Kinetics and Mechanism of the Bromination of Acetanilide

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ABSTRACT

Kinetics of the bromination of acetanilide acid in aqueous solution by bromine has been studied potentiometrically. The rate shows second order kinetics i.e. first order with respect to acetanilite and bromine. A suitable mechanism in conformity with the kinetic observations has been proposed. Various activation parameters such as frequency factor, energy of activation and entropy of activation are calculated from kinetic measurements.

Key words: Kinetics, Bromination, Acetanilide, Steady State Principle.

INTRODUCTION

During last few decades, as a result of the advancement of electronic and rapid monitoring technique,[1-5] a good deal of efforts has been devoted to study rapid reactions which can not be studied by conventional techniques. Many workers used potentiometric method to follow the bromination reactions.[6-10] Speneer and Bell[11-12] used rotating platinum electrode technique to study the kinetics of the base catalysed bromination of ethyl nitro acetate.

The reaction between acetanilide and bromine in aqueous solution is very rapid to be studied by conventional techniques. Therefore, the kinetics of this bromination reaction have been studied by a very simple electrochemical technique such as steady state technique by generating brominating reagent in situ in solution of acetanilide by means of acidic bromate – bromide reaction. The rate of generation of bromine is evaluated by noting the time required for reaction with known concentration of allyl alcohol. The steady state concentration of bromine – acetanilide reaction is evaluated potentiometrically. Separate order of acetanilide and bromine is determined. From the results the rate of bromination of acetanilide is evaluated.

The study is carried out at various temperatures to evaluate kinetic parameters such as frequency factor, energy of activation and entropy of activation. From the foregoing results the most probable mechanism for the bromination of acetanilide has been suggested.

EXPERIMENTAL

Preparation of solutions

The solutions were prepared fresh for each set of experiments. water, double distilled in glass, was used for preparing the various solutions. All the glass ware was cleaned with Surf excel, washed repeatedly with hot distilled water and rinsed with double distilled water before being used for preparing the solutions.

The stock solutions were prepared of allyl alcohol (0.01M), hydrochloric acid (0.05M) and potassium bromide (0.02 M) in distilled water. Further, a stock solution of (0.04M) potassium bromate was also prepared.

The required volume of stock solutions were mixed and diluted to obtain the following solutions :

Solution A

Allyl alcohol (2.5×10^{-4} M) + hydrochloric acid (3.0×10^{-2} M) + potassium bromate (5.0×10^{-3} M).

Solution B

Potassium bromide (2.5×10^{-2} M)

A bright platinum foil electrode and saturated calomel electrode were introduced into the reaction mixture and EMF of the cell was measured at the intervals of 50 second using Digital potentiometer. The measurements were continued until there was a sharp rise followed by gradual increase in the EMF values. The EMF versus time curve gives the time of inflexion. From the result the rate of production of bromine can be evaluated.

The above procedure was repeated by taking acetanilide in place of allyl alcohol. The EMF measurements were made at the intervals of 50 second. From the EMF values the redox potential of bromine, could be evaluated. Having evaluated the redox potential of bromine, the steady state concentration of bromine and hence the specific reaction rate of bromination of acetanilide could be determined.

The procedure described above in both the paragraphs were repeated at various temperature in the range of 25.0 ^{0}C to 40.0 ^{0}C and from the results the energy of activation, frequency factor, entropy of activation for the reaction was evaluated.

The kinetic measurements were also carried out as mentioned in above but with several different concentrations of the acid. For this purpose, from the stock solutions required volume of potassium bromide and allyl alcohol were mixed together and diluted to 250 cm^{3}.

It is solution C : Allyl alcohol (2.5×10^{-4}M) + Potassium bromide (2.5×10^{-2}M).

In each of four stoppered bottles required volume of potassium bromate was taken and various amount of hydrochloric acid was added to these bottles. The contents of each were diluted to 100 cm^{3}.

It is solution D

Potassium bromate (5.0×10^{-3}M) + hydrochloric acid
(3.0×10^{-2}M, 4.0×10^{-2} M, 5.0×10^{-2} M, 6.0×10^{-2} M).

The solutions were kept in a thermostat at 25.0 ^{0}C. After acquiring temperature of thermostat, 10.0 cm^{3} each of solution - C and solution –D were mixed in a beaker kept in the thermostat. The time of inflexion in presence of these various concentrations of the acid was determined . The solution – C was then prepared containing acetanilide instead of allyl alcohol. The kinetics was carried out and results are presented in table.

RESULTS AND DISCUSSION

The concentrations of bromate, bromide and acid are greater than that of allyl alcohol. Hence, during the production of bromine these concentrations remain unchanged. Therefore the rate of production of bromine can be considered as constant. It can be obtained by the ratio

$$\text{Rate of production} = \frac{\text{Concentration of bromine produced}}{\text{Time of inflexion point}}$$

Table 1: Kinetics of bromination of acetanilide:
Rate of generation of bromine at 25.0 ^{0}C.

