Asian Journal of Chemistry Vol. 22, No. 7 (2010), 5072-5076

Kinetics and Mechanism of the Bromination of Salicylic Acid

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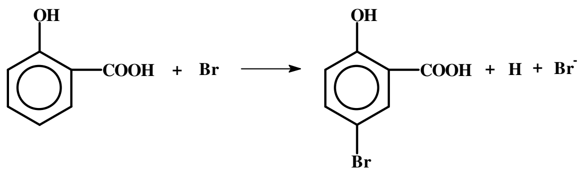
Kinetics of the bromination of salicylic acid in aqueous solution by bromine has been studied potentiometrically. The rate shows second order kinetics *i.e.*, first order with respect to salicylic acid and bromine. A suitable mechanism in conformity with the kinetic observations has been proposed. Various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

Key Words: Kinetics, Bromination, Salicylic acid, Steady state principle.

INTRODUCTION

It is natural that majority of the kinetic work has been done on the reactions whose rates can be measured easily, with conventional techniques. Bell and Ramsdent[1] have studied the bromination of N,N-diethyl-*m*-toludine potentiometrically. They have also adopted potentiometric[2-4] method to follow the bromination of 2,3-dimethyl-1,4-dizopinium cations[5]. Speneer and Bell[6,7] used rotating platinum electrode technique to study the kinetics of the base catalyzed bromination of ethyl nitroacetate. During last few decades, as a result of the advancement of electronic and rapid monitoring[8-12] techniques, a good deal of efforts has been devoted to study rapid reactions which cannot be studied by the conventional techniques.

The bromination of aromatic compounds in aqueous solutions are very rapid[13] and studies on their kinetics are scarce, probably because of the extreme rapidity of the reactions. Conventional methods of determination of specific reaction rates are of no avail in these cases under such circumstances in the present work, we have studied the kinetics of bromination of salicylic acid by bromine in aqueous solution. The reaction can be represented by the equation,



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We have determined its specific reaction rate by the steady state technique. In this method the bromine is generated *in situ*, at controlled rate, by well known bromate-bromide reaction[14-16]:

$$BrO_3^- + 5Br^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O \qquad \text{(ii)}$$

The specific reaction rate at various concentration of salicylic acid were determined. The bromination reaction was carried out at various temperatures to determine activation parameters. The most probable mechanism for this bromination reaction was proposed.

EXPERIMENTAL

Analytical grade chemicals were used to prepare stock solutions in glass distilled water. Solution **A**: 2.0 × 10^{-4} M salicylic acid in 1.5 × 10^{-2} M potassium bromide and 0.3 M sulphuric acid. Solution **B**: 3.0 × 10^{-3} M potassium bromate.

Kinetic measurement: 50 cm^3 of solution **A** and 50 cm^3 of solution **B** were maintained in a thermoastat. When the experimental temperature was attained, they were mixed in a beaker and a stop-watch was simultaneously started. A bright platinum foil electrode and saturated calomel electrode (SCE) were introduced into the reaction mixture and the EMF of the system was measured at intervals of 25 s with electronic voltmeter.

Specific reaction rate: The specific reaction rate was calculated from the ratio of the rate of production of bromine to the initial concentration of salicylic acid and bromine. The rate of production of bromine was obtained from the ratio of initial concentration of salicylic acid to the time of inflexion in the EMF *versus* time curve (Table-1 and Fig. 1).

TABLE-1
KINETICS OF THE BROMINATION OF SALICYLIC ACID
Concentration of potassium bromide : 7.5 × 10^{-3} M; Concentration of potassium bromate: 1.5 × 10^{-3} M; Concentration of sulphuric acid: 0.15 M; Concentration of salicylic acid: 1.0 × 10^{-4} M; Temperature : 25 ºC

Time (s)	EMF (V)	Time (S)	EMF (V)	Time (s)	EMF (V)
25	0.640	150	0.730	275	0.810
50	0.660	175	0.750	300	0.810
75	0.680	200	0.790	325	0.815
100	0.695	225	0.800	350	0.815
125	0.715	250	0.805	375	0.815

Extrapolated value of EMF at zero time = 0.625 V; Time to reach inflexion point = 190 S; Rate of generation of bromine = 5.26 × 10^{-7} M S^{-1}; Specific reaction rate, k_2 = 4.42 × 10^9 M^{-1} S^{-1}.

The steady state concentration of bromine was obtained by substituting the extrapolated EMF at zero time into the Nernst equation with substracted calomel electrode potential, $E = 0.978 + 0.0296 \log [Br_2]$ (Table-1 and Fig. 1).

Such determinations of specific rates were made with various concentrations of salicylic acid ranging from 1 × 10^{-4}-2 × 10^{-4} M at 25 ºC to obtain the order of reaction.

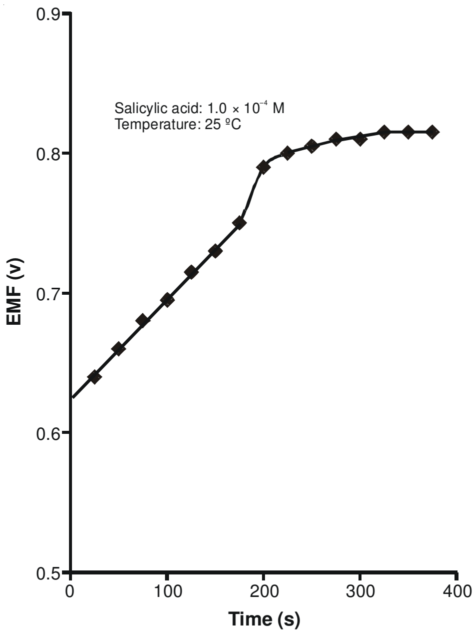


Fig. 1. Kinetics of the bromination of salicylic acid

The specific reaction rate measured at various temperature ranging from 20-40 ºC (Table-2). From the observations activation parameters such as energy of activation, frequency factor and entropy of activation were determined (Table-3).

