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Kinetics of Bromination of Acetanilide

Tyagi Divya

School of Physical Sciences, Department of Chemistry
Starex University,Gurugram,122001 Email Id- divyatyagi77@gmail.com

ABSTRACT

Bromination of Acetanilide is very slow in chloroform or other solvent while it is very fast in aqueous solution. To study Kinetics of reaction, studies are carried at different temperature in range of 20^0C to 40^0C. Bromination reaction in aqueous solution follow 2^{nd} order of reaction

Keywords- Oxidation, activation energy, specific conductivity, Transference Number, Rate Constant

***Corresponding Author**

Dr, Divya Tyagi

Department of Chemistry

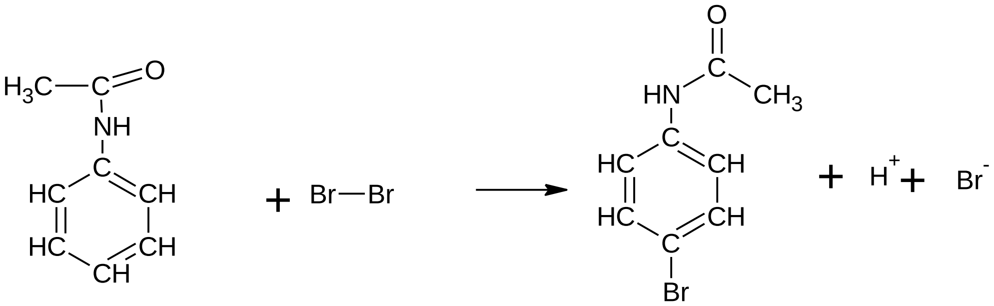
Starex University, Gurugram 122001

Email: divyatyagi77@gmail.com, Mobile No. 9871089402

I. INTRODUCTION

Bromination of aromatic amines and their derivatives are known to be fast reactions in aqueous solution.

Bromination of acetanilide occur as



The product of bromination is almost entirely the para Isomer, the ortho isomer being in traces[1]. The reaction occurs quite slowly in solvents like glacial acetic acid, chloroform or carbon tetrachloride[2],but in aqueous solution it is quite fast. With solutions of a few tenths molar concentration, the reaction would be all over in a fraction of a second.

In the reaction under study, there is the formation of hydrobromic acid, which is a strong acid and therefore gives rise to considerable electrical conductance in the solution. On the other hand both the reactants as well as the other product of the reaction do not have any appreciable electrical conductance. Hence the progress of the reaction can be followed by measuring the electrolytic conductance of the reaction mixture[3] .

EXPERIMENTAL:

PREPARATION AND STANDARDISATION OF SOLUTION:

Bromine Solution: A saturated bromine solution in distilled water is prepared by adding pure liquid to a adding to a stopper bottle containing distilled water, till excess bromine settles at the bottom. The bottle Is shaken after a regular interval of time and kept for a day.

The upper saturated solution Is decanted into another bottle as

a stock bromine solution. To a known volume of the saturated bromine solution, an excess o f potassium Iodide solution (10 %) is added and the liberated Iodine Is titrated against 0.1 M sodium thiosulpate using fresh starch solution as indicator. From the mean titre value the strength of the saturated bromine solution is calculated. Then by dilution of this solution a stock of 20 L of 0.01 M bromine solution is prepared and stored in bottle.

Acetanilide Solution: Acetanilide is recrystallised[4] from hot water containing 5% alcohol. The crystals are dried and kept in a desiccator. A saturated solution of acetanilide in distilled water is prepared by dissolving recrystallised acetanilide in hot distilled water, cooling the hot solution and filtering the solution. The concentration of the saturated acetanilide solution is determined by treating a known volume of the solution with a known excess of standardized bromine solution, then treating the bromine remaining unreacted with excess potassium iodide and titrating the liberated iodine against 0.1 M sodium thiosulpate. From the saturated solution a stock solution of 20 L of 0.01M acetanilide is prepared by dilution using distilled water.

