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REVIEW

Effect of bromide ion on the kinetics of bromination of *o*-hydroxy benzoic acid by bromine in aqueous solution

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Abstract The kinetics of the bromination of *o*-hydroxy benzoic acid has been studied by rotating platinum electrode (RPE) technique. The bromide ion has been found to remarkably enhance the specific reaction rate. This is associated with a fall in energy of activation. The other added ions like nitrate, acetate and bicarbonate have shown that the base catalysis or salt effect is improbable. The mechanism suggested to explain the catalytic effect of bromide ions.

Contents

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1. Introduction

Introduction of bromine into organic molecule is an important and fundamental reaction in organic chemistry, owing to considerable commercial importance of such compounds. They can be used as potential antitumour, antibacterial, antifungal, antineoplastic, antiviral and antioxidising agents and also industrial intermediates in the manufacture of pharmaceuticals, agrochemicals and other special products, for instance flame retardants (Kirk-Othmar, 1997; Butler and Walker, 1993; Kinnic and Bonnic, 1999; Gribble, 1998a,b).

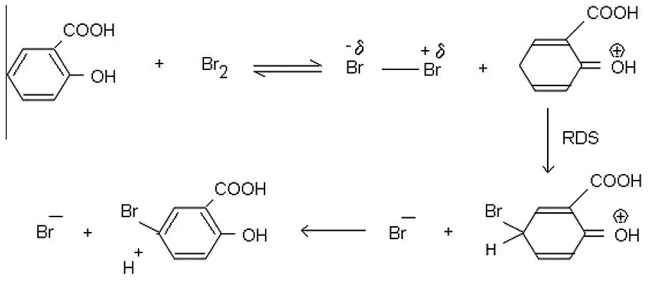
They also play a key role in the preparation of organometallic reagents (Cannon and Krow, 1996; Davies, 1982) and a vital role in the transition metal mediated coupling reaction (Beletskaya and Chepraker, 2000; Maijere and Mayor, 1994; Cabri and Candiani, 1995).

The accepted mechanisms for the bromination of *o*-hydroxy benzoic acid by molecular bromine involve polarisation of the Br–Br bond followed by electrophilic attack by the positive end of the dipole (Scheme 1). The substitution of bromine takes place at ortho and meta positions (De la Mare and Ridd, 1959) or formation of dibromo derivative (Allen, 1914), and other reactions (Fresenius, 1900) and hence are of less importance. The mechanism hardly suggested any possibility of influence of bromide ion on the reaction rate. We have, however, investigated that the bromide ion remarkably enhances the rate of bromination of *o*-hydroxy benzoic acid.

The reaction under study is too rapid to be studied by conventional technique and hence has been studied by the voltametric principle using rotating platinum electrode (RPE) Kolthoff and Lingane, 1952. Bromine gives diffusion current proportional to its concentration at RPE, whereas neither the *o*-hydroxy benzoic acid nor the product yield any diffusion current. Hence the course of reaction can be followed by measuring diffusion current at intervals of time. The technique is quite accurate and reproducible (Rao and Mali, 1976; Rao et al., 1978).

2. Experimental

Analytical grade chemicals were used to prepare stock solution. In each experiment, the required volume of stock solutions was diluted to obtain the following solution:



Scheme 1

Solution A: 2.0×10^{-4} M bromine in 1.0×10^{-2} M potassium nitrate.
Solution B: 2.0×10^{-4} M *o*-hydroxy benzoic acid in 1.0×10^{-2} M potassium nitrate.
Solution C: 1.0×10^{-2} M potassium nitrate.

All the solutions were kept in stoppered flask in a thermostat maintained at 25.0 °C.

2.1. Calibration curve for bromine

The RPE and Saturated Calomel Electrode (SCE) were introduced into several bromine solution of concentration 0.2×10^{-4} M to 1.0×10^{-4} M, each in 1.0×10^{-2} M potassium nitrate. The diffusion current was measured and plotted against concentration of bromine.

2.2. Kinetic measurements

50.0 cm^3 each of solution A and B, previously thermostated at 25.0 °C were quickly poured into a beaker and stop-watch was simultaneously started. The resulting reactant concentration was each 1.0×10^{-4} M and ionic strength was 1.0×10^{-2} M and the diffusion current was noted at various intervals of time during the course of reaction. The reciprocal of concentration of unreacted bromine obtained from calibration curve was plotted versus time. A straight line was obtained whose slope was the specific reaction rate, k_2. The specific reaction rate determined by this technique was satisfactorily reproducible within ±2.0%.

