



Catalytic Effect of Bromide ion on the Kinetics of the Bromination of O-acetotoluidide in Aqueous solution

D.B. PATIL¹ and S.B. KAPOOR²

¹Department of Chemistry, Institute of Science, Nagpur - 440 001 (India).

²Department of Chemistry, Arts, Commerce and Science College,
Tukum, Chandrapur - 442 401 (India).

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ABSTRACT

The kinetics of the bromination of o-acetotoluidide by bromine in aqueous medium has been studied voltametrically. The specific reaction rate is $1.78 \text{ M}^{-1}\text{S}^{-1}$ at 25.0°C . The energy of activation is 59.8 KJ mol^{-1} . The entropy of activation is $-132.7 \text{ J mol}^{-1}\text{K}^{-1}$. The specific reaction rate is influenced by added bromide ion and the specific reaction rate, energy of activation and entropy of activation are $54.7 \text{ M}^{-1}\text{S}^{-1}$, 25.8 KJmol^{-1} and $-133.4 \text{ Jmol}^{-1}\text{K}^{-1}$ respectively. The most likely mechanism has been suggested.

Key words: Catalytic effect, Bromination, o-acetotoluidide, Bromine, Voltametry.

INTRODUCTION

Bromine reacts with o-acetotoluidide to produce p-bromoderivative and hydrobromic acid. In aqueous solution it is very fast reaction and its kinetics can not be measured by any conventional method. Various workers have investigated the kinetics of fast bromination of aromatic compounds in aqueous and non-aqueous solutions¹⁻¹².

In present investigation since bromination of o-acetotoluidide is a fast reaction, a special improvised technique has been used for the determination of reaction rate. Kinetics is studied by recording diffusion current due to bromine,

developed at a rotating platinum electrode in the reaction mixture during the course of reaction. Further the effect of added bromide ions on the bromination of the o-acetotoluidide have been investigated.

EXPERIMENTAL

Preparation of Solutions

Analytical grade chemicals were used to prepare stock solutions. Doubly glass distilled water was used to prepare all the solutions.

In each experiment the required volume of the stock solutions were diluted to obtain the

following solutions.

- A : 2.0×10^{-4} M bromine in 1.0×10^{-2} M potassium nitrate.
 B : 2.0×10^{-4} M o-acetotoluidide in 1.0×10^{-2} M potassium nitrate.
 C : 1.0×10^{-2} M potassium nitrate.

All solutions were placed in stoppered bottles and were maintained in a thermostat at 25.0 °C.

Kinetic Determination

The saturated calomel electrode (SCE) was dipped into an empty beaker in which the rotating platinum electrode was already rotating. The whole assembly was maintained in thermostat at 25.0 °C. 50.0 cm³ of solution A and 50.0 cm³ of solution B was thermostated at 25° c for half an hour. Then they were quickly poured into the beaker in which SCE and RPE was already introduced. The stop-watch was simultaneously started. The initial concentration of o-acetotoluidide and bromine were each 1.0×10^{-4} M in the reaction system. The change in galvanometer deflection was noted at intervals of 10 seconds for several minutes.

From calibration curve and galvanometer deflection concentration of bromine unreacted could be estimated.

From this the specific reaction rate, k_2° in absence of added bromide ions was determined. Similar determinations were made in presence of added bromide ions. Further the effect of H⁺ ions, base effect and salt effect have also been investigated.

RESULTS AND DISCUSSION

The results presented in Fig. 1 shows the remarkable effect of bromide ion in enhancing the specific reaction rate of the reaction by many fold. A linear plot of $k_2^{Br^-}/k_2^\circ$ versus $[Br^-]/[Br_2]$ and energy of activation for the bromination of o-acetotoluidide in presence of 100 fold relative concentration of bromide ions (Table 1 and 2, Fig. 1) strongly suggest that bromide ion has a catalytic effect on bromination of o-acetotoluidide in aqueous solution.

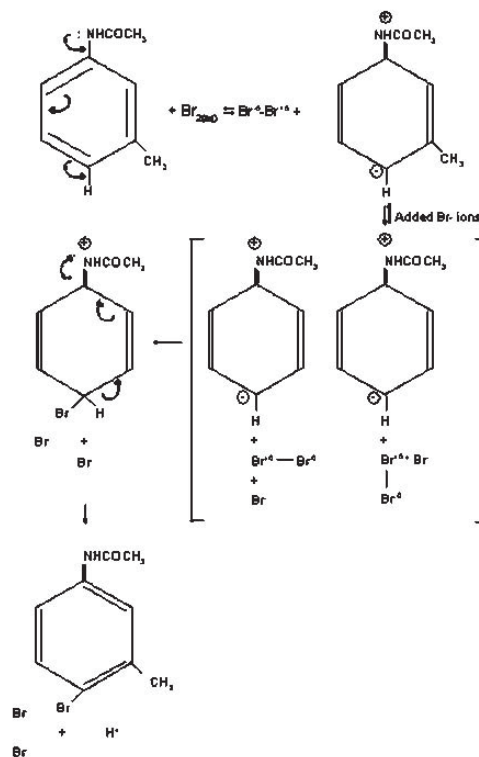
Bromine in aqueous solution hydrolysed according to the equation,



The added H⁺ ions increases the specific reaction rate from $1.78 \text{ M}^{-1}\text{S}^{-1}$ to $8.60 \text{ M}^{-1}\text{S}^{-1}$, while added bromide ions increases it to $54.7 \text{ M}^{-1}\text{S}^{-1}$ which is much more (Table 1). It indicates the shifting of above equilibrium and catalytic role played by the bromide ions

It might possible that bromide ion serve as a base. Such possibility is unlikely since the bromide ion in aqueous solution is known to be a weak base. If the reaction is at all base catalysed the added acetate and bicarbonate ions should have increased the specific reaction rate. Both these expectations are not true (Table 3) Hence the role of bromide ions as a base is highly improbable.

