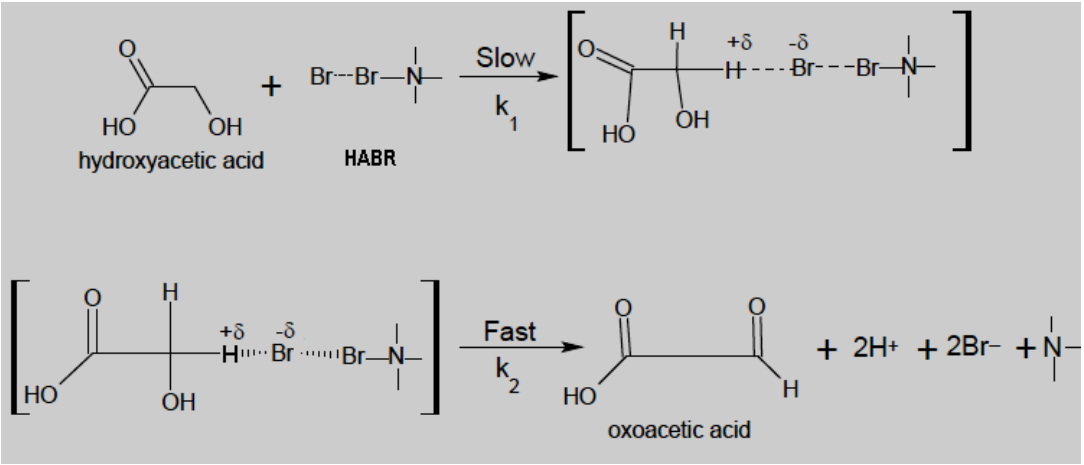
From the above graph it is observed that, as the ionic strength of the solution increase the reaction rate also increase (Figure 5). The observed effect (reaction rate increases with increasing ionic strength) can be explained simply the positive ion involvement in the transition state. The Debye-Hückel theory of ionic solutions and the affect of 'ionic atmosphere' on ion support the observation[17].

4. Reaction Mechanism

Absence of any effect of added acrylonitrile on the reaction discounts the possibility of a one-electron transfer oxidation, leading to the formation of free radical intermediate. The transition state thus approaches separation of charge. This is supported by the solvent effect also. Greater role played by the positive species solvating power of the solvents supported the postulation of a carbonation character in the transition state. Thus, the transfer of a hydride ion from the glycolic acid to HABR is indicated. The hydride ion transfer may take place through complex formation. Thus, the overall mechanism is proposed to involve the formation of a complex between glycolic acid and HABR in a rate determining step. The observed negative entropy of activation also supports the above observation. As the charge separation takes place, the charged ends become highly solvated. This results in an immobilization of a large number of solvent molecules, reflected in the loss of entropy [18].

The transition state theory, can support the observed result according transition state theory, reaction is assumed to involve the formation of activated complex that goes on to product at an extremely rapid rate and involves proton transfer in a rate determine step. The reaction centre in the rate-determining transition state is highly polarized suggests that the activated complex has a considerable carbocationic character. Based on the above observation the following mechanistic approach is suggested:

Figure 6: Reaction mechanism of the oxidation of glycolic acid by HABR.



The rate law of the reaction can be calculated based upon the above proposed mechanism by applying steady state approximation.

Rate = k_1[HOCOCH$_2$OH][HABR]

Since the rate law calculated from the proposed mechanism the same as experimentally observed indicates proposed mechanism has an agreement with the experimental observations.

4. Conclusions

The oxidation of glycolic acid by HABR in glacial acetic acid medium at constant temperature found to follow a second order kinetics, first order with respect to each reactant. The mechanism of the reaction involves formation of complex in the transition state. The rate of the reaction, product analysis, stoichiometric determinations and other experimental data indicates that the product of oxidation was glyoxylic acid and the ratio of glycolic acid to HABR were 2:1. The overall reaction written as:

2HOCH$_2$COOH + (CH$_2$)$_6$N$_4$Br$_4$ → 2HCOCOOH + (CH$_2$)$_6$N$_4$ + 4HBr

The transition state was found much more polar than the intermediate and the former more stabilized by the presence of ion atmosphere than the latter. Thus an increase in ionic strength favor the transition state; there by increasing the k_{obs} as observed in the present investigation. Comparing the oxidation of lactic and mendelic acid by HABR with glycolic acid large negative entropy of activation was observed in the case of glycolic acid this due to the presence of strong intramolecular H-bonding.

Comparing HABR with other oxidant like bromine in water, HABR avoid the possibilities of participation of many oxidants in a given reaction medium. For example oxidation by bromine in water possible oxidants are HOBr, Br_2 and Br_3^- which make the mechanism complicated. The oxidation of glycolic acid by chromium (IV) with the decrease in $[H^+]$ (increase in pH), in aqueous solution, various species of chromic acid exist in equilibrium. The nature of these species depends up on the pH and the concentration of potassium dichromate and result in loss of carbon dioxide.

But the oxidation of glycolic acid by HABR permit possibility of oxidation of glycolic acid in lower pH and the use of HABR as oxidant instead of bromine reduce the toxic and offensive odor of bromine.

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