2.3. Effect of bromide ions on the kinetics

The study was repeated several times using the same volume and concentration of the solution but increasing only the concentration of potassium bromide, ten fold at a time relative to that of bromine until the bromide ion concentration was hundred fold i.e., $[Br^-]/[Br_2]$ was varied from 10 to 100 (Table 1 and Figs. 1 and 2) the concentration of the bromide ions produced in the reaction was negligible as compared to added bromide ions.

2.4. The energy of activation

The activation energies in the absence of added potassium, and in the presence of hundred fold potassium bromide were determined by measuring the specific reaction rate at several temperatures (Tables 2 and 3).

2.5. Effect of H^+ aq

The specific reaction rate was also determined in the presence of hundred fold of perchloric acid to determine the effect of suppression of hydrolysis of bromine (Table 4).

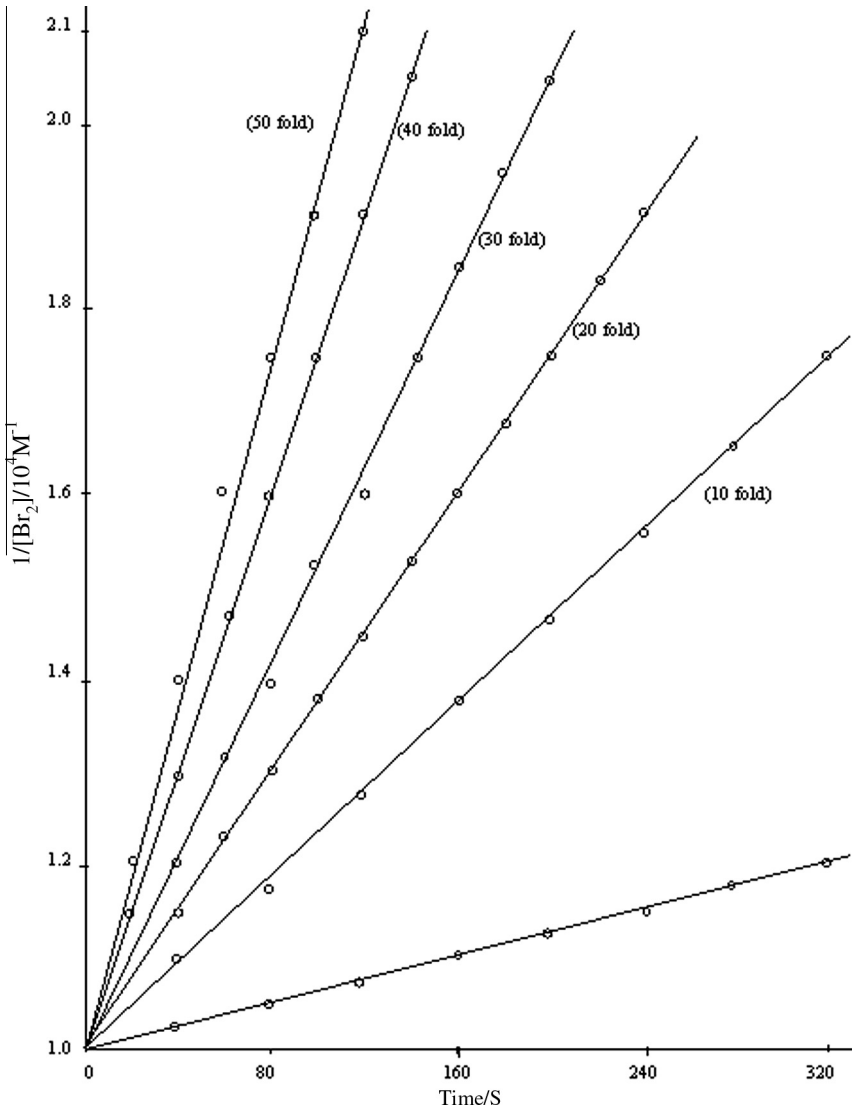


Figure 1 Kinetics of bromination of *o*-hydroxy benzoic acid: effect added bromide ions.

2.6. Effect of bases

To investigate the base catalysis, the specific reaction rate was measured in the presence of bases whose concentrations were hundred fold that of bromine. The bases used were the acetate ions and bicarbonate ion (Table 4).

2.7. Salt effect

The specific reaction rate was determined in the presence of hundred fold of potassium nitrate, besides that already present as the supporting electrolyte, to investigate the possibility of salt effect (Table 4).