A hundred fold relative concentration of potassium nitrate in place of potassium bromide does not at all increase the specific reaction rate. This discard the possibility of bromide ion affecting the specific reaction rate by salt effect.



Scheme 1:

All above observation leads to the conclusion that a different mechanism operates for the bromination of o-acetotoluidide by bromine in aqueous solution in presence of the added bromide ions. The most probable mechanism for the reaction is as under.

Table 1: Kinetics of bromination of o-acetotoluidide : effect of added bromide ions

Concentration of o-acetotoluidide solution	:	1.0x 10 ⁻⁴ M
Concentration of bromide solution	:	1.0x 10 ⁻⁴ M
Concentration of potassium nitrate	:	1.0x 10 ⁻² M
Temperature	:	25.0°C
Specific reaction rate without adding bromide ions, K ₂ ^o =1.78 M ⁻¹ s ⁻¹		

[Bromide ion]/10 ⁻³ M	Relative concentration of added bromide ions	Specific reaction rate, K ₂ ^{Br} / M ⁻¹ s ⁻¹	K ₂ ^{Br} / K ₂ ^o
1.0	10	6.25	3.51
2.0	20	9.28	5.21
3.0	30	13.7	7.70
4.0	40	18.7	10.5
5.0	50	21.8	12.2
6.0	60	24.1	13.5
7.0	70	27.0	15.6
8.0	80	35.4	19.9
9.0	90	42.5	23.9
10.0	100	54.7	30.7

Table 2: Kinetics of bromination of o-acetotoluidide : effect of temperature, in presence of hundred fold potassium bromide

Concentration of o-acetotoluidide solution	:	1.0x 10 ⁻⁴ M
Concentration of bromide solution	:	1.0x 10 ⁻⁴ M
Concentration of potassium nitrate solution	:	1.0x 10 ⁻² M

Temp./ °C	Temp. T/K	1/T/ 10 ⁻³ K ⁻¹	Specific reaction rate, K ₂ ^{Br} / M ⁻¹ s ⁻¹	log K ₂
10	283.0	3.534	32.6	1.513
15	288.0	3.472	39.3	1.594
20	293.0	3.413	46.3	1.665
25	298.0	3.356	54.7	1.738
30	303.0	3.300	64.4	1.809

$$\text{Energy of activation} = \frac{-2.303 \times 8.314 \times (1350)}{1000} = 25.8 \text{ Jmole}^{-1}$$

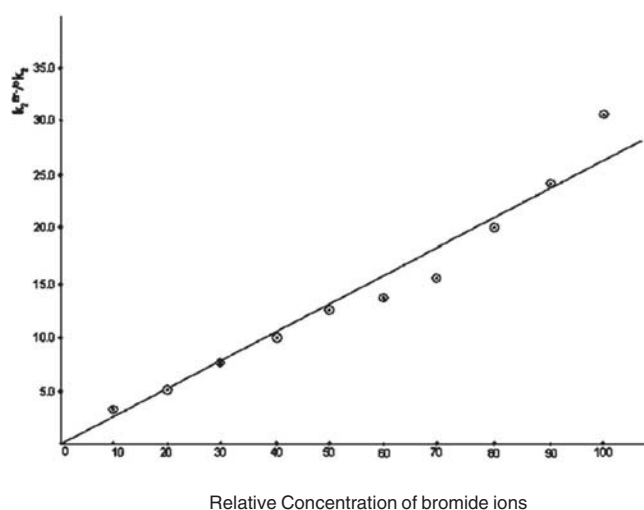
$$\text{Entropy of activation} = -133.4 \text{ JK}^{-1} \text{ mole}^{-1}$$

$$\text{Frequency Factor} = 1.81 \times 10^6 \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$$

Table 3: Kinetics of bromination of o-acetotoluidide : effect of added species

Concentration of o-acetotoluidide solution	:	1.0x 10 ⁻⁴ M
Concentration of bromide solution	:	1.0x 10 ⁻⁴ M
Concentration of potassium nitrate solution	:	1.0x 10 ⁻² M
Temperature	:	25.0°C

Concentration of M species added, 1.0x10 ⁻²	Absence of added species	NO ₃ ⁻	HCO ₃ ⁻	CH ₃ COO ⁻	H ⁺	Br ⁻
Specific reaction rate, K ₂ / M ⁻¹ s ⁻¹	1.78	1.74	1.82	1.92	8.60	54.7

**Fig. 1: Catalytic effect of bromide ions on the kinetics of bromination of o-acetotoluidide**

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