KINETIC REQUIREMENTS:

The two 10 l reagent containers are filled with 0.01M bromine solution and 0.01M acetanlilde respectively and are kept in a thermostat at 25.0^{0}C|, for a period of two hours so as to ensure thermal equilibrium in the system. The conductance cell is Introduced into the observation tube at a distance of 20 cm from the mixing chamber. When the solutions have acquired the thermostat temperature, compressed air at a pressure o f 33 cm of mercury is applied at the reactant solution containers. The two reactant solutions flow out of the outlet tubes, get mixed in the mixing chamber within a few milliseconds and flow along the observation tube. The electrical resistance o f the solution is measured and the reciprocal of it gives the conductance. Similar measurements are repeated by inserting the conductance cell at various distances such as 30, 40, 60, 60, 70 and 80 cm from mixing chamber in the observation tube and the electric resistance of the reaction mixture is measured each time. These measurements are carried out with a semax resistance bridge instrument and sigma electronic appliances. An input of 230 V, 50Hz is stabilized by voltage stabilizer. This voltage is supplied to an oscillator. The output of the oscillator is 3 volts, 1000 Hz. This output voltage is fed to the resistance bridge instrument. The null point is obtained using a 'magic eye' in the instrument.

The actual concentration (x) of hydrobromic acid produced is evaluated from the conductance measurements depending upon a calibration o f these measurements with hydrobromic acid solutions of known concentration. The calibration is carried out. The reaction Mixture flowing out of the observation tube is collected and filtered. This filtrate contains 0.005M hydrobromic acid. From this hydrobromic acid, solutions of different concentrations are prepared. Although the conductance of the reaction mixture is mostly due to the hydrobromic acid produced in the reaction, yet there is a small contribution by the acid produced due to the hydrolysis of unreacted bromine[6]. Therefore appropriate amounts of 0.005 M bromine solution are added to the solutions of hydrobromic acid prepared above. Thus the composition of these solutions are closely similar to those of the reaction mixture at various stages of the reaction. The conductance of these solutions are measured using the same conductance cell and plotted against the concentrations of hydrobromic acid. From this calibration curve fig.1 and 2 and from the conductance measurements during the kinetic study the concentration (x) of the hydrobromic acid can be evaluated.

The duration over which the reaction has occurred at a certain distance from the mixing chamber is evaluated from the flow rate of the solution in cm^{3}per second and the area of cross section of the observation tube. The area of cross section of the observation tube is 0.052 cm^2 and the flow rate of the solution is 7.67 cm^3 per second. Therefore the linear velocity of the solution is 7.67/0.062 = 146.9 cm per second. Thus at a distance, say10 cm from the mixing chamber, the duration (t) of the reaction is 10/146.9 = 0.068 sec. Similarly the duration of reaction at various other distances from mixing chamber are found out.

Thus the concentration (x) of hydrobromic acid at a time (t) is now known. The concentrations of bromine and acetanilide taken in the containers are 0.01M, but when they get mixed in the mixing chamber the concentrations are automatically diluted twice. Therefore the in initial concentrations (a) of bromine and acetanilide are each 0.005 M. A plot of l /a- x versus time t is found to be a straight line (fig 3) Hence the reaction is concluded to be of the second order. The slope of the linear plot of l/a-x versus t gives the specific rate constant o f the reaction.

In order to determine the activation energy of the reaction, the studies are carried out at various temperatures in the range 20-40^{0}C. The results at these temperatures are presented in Table 5A, Table 5B, fig 1 and 2, and fig 3.

The plot of log K_2vs 1/T is also linear (fig 4). The slope of this linear curve is -Ea/2.303 R, from which the activation energy (Ea) for the reaction is found out. The results are presented in table 6.

Knowing the energy of activation, the frequency factor (A) for the reaction is evaluated using the equation

$$K_2 = A \exp^{(-Ea/RT)}$$

Knowing tha frequency factor, the entropy o f activation, is evaluated using the equation

$$A = e^{KT/h} \exp (\Delta S^a/R)$$

where, k= Boltman constant, 1.38 x 10^{-16} erg/degree

T = Absolute temperature

ΔS^a = The entropy o f activation

and h = Planck's constant, 6.62 x 10-^{27} erg / sec

Initial concentration of Acetanilide and bromine (a) = 0.0050M

Flow Rate of reaction solution (V) = 7.67 cm^3/ sec^{-1}

Diameter of the observation tube (2r) = 2.50 mm

Area of cross section of observation tube (A) = 0.052 cm^2

Linear velocity of solution (u) = 146.9 cm / sec

Table 1 A- Calibration of conductance of the hydrobromic acid solutions at 20.0^0C