3. Results and discussion

The bromination of *o*-hydroxy benzoic acid is second order kinetics. The analysis of product by standard technique (Weissberger, 1956) shows the mono bromo derivative i.e., 5-bromo derivative. The other derivative is in traces.

The results presented in Figs. 1 and 2 show the remarkable effect of the bromide ion in enhancing the specific reaction rate of the reaction by many fold. A plot of $k_2^{Br^-}/k_2^\circ$ versus $[Br^-]/[Br_2]$ is linear in this case Fig. 3 $k_2^{Br^-}$ is the second order specific reaction rate in the presence of bromide ions and k_2° is the second order specific reaction rate in the absence of bromide ion or second order specific reaction rate of bromination of *o*-hydroxy benzoic acid by bromine in aqueous solutions. The energy of activation for the bromination of *o*-hydroxy benzoic acid in the presence of hundred fold relative concentration of bromide ion is 15.8 kJ mole^{-1} which is significantly lower than in the absence of added bromide ion, i.e., 24.4 kJ mole^{-1} (Tables 3 and 2). This fact, together with the observation that $k_2^{Br^-}/k_2^\circ$ varies linearly with relative concentration of the bromide ion, strongly suggests that the bromide ion has a catalytic effect on the bromination reaction.

Bromine in aqueous solution is extensively hydrolysed according to the equation.

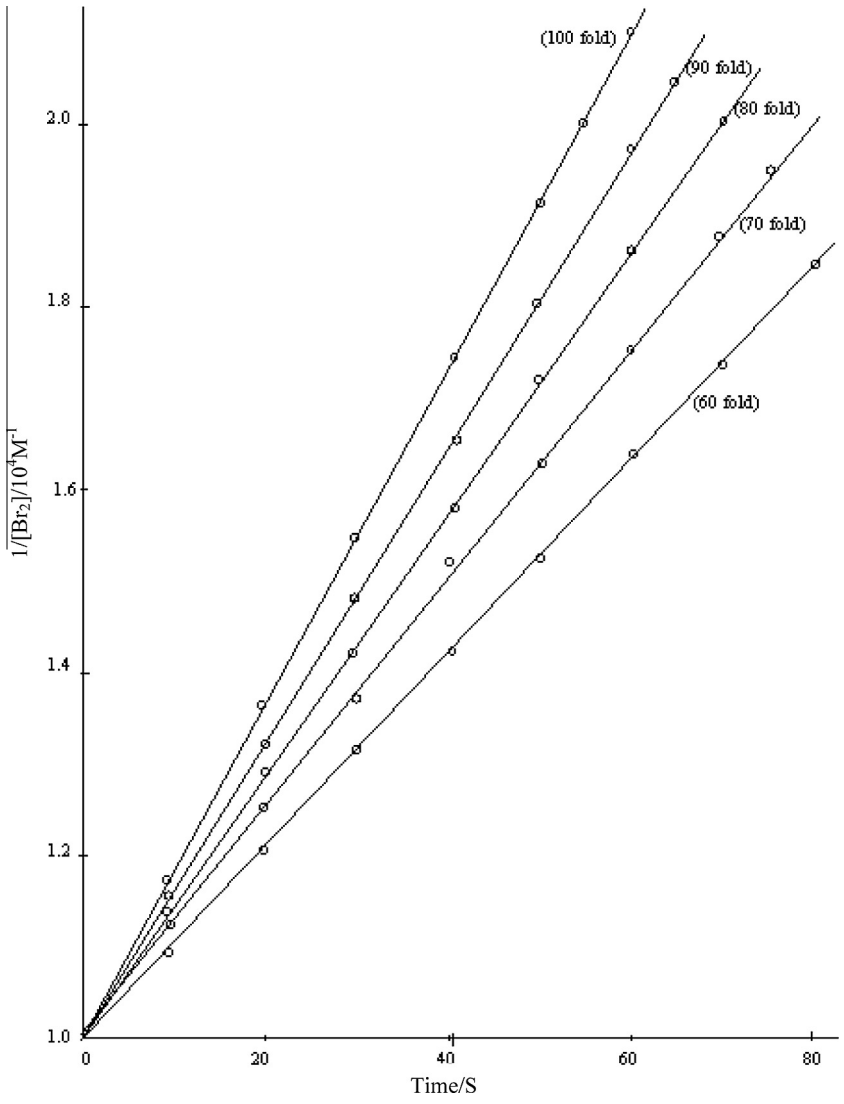


Figure 2 Kinetics of bromination of *o*-hydroxy benzoic acid: effect of added bromide ions.