Concentration of potassium bromate   : 5.0×10^{-3} M
Concentration of potassium bromide   : 2.5×10^{-2} M
Concentration of hydrochloric acid   : 3.0×10^{-2} M
Concentration of allyl alcohol   : 2.5×10^{-4} M

Time/S	EMF/mV	Time/S	EMF/mV
50	700	500	783
100	702	550	789
150	705	600	794
200	709	650	800
250	712	700	804
300	716	750	808
350	722	800	810
400	749	850	812
450	774	900	814

Time to reach inflexion point   =   350 S
Rate of generation of bromine   = 7.14×10^{-7} MS^{-1}

Table 2: Kinetics of bromination of acetanilide at 25.0 °C

Concentration of potassium bromate   : 5.0×10^{-3} M
Concentration of potassium bromide   : 2.5×10^{-2} M
Concentration of hydrochloric acid   : 3.0×10^{-2} M
Concentration of Acetanilide   : 2.5×10^{-4} M

Time/S	EMF/mV	Time/S	EMF/mV
50	756	500	796
100	760	550	800
150	763	600	805
200	768	650	808
250	772	700	810
300	776	750	812
350	780	800	813
400	786	850	
450	790	900	

Extrapolated value of EMF at zero time   =   0.752 V
Steady state concentration of bromine   = 5.14×10^{-7} M
Specific reaction rate, k   = 5.56×10^{3} M^{-1} S^{-1}

In present study, the time of inflexion point was 350 S and the concentration of allyl alcohol was 2.5 ×10⁻⁴ M (Ref. Table1 and Fig.1). Therefore the rate production of bromine 7.14 × 10⁻⁷ M S⁻¹.

As the concentration of acetanilide was accurately known, the steady state concentration of bromine was evaluated at t = 0. It was obtained by extrapolating the plot of EMF versus time to zero and obtaining bromine " bromide system at that

Table 3: Kinetics of the bromination of acetanilide effect of temperature

[KBr] = 2.5×10^{-2} M, [KBrO$_3$] = 5.0×10^{-3} M, [HCl] = 3.0×10^{-2} M [Acetanilide] = 2.5×10^{-4} M

Temperature ^{0}C	Specific reaction rate k / 10^3 M^{-1}S^{-1}
25.0	5.56
30.0	5.80
35.0	6.07
40.0	6.41

Table 4: Kinetics of bromination of acetanilide At 25.0 ^{0}C

[KBr] = 2.5×10^{-2} M, [KBrO$_3$] = 5.0×10^{-3} M, [HCl] = 3.0×10^{-2} M [Acetanilide] = 2.5×10^{-4}

Energy of activation, Ea	=	63.2 KJ
Frequency factor, A	=	4.47×10^{11} M^{-1}S^{-1}
Entropy of activation, ∆S*	=	30.2 J K^{-1} Mole^{-1}

Table 5: Kinetics of bromination of acetanilide effect of acid concentration

[KBr] = 2.5×10^{-2} M, [KBrO$_3$] = 5.0×10^{-3} M, [Acetanilide] = 2.5×10^{-4} Temperature : 25.0 ^{0}C

Concentration of acid / 10^{-2} M	Specific reaction rate, k_2 / M^{-1}S^{-1}
3.0	5.56×10^3
4.0	6.84×10^3
5.0	7.42×10^3
6.0	12.97×10^3

instant. At constant temperature and concentration of Acetanilide the specific reaction rate remains constant. Therefore, when rate of production of bromine changes from 7.14 × 10⁻⁷ M S⁻¹ to 7.77 × 10⁻⁷ M S⁻¹, the corresponding steady state concentration of bromine changes in the same proportion from 5.14 × 10⁻⁷ M to 5.58 × 10⁻⁷ M. This is possible only when the exponent of concentration of bromine is 1.

Therefore the reaction is of first order with respect to bromine. When concentration of acetanilide is varied from 2.5 × 10⁻⁴ M to 4.5 × 10⁻⁴ M at constant rate of production of bromine, the steady state concentration of bromine changes from 5.14 × 10⁻⁷ M to 2.85 × 10⁻⁷ M. That is by changing the concentration of acetanilide approximately double the steady state concentration of bromine is almost half of its value. This is possible only when the exponent of concentration of acetanilide is 1.

Hence the reaction is first order with respect to acetanilide. Hence the overall reaction is second order. We know the steady state concentration of bromine at t = o, rate of production of bromine and initial concentration of acetanilide. Therefore the specific reaction rate of bromination of acetanilide can be evaluated as,

$$k = \frac{\text{Rate of production of bromine}}{[\text{Acetanilide}] [Br_2]}$$

The specific reaction rates are evaluated at various temperatures ranging from 25^{0}C to 40^{0}C. The plot of logk versus the reciprocal of absolute temperature gives straight line with negative slope, from which the energy of activation is evaluated.

The specific reaction rate and the energy of activation are found to be 5.56 ×10³ M⁻¹S⁻¹ and 63.2 KJ Mole⁻¹ respectively at 25 ^{0}C. The frequency factor and entropy of activation are 4.47×10¹¹ M⁻¹S⁻¹ and 30.2J K⁻¹M⁻¹ respectively at 25 ^{0}C.