Volume of 0.005M Hydrobromic acidl (ml)	Volume of 0.005M Bromine (ml)	Conc. of hydrobromic acid (M)	Resistance (ohm)	Conductance (mho)
0.0	20.0	$0.00X10^{-3}$	$24.0X10^{3}$	$0.417X10^{-4}$
2.0	18.0	0.50	15.5	0.646
4.0	16.0	1.00	7.75	1.29
6.0	14.0	1.50	5.36	1.86
8.0	12.0	2.00	4.10	2.44
10.0	10.0	2.50	3.36	2.98
12.0	8.0	3.00	2.80	3.57
14.0	6.0	3.50	3.50	4.00

Table 1 B - Kinetic study at 20.0^0C

Distance from mixing chamber (cm)	Time (t) (sec)	Resistance of reaction mixture (ohm)	Conductance of reaction mixture (mho)	Concentration of HCl x (M)	a – x (M)	1/ a – x (M^{-1})
20	0.136	$12.0X10^{3}$	$0.833X10^{-4}$	$0.660X10^{-3}$	$4.36X10^{-3}$	229.9
30	0.204	6.50	1.54	1.23	3.77	266.3
40	0.272	6.10	1.96	1.60	3.40	294.1
50	0.341	4.45	2.25	1.83	3.17	315.5
60	0.409	4.00	2.50	2.07	2.93	341.3
70	0.477	3.70	2.70	2.25	2.75	363.6
80	0.545	3.40	2.94	2.45	2.55	392.1

Slope of 1/ a-x vrs t curve = Specific reaction rate, K_2 = 347.6 M^{-1} sec^{-1}

Table 2 A- Calibration of conductance of the hydrobromic acid solutions at 25.0^0C

Volume of 0.005M hydrobromic acid (ml)	Volume of 0.005M Bromine (ml)	Conc. of hydrobromic acid (M)	Resistance (ohm)	Conductance (mho)
0.0	20.0	$0.0X10^{-3}$	$20.40X10^{3}$	$0.488\ X10^{-4}$
2.0	18.0	0.50	15.50	0.645
4.0	16.0	1.00	7.60	1.32
6.0	14.0	1.50	5.20	1.92
8.0	12.0	2.00	3.95	2.53
10.0	10.0	2.50	3.20	3.13
12.0	8.0	3.00	2.66	3.77
14.0	6.0	3.50	2.36	4.26

Table 2 B - Kinetic study at 25.0^0C

Distance from mixing chamber (cm)	Time (t) (sec)	Resistance of reaction mixture (ohm)	Conductance of reaction mixture (mho)	Concentration of HCl x (M)	a – x (M)	1/ a – x (M^{-1})
20	0.136	$7.10X10^{3}$	$1.40X10^{-4}$	$1.12\ X10^{-3}$	$3.88X10^{-3}$	257.4
30	0.204	5.20	1.93	1.53	3.47	288.3
40	0.272	4.10	2.44	1.93	3.07	325.2
50	0.341	3.65	2.74	2.18	2.82	254.5
60	0.409	3.35	2.99	2.38	2.62	381.3
70	0.477	3.10	3.23	2.58	2.42	413.5
80	0.545	2.95	3.39	2.70	2.30	434.1

Slope of 1/ a-x vrs t curve = Specific reaction rate, K_2 = 445.0 M^{-1} sec^{-1}

Table 3 A- Calibration of conductance of the hydrobromic acid solutions at 30.0^0C

Volume of 0.005M Hydrobromic acidl (ml)	Volume of 0.005M Bromine (ml)	Conc. of hydrobromic acid (M)	Resistance (ohm)	Conductance (mho)
4.0	16.0	1.00X10^{-3}	5.80X10^{3}	1.72X10^{-4}
6.0	14.0	1.50	4.20	2.41
8.0	12.0	2.00	3.20	3.13
10.0	10.0	2.50	2.70	3.79
12.0	8.0	3.00	2.30	4.36
14.0	6.0	3.50	2.10	4.76

Table 3 B - Kinetic study at 30.0^0C

Distance from mixing chamber (cm)	Time (t) (sec)	Resistance of reaction mixture (ohm)	Conductance of reaction mixture (mho)	Concentration of HCl x (M)	a – x (M)	1/ a – x (M^{-1})
20	0.136	5.30X10^{3}	1.89X10^{-4}	1.15X10^{-3}	3.85X10^{-3}	269.7
30	0.204	3.60	2.76	1.78	3.22	310.6
40	0.272	3.10	3.25	2.15	2.86	360.9
50	0.341	2.80	3.57	2.40	2.60	384.0
60	0.409	2.60	3.86	2.62	2.38	420.2
70	0.477	2.40	4.17	2.86	2.15	466.1
80	0.545	2.30	4.35	3.00	2.00	500.0