$$Br_2 + H_2O \leftrightarrows HBrO + H^+ + Br^- \quad (1)$$

Although, HBrO is a brominating agent, it is known that Br_2 reacts very much faster than HBrO (Eigen and Kustin, 1962; Wilson and Soper, 1949). Any added Br^- or H^+ shift the equilibrium to increase the concentration of bromine and hence the rate constant. Therefore the addition of hundred fold concentration of Br^- or H^+ relative to the bromine should shift the equilibrium to the same extent and hence increase the rate of reaction to the same extent. The added H^+ ions increase the specific reaction rate at 25.0 °C from 6.25 to 30.3 $M^{-1}\,S^{-1}$ while the Br^- increases it much more i.e., up to 183 $M^{-1}\,S^{-1}$ (Table 4). Evidently the bromide ion, in addition to shifting the equilibrium, also plays a catalytic role.

From the remarkable catalytic effect of bromide ion, it might appear that the bromide ion acts as a base. Such possibility is indeed unlikely since the bromide ion in aqueous solution is known to be a very weak base. If the reaction is at all base catalysed a stronger base like the bicarbonate and acetate ions should have enhanced the specific reaction rate significantly. Both these expectations are belied in reality (Table 4 and Fig. 4). Hence the possibility of bromide ion acting as a

Table 1 Kinetics of bromination of *o*-hydroxy benzoic acid: effect of added bromide ions.

Bromide ions 10^{-3} M	Relative concentration of added bromide ions	Specific reaction rate, $K_2^{Br-}/M^{-1}S^{-1}$	k_2^{Br-}/k_2°
1.0	10	23.4	3.7
2.0	20	37.5	6.0
3.0	30	52.5	8.4
4.0	40	75.0	12.0
5.0	50	91.7	14.7
6.0	60	106	17.0
7.0	70	123	19.7
8.0	80	143	22.9
9.0	90	162	25.9
10.0	100	183	29.3

Concentration of *o*-hydroxy benzoic acid solution: 1.0×10^{-4} M.
Concentration of bromine solution: 1.0×10^{-4} M.
Concentration of potassium nitrate: 1.0×10^{-2} M.
Temperature: 25.0 °C.
Specific reaction rate without adding bromide ions, k_2°: 6.25 $M^{-1}\,S^{-1}$.

Table 2 Kinetics of bromination of *o*-hydroxy benzoic acid: effect of temperature, in the absence of added bromide ions.

Temp/°C	Temp, T/K	$\frac{1}{T}/10^{-3}K^{-1}$	Specific reaction rate, $k_2^{Br^-}/M^{-1}S^{-1}$	$\log k_2$
20	293.0	3.413	5.75	0.760
25	298.0	3.356	6.25	0.796
30	303.0	3.300	7.35	0.866
35	308.0	3.247	8.65	0.937
40	313.0	3.195	10.0	1.000

Energy of activation = 24.4 K J mol^{-1}.
Entropy of activation = −156.1 J K^{-1} mol^{-1}.
Frequency factor = 1.18×10^5 cm^3 mol^{-1} s^{-1}.
Concentration of *o*-hydroxy benzoic acid solution: 1.0×10^{-4} M.
Concentration of bromine solution: 1.0×10^{-4} M.
Concentration of potassium nitrate: 1.0×10^{-2} M.

Table 3 Kinetics of bromination of *o*-hydroxy benzoic acid: effect of temperature, in the presence of a hundred fold potassium bromide.

Temp/°C	Temp, T/K	$\frac{1}{T}/10^{-3}K^{-1}$	Specific reaction rate, $k_2^{Br^-}/M^{-1}S^{-1}$	$\log k_2$
10.0	283.0	3.534	111	2.045
15.0	288.0	3.472	133	2.124
20.0	293.0	3.413	156	2.193
25.0	298.0	3.356	183	2.262
30.0	303.0	3.300	215	2.332

Energy of activation = 15.8 K J mol^{-1}.
Entropy of activation = −156.8 J K^{-1} mol^{-1}.
Frequency factor = 1.08×10^5 cm^3 mol^{-1} s^{-1}.
Concentration of *o*-hydroxy benzoic acid solution : 1.0×10^{-4} M.
Concentration of bromine solution: 1.0×10^{-4} M.
Concentration of potassium nitrate solution: 1.0×10^{-2} M.

base is highly improbable. These observations also confirmed the well established idea that the last step in the general mechanism (Scheme 1) which involves deprotonation, can not be the rate determining one, as added bases would then definitely enhance the specific reaction rate of the reaction.