TABLE-2
KINETICS OF THE BROMINATION OF SALICYLIC ACID EFFECT OF TEMPERATURE
[KBr] = 7.5 × 10^{-3} M, [$KBrO_3$] = 1.5 × 10^{-3} M, [H_2SO_4] = 0.15 M [salicylic acid] = 1.0 × 10^{-4} M

Temperature (ºC)	Specific reaction rate (k/10^9 M^{-1} S^{-1})
20	3.61
25	4.42
30	5.92
35	6.79
40	7.77

TABLE-3
KINETICS OF THE BROMINATION OF SALICYLIC ACID
[KBr] = 7.5 × 10^{-3} M, [$KBrO_3$] = 1.5 × 10^{-3} M, [H_2SO_4] = 0.15 M, [salicylic acid] = 1.0 × 10^{-4} M; Temperature 25 ºC

Activation parameters	Value	Unit
Energy of activation (Ea)	33.5	KJ mol^{-1}
Frequency factor (A)	3.31 × 10^{15}	M^{-1} S^{-1}
Entropy of activation (ΔS*)	-43.85	K^{-1} mol^{-1}

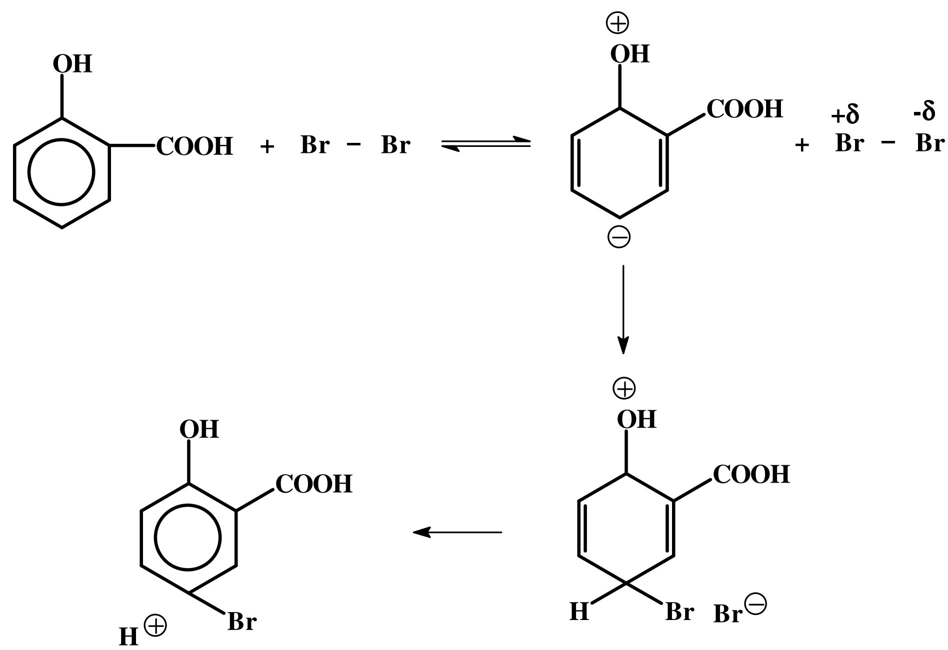
RESULTS AND DISCUSSION

By varying the concentration of salicyclic acid from 1×10^{-4}-2×10^{-4} M, the value of specific rate almost remains constant within the limits of experimental error. These observations indicated that the reaction was of overall second order *i.e.*, first order with respect to salicylic acid and bromine.

The specific reaction rates, k were evaluated at various temperatures, plot of log k *versus* reciprocal of absolute temperature gave a good straight line with slope of (-Ea/2.303 R) from which energy of activation was calculated. The specific reaction rate, k and energy of activation were found to be 4.42×10^9 M^{-1} S^{-1} and 33.5 KJ mol^{-1}, respectively at 25 ºC. The frequency factor and entropy of activation were 3.31×10^{15} M^{-1} S^{-1} and -43.85 K mol^{-1}, respectively at 25 ºC.

In the bromate-bromide reaction in acid media, bromine might be produced either in the molecular form Br_2 or in the hydrolyzed form, HOBr ($Br_2 + H_2O \rightleftharpoons HOBr + H^+ + Br^-$) out of which one species could brominates the salicylic acid. But the rate of bromination was about thousand times faster than the rate of hydrolysis. If the bromine were to first hydrolyzes and then brominates salicylic acid, the overall reaction could not have a rate which was so many times higher than the rate of hydrolysis. Since the rate determining step is the slowest step, the rate of the overall reaction could not exceed that of the slowest step. Hence the hydrolysis of bromine was not one of the steps in the mechanism of the bromination of salicylic acid.

Thus if the bromine was produced as Br_2, it must react in the same form. Hence the accepted mechanism for the reaction was.



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(*Received*: 5 June 2009; *Accepted*: 19 March 2010) AJC-8517