Slope of 1/ a-x vrs t curve = Specific reaction rate, K_2 = 545.0 M^{-1} sec^{-1}

Table 4 A- Calibration of conductance of the hydrobromic acid solutions at 35.0^0C

Volume of 0.005M Hydrobromic acidl (ml)	Volume of 0.005M Bromine (ml)	Conc. of hydrobromic acid (M)	Resistance (ohm)	Conductance (mho)
4.0	16.0	1.00X10^{-3}	5.55X10^{3}	1.80X10^{-4}
6.0	14.0	1.5	4.10	2.44
8.0	12.0	2.0	3.15	3.18
10.0	10.0	2.5	2.60	3.86
12.0	8.0	3.0	2.25	4.44
14.0	6.0	3.5	3.00	5.00
16.0	4.0	4.0	1.90	5.26
18.0	2.0	4.5	1.80	5.56

Table 4 B - Kinetic study at 35.0^0C

Distance from mixing chamber (cm)	Time (t) (sec)	Resistance of reaction mixture (ohm)	Conductance of reaction mixture (mho)	Concentration of HCl x (M)	a – x (M)	1/ a – x (M^{-1})
20	0.136	4.25X10^{3}	2.36X10^{-4}	1.42X10^{-3}	3.65X10^{-3}	279.3
30	0.204	3.15	3.18	2.00	3.00	333.3
40	0.272	2.70	3.70	2.40	2.60	384.6
50	0.341	2.45	4.08	2.70	2.30	434.8
60	0.409	2.35	4.26	2.85	2.15	465.1
70	0.477	2.20	4.55	3.07	1.93	518.1
80	0.545	2.10	4.76	3.26	1.76	571.4

Slope of 1/ a-x vrs t curve = Specific reaction rate, K_2 = 660.0 M^{-1} sec^{-1}

Table 5 A- Calibration of conductance of the hydrobromic acid solutions at 40.0^{0}C

Volume of 0.005M Hydrobromic acidl (ml)	Volume of 0.005M Bromine (ml)	Conc. of hydrobromic acid (M)	Resistance (ohm)	Conductance (mho)
6.0	14.0	$1.5X10^{-3}$	$3.86X10^{3}$	$2.60X10^{-4}$
8.0	12.0	2.00	2.90	3.45
10.0	10.0	2.50	2.40	4.17
12.0	8.0	3.00	2.06	4.88
14.0	6.0	3.50	1.90	5.26
16.0	4.0	4.00	1.86	5.41
18.0	2.0	4.50	1.80	5.58
20.0	0.0	5.00	1.75	5.71

Table 5 B - Kinetic study at 40.0^{0}C

Distance from mixing chamber (cm)	Time (t) (sec)	Resistance of reaction mixture (ohm)	Conductance of reaction mixture (mho)	Concentration of HCl x (M)	a – x (M)	1/ a – x (M^{-1})
20	0.136	$3.40X10^{3}$	$2.94X10^{-4}$	$1.72X10^{-3}$	$3.28X10^{-3}$	304.9
30	0.204	2.65	3.77	2.23	2.77	361.0
40	0.272	2.35	4.25	2.55	2.45	408.2
50	0.341	2.15	4.65	2.83	2.17	460.8
60	0.409	2.05	4.88	3.00	2.00	500.0
70	0.477	1.95	5.13	3.22	1.78	561.8
80	0.545	1.90	5.26	3.50	1.50	666.7

Slope of 1/ a-x vrs t curve = Specific reaction rate, $K_2 = 770.0 \ M^{-1} \ sec^{-1}$