The argument that the bromide ion does bring about base catalysis but the effect of the base catalysis is offset by the base hydrolysing the bromine, can be shown to be invalid. Eq. (1) shows the hydrolysis equilibrium of bromine, the constant for which is 4.56×10^3 M^{-2} at 20.0 °C, at 1.0×10^{-4} M, more than 99% of bromine is already hydrolysed and the addition of base does not significantly enhance the extent of hydrolysis. In fact, the bromination occurs through molecular bromine and since the reverse reaction in Eq. (1) is rapid, with the rate constant of 1.6×10^{10} M^{-2} S^{-1}, molecular bromine is regenerated as fast as it is consumed.

The formation of tribromide ion Br_3^- and its electrophilic attack on the *o*-hydroxy benzoic acid does not offer a plausible explanation for the observed catalytic effect of the bromide ion. For one, Br_3^-, a negatively charged species, would be a poorer electrophile than Br_2, secondly the equilibrium constant, for the formation of Br_3^- in,

$$Br_2 + Br^- \leftrightarrows Br_3^- \quad (2)$$

is only 0.20 at 25.0 °C and hence the concentration of Br_3^- would be very low especially at low concentration of Br_2 used in the present study. Further, since the equilibrium constant for Eq. (2) is given by,

$$K = \frac{[Br_3^-]}{[Br_2][Br^-]} \quad (3)$$

The concentration of Br_3^- would be proportional to $(K^{-1}[Br^-]^{-1} + 1)^{-1}$ for the given initial concentration of Br_2 and hence the concentration of Br_3^- would tend to a limiting value at higher concentration of bromide ion. Therefore if Br_3^- is the active species, the specific reaction rate should have reached a limiting value at higher concentration of the bromide ion. The observed fact contrary to this expectation shows that Br_3^- can not be the active brominating agent.

The possibility of the bromide ion forming a complex with *o*-hydroxy benzoic acid can also be eliminated because, similar to the case with the Br_3^-, the concentration of the complex would also reach a limiting value at higher concentration of bromide ion and any further addition of it should not increase concentration of the complex and the specific reaction rate.

A hundred fold relative concentration of potassium nitrate does not increase the specific reaction rate. This reasonably discards the possibility of the bromide ion affecting the specific rate due to salt effect.

All the above observations come to conclusion that a different mechanism operates for the bromination of *o*-hydroxy benzoic acid by bromine in aqueous solution in the presence of added bromide ions. The reaction is second order in the presence and absence of added bromide ion. Therefore the bromine and *o*-hydroxy benzoic acid are involved in the rate determining step. The fact that bromide ion catalyses the bromination by bromine, suggests that in the rate determining step the bromide ion is also involved. We therefore suggest the mechanism (Scheme 2) which meets all the observed facts.

The *o*-hydroxy benzoic acid, with its electron rich site, polarises the bromine molecule. In the presence of the very high number of bromide ion as compared to bromine molecule reacting with the *o*-hydroxy benzoic acid, there will be many bromide ions in its near vicinity. In this environment it may be possible that $Br^{+\delta}$–$Br^{-\delta}$ can have a longer mean life by a rearrangement

Table 4 Kinetics of bromination of *o*-hydroxy benzoic acid: effect of added species.

Concentration of species added 1.0×10^{-2} M	Absence of added species	NO_3^-	HCO_3^-	CH_3COO^-	H^+	Br^-
Specific reaction rate, k_2/M^{-1} S^{-1}	6.25	6.20	6.30	6.40	30.3	183

Concentration of *o*-hydroxy benzoic acid solution: 1.0×10^{-4} M.
Concentration of bromine solution: 1.0×10^{-4} M.
Concentration of potassium nitrate: 1.0×10^{-2} M.
Temperature: 25.0 °C.