The acid concentration was varied from 3.0 × 10⁻² M to 6.0 × 10⁻² M. It was observed that the specific reaction rates increases from 5.56×10³M⁻¹S⁻¹ to 12.97 ×10³ M⁻¹S⁻¹ (Table 5).
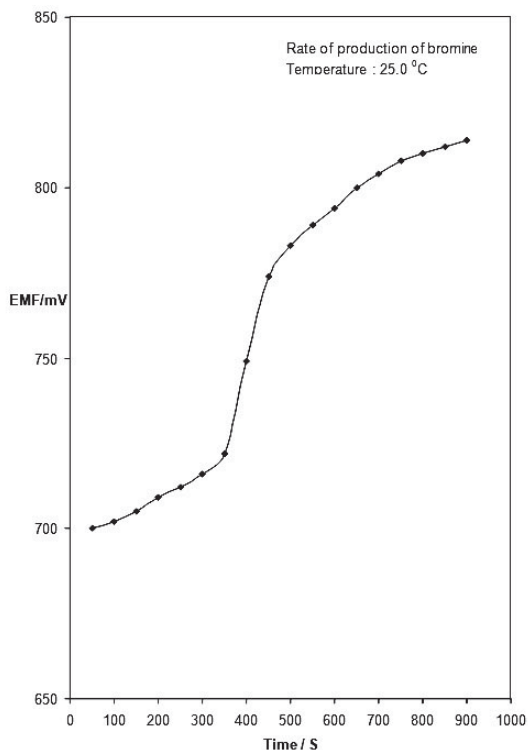
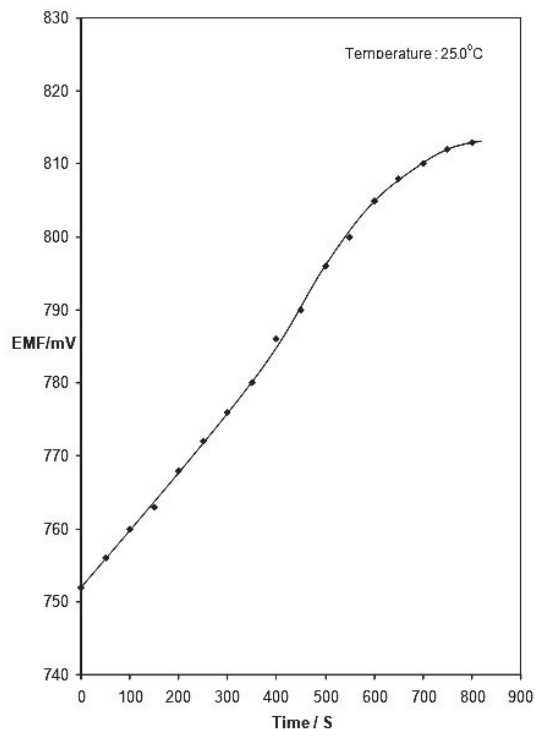**Fig. 1: Kinetics of bromination of acetanilide**

Fig. 2: Kinetics of bromination of acetanilide

It is well known that in aromatic electrophilic substitution reactions bromine is much faster brominating agent than that of HOBr. Therefore in aqueous solution bromine is brominating agent than HOBr. However, in presence of strong acids hypobromous is faster brominating agent than the bromine. In presence of hydrochloric acid, H_2OBr^+ has been suggested as brominating agents.[13-158]

In present study, bromine is produced in the reaction of bromate, bromide and acid via HOBr due to the reduction of BrO_3^- and oxidation of Br^-. The effective concentration of bromine produced at steady state is 5.14×10^{-7} M. If HOBr is a brominating agent , in presence of acid it will be very fast brominating agent than the bromine. Therefore bromination of acetanilide must have occured by H_2OBr^+. Hence most probable mechanism of bromination of acetanilide in presence of acid can be proposed as follows:
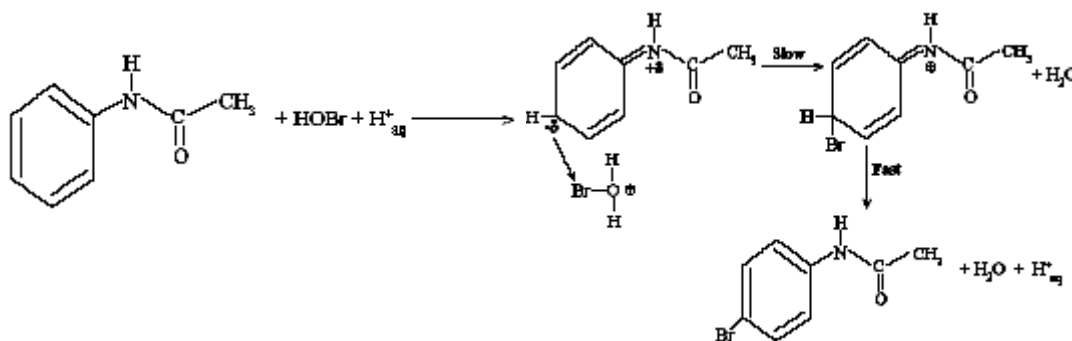
Scheme

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