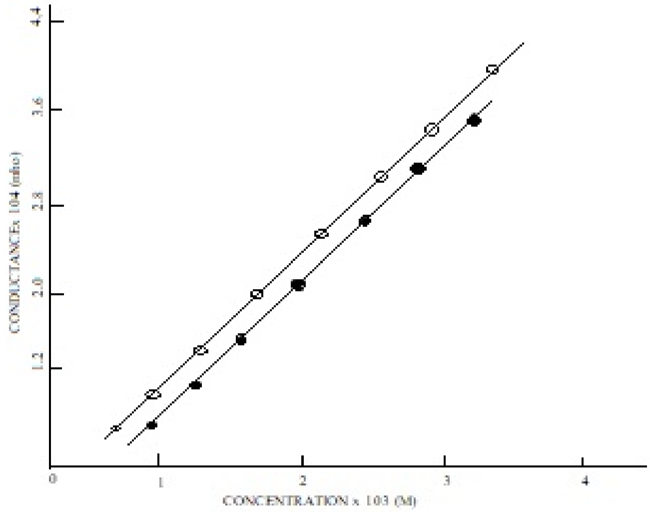


Fig 1 Calibration Of The Conductance Of Hydrobromic Acid At 20^0 and 25^0 C

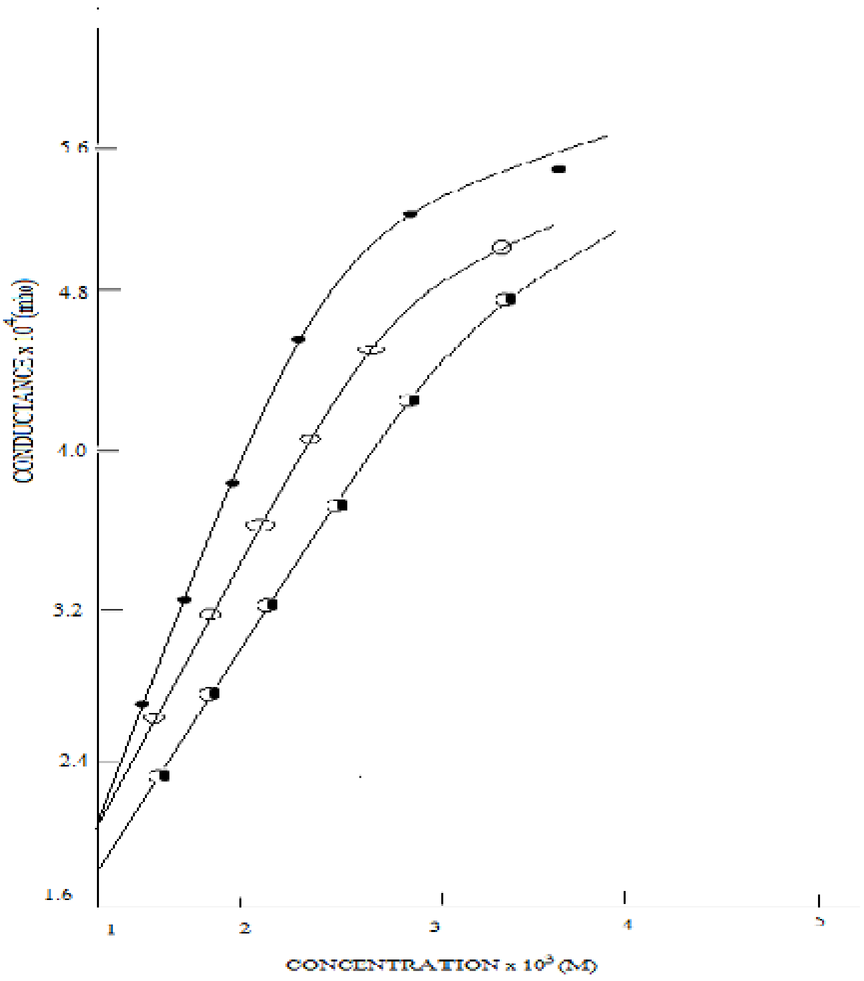


Fig-2 Calibration Of The Conductance Of Hydrobromic Acid At 30^0, 35^0 And 40^{0}C

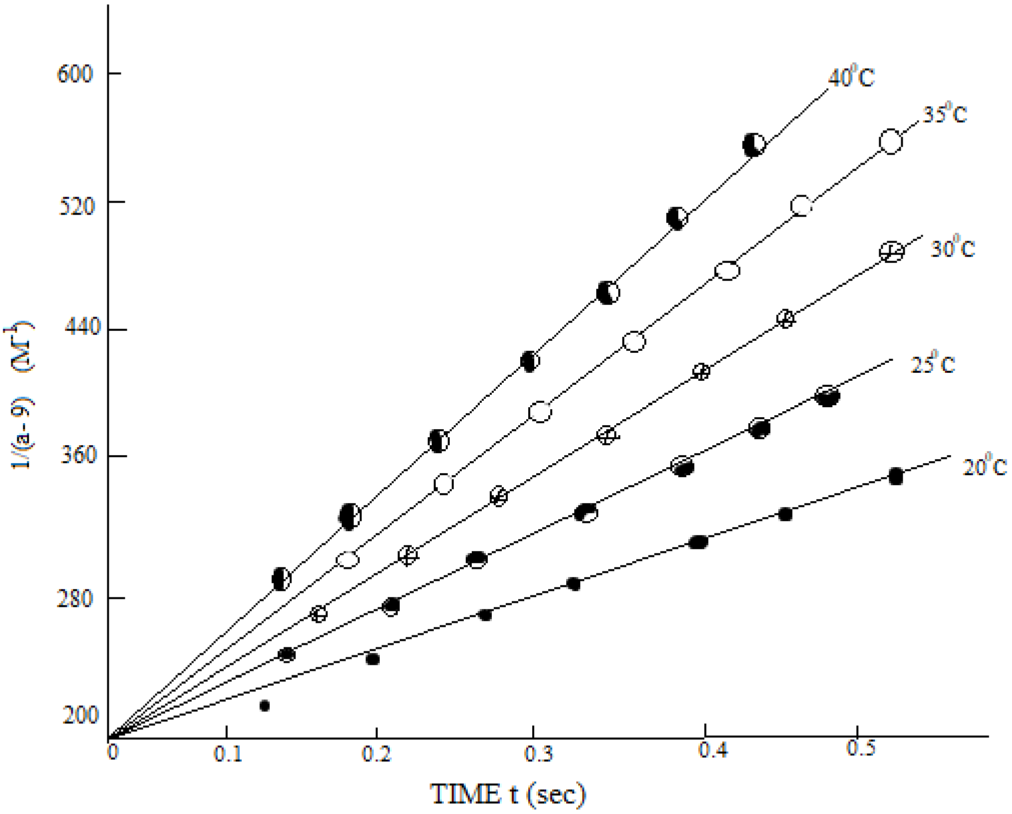


Fig.3 – The Kinetics Of Bromination Of Acetanilide At Various temperatures

Table 6 – Variation of the specific reaction rate with temperature

Temperature		**1/T**	**Specific reaction rate, K_2 M^{-1}/Sec**	**Log K_2**
^{0}C	T^{0}K			
20	293	3.413	347.5	2.541
25	298	3.360	445.0	2.648
30	303	3.300	545.0	2.736
35	308	3.250	660.0	2.813
40	313	3.196	770.0	2.886

Energy of activation Ea = -2.303 X R X Slope of log K_2 vs 1/T Curve

= -2.303 X 1.98 X (-1.48X10^3)

= 6670 cal/mole

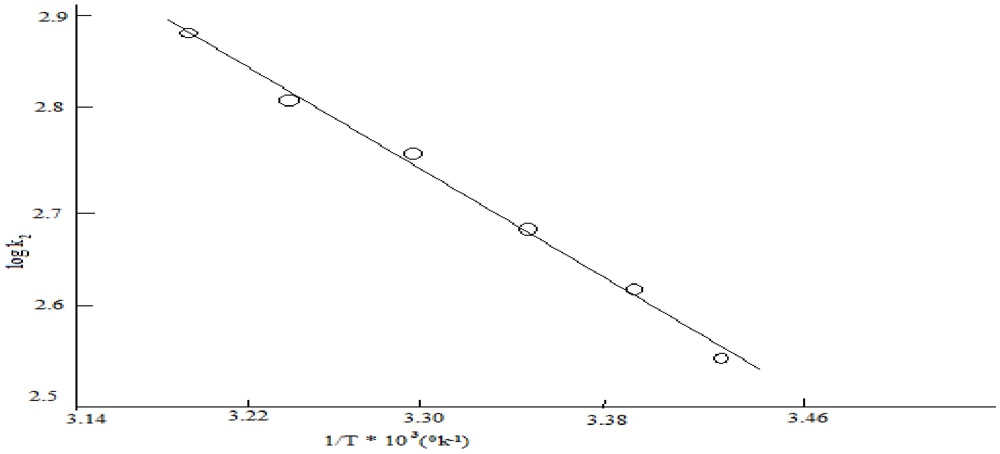


Fig.4 – Variation Of Specific Reaction Rate With Temperature

RESULT AND DISCUSSION

The bromination of the acetanilide in aqueous solution is found to obey second order kinetics since the plot of 1/a-x versus time yields a straight line. The specific rate constant for this reaction is 445.0 M^{-1}/ Sec at 25^0C. The activation energy and the entropy of activation are respectively 6.67 Kcal/mole and -24.9 cal/mole degree while the frequency factor at 25.0^0C is $3.45X10^7$ M^{-1}/Sec

As mentioned earlier the progress of the reaction is followed by measuring the conductance of the reaction mixture due to the hydrobromic acid produced in the reaction It is however known that bromine undergoes hydrolysis[6] in aqueous solution according to the equation:

$$Br_{2aq} + H_2O \rightleftharpoons H^+_{aq} + HOBr_{aq}$$

and thus produces extra hydrobromic acid which would contribute to the conductance of the solution. At early stages of the reaction the concentration of hydrobromic acid formed is small and is comparable to that produced as a result of the hydrolysis of bromine. Therefore there is the possibility of error in estimating its concentration arising out of the bromination reaction. In order to eliminate this error during the calibration, solutions of hydrobromic acid of various concentrations are prepared containing bromine at such concentrations as would be occurring at various stages of the reaction. Any hydrobromic acid arising out of the hydrolysis of bromine would also contribute to the total conductance, thereby simulating accurately the conditions occurring during the actual brominating reaction.

The conductance measurements have a precision of nearly ±1.0%, which introduces an error of 2% in the final results. The errors due to mixing efficiency and deviation from mass flow are within 2% while the entities such as the flow rate, area of cross section of the observation tube are accurately calculated. Hence the overall error in the rate constants is not more than 3%.

It is interesting to note that the solvent has profound influence on the order and specific rate constant of the reaction. Robertson et al[7] have studied the bromination of acetanilide in glacial acetic acid, in aqueous acetic acid and in other solvents like chloroform and carbon tetrachloride. They found that the reaction order, mechanism and the activation energy of the reaction depend upon the relative concentrations of the reactants. Further, the authors found that the influence of water on the bromination in acetic acid is to increase the rate and cause a gradual change from third order to second kinetics. The following data give an idea of their work.

Concentration of acetanilide	M/20	M/40	M/80	M/160	M/320	M/640
X_1(Br_2 absorbed in %)	20	20	20	20	20	20
$K_2M^{-1}Min^{-1}$	9.5	4.9	2.5	1.4	0.86	0.57
Reaction order	2.9	3.0	2.9	2.7	2.6	
K_a cal/mole	3300			11,000		

On comparing these studies with the present study in purely aqueous solution it is found that the rate constant of the reaction in aqueous solution is more than 3000 times higher than those in the solvents mentioned above.

MECHANISM OF BROMINATION:

It has been widely accepted that bromination in aqueous media is mainly molecular bromine[8]. Many authors have shown that molecular bromine is directly involved in the rate determining step. Thus in aqueous media the rate of bromination is given by

$$-d[Br_2]/dt = K_2[ArH][Br_2]$$

But the bromination in organic solvents such as acetie acid, chloroform, carbon tetrachloride is of oomplex nature. Robertson at al[9] have shown that bromination involves kinetic terms of order higher than one with respect to bromine. Therefore more general kinetic form of the bromination is given by[10]

$$-d[Br_2]/dt = K_2[ArH][Br_2] + K_3[ArH][Br_2]^2 + K_4[ArH][Br_2]^3$$

A number of mechanisms have been suggested to interpret the above equation

1) $ArH + Br_2 \rightarrow ArHBr_2 \rightarrow$ Products (Second order)
2) $ArH + Br_2 \rightarrow ArHBr_2 \rightarrow$ Products (Third order)
3) $Br_2 + Br_2 \rightarrow Br_4 + ArH \rightarrow ArHB_4 + Br_2 \rightarrow$ Products (Fourth order)

Further, bromination is catalysed by strong acids such as perchloric acid, sulphuric acid etc. Thus the aqueous hypobromous acid in the presence o f perchloric acid becomes a much more active brominating agent[11] than bromine water. Then the bromination is represented in the kinetic form as

$$-d[BrOH]/dt = k_2 [ArH][BrOH][H^+]$$

Bronination in acetic medium involves the hypobromous acidium ion i.e. $BrOH^+_2$ or the brominium ion Br^+ obtained by following processes[12,13]

$BrOH + H^+ \rightarrow BrOH_2^+$, $BrOH_2^+ + ArH \rightarrow$ Products
$BrOH + H^+ \rightarrow BrOH_2^+ \rightarrow Br^+ + H_2O$
$ArH + Br^+ \rightarrow$ Products

further it is found that the rates of bromination depend upon the acidity function rather than the pH. There are two types of acidity functions, Hammett's acidity function H_0 given as

$$H_0 = pK_{BrOH2+} + + \log[BrOH]/ BrOH_2^+$$

And, J_0 function given by

$$J_0 = pK_{BrOH} + \log[BrOH]/ [Br^+]$$

Thus if one finds that the rate constants vary with H_0 function, then the main brominating species is $BrOH_2^+$ while if the rate constants vary with $J_{0,}$ then the main brominating species is Br^+. But a lot of work needs to be done to confirm this idea.

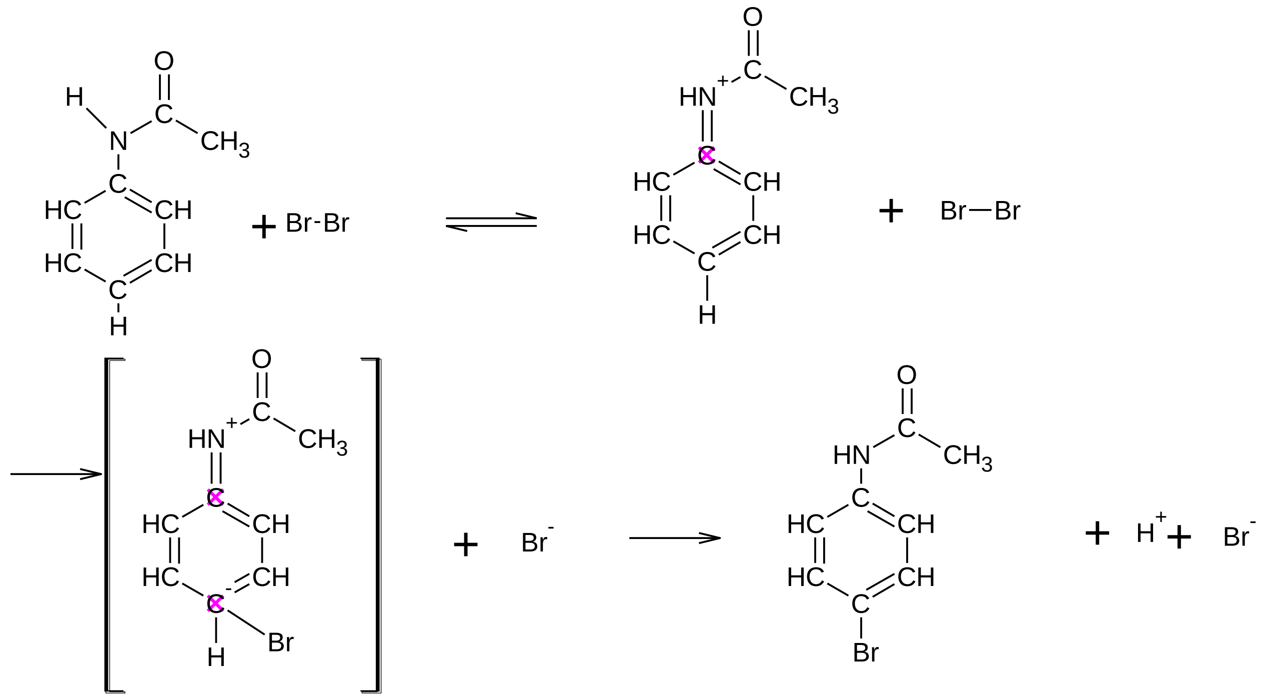
Tribromide[14] ion is also known to be a brominating agent. But its activity is nearly 200 times less than that of molecular bromine.

The relative reactivities of the various brominating agents is found to be in the following order[15]

$$Br^{+} > Br_2 > BrOH > Br^{-}_3$$

Further the rate constants of bromination also depend upon the nature of the substituted group i.e. whether it is electron withdrawing or electron releasing, orientation effects and steric effects. An excellent account of the effects of these factor has been given by de la Mare in his book[16]

The reaction under study has been carried out in purely aqueous medium and hence the main brominating agent is the molecular bromine. As there is the formation of hydrobromic acid| Br_3^{-} species which are known to be brominating species are invariably formed, yet its reactivity being very much less than that of Br_3, the bromination due to Br_3^{-} can be neglected. Thus the most probable mechanism would be



The π electrons of the nucleus readily react with the bromine and form an adduct which then gives rise to the intermediate. The formation of this intermediate is the rate determining step[17] while the removal of proton is very fast[18]. Therefore the kinetic equation for this mechanism would be

$$\text{Rate} = k_2\,[\text{Acetanilide}]\,[Br_2]$$

which implies that the reaction is of the second order.

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