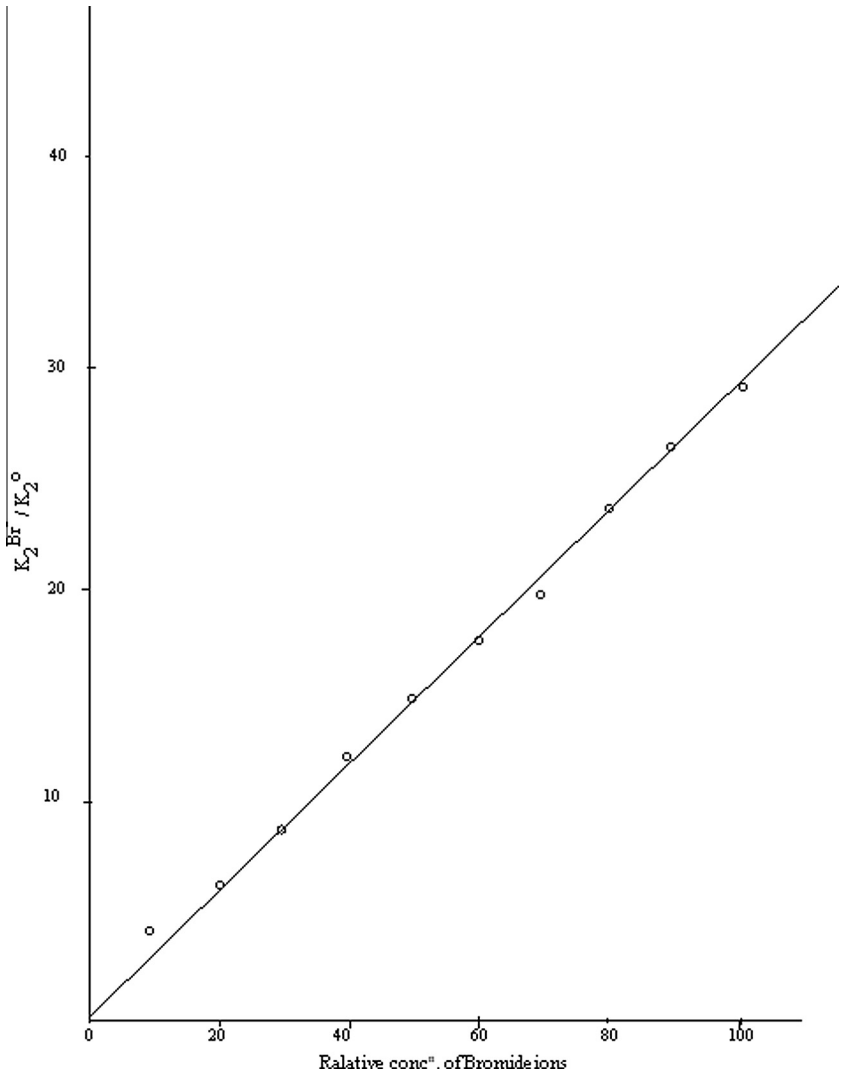


Figure 3 Catalytic effect of the bromide ions on the kinetics of bromination of *o*-hydroxy benzoic acid.

of electrons with a bromide ion in the vicinity (Scheme 2). This enhances the electrophilic attack by the $Br^{+\delta}$–$Br^{-\delta}$ on the *o*-hydroxy benzoic acid in the rate determining step involving the breaking of the $Br^{+\delta}$–$Br^{-\delta}$ bond and formation of the positive intermediate. In the absence of added bromide ion (Scheme 1), there is no such facility for the $Br^{+\delta}$–$Br^{-\delta}$. The rapid deprotonation of intermediate yields a bromo derivative.

Since the rate determining step involves the bromide ion, there should be linear dependence of the specific reaction rate on the concentration of the bromide ion. The rate of the bromide ion catalysed reaction should be given by,

$$\text{Rate} = K_3[o\text{-hydroxybenzoic acid}][Br_2][Br^-]$$

Since the concentration of bromide regenerated and remains constant and may be incorporated with K_3 to give new constant K_2^1:

$$\text{Rate} = K_2^1[o\text{-hydroxybenzoic acid}][Br_2]$$

This clearly shows the second order kinetics even in the presence of the bromide ions. The observed rate of reaction is the sum of rate of uncatalysed reaction and catalysed reaction.

Therefore,

$$k_2^{Br-}[o\text{-hydroxybenzoic}][Br_2] = k_2^{\circ}[o\text{-hydroxybenzoic acid}][Br_2] + k_3[o\text{-hydroxybenzoic acid}] \times [Br_2][Br^-]$$

$$\text{i.e., } k_2^{Br-} = k_2^{\circ} + k_3[Br^-]$$

$k_2^{Br-}/k_2^{\circ} = 1 + k_3[Br^-]/k_2^{\circ}$ therefore the plot of k_2^{Br-}/k_2° against $[Br^-]$ should be a straight line. If this is true then the plot of k_2^{Br-}/k_2° against $[Br^-]/[Br_2]$ should also be a straight line. Both these expectations were found to be true in the reaction under study (Fig. 3).

The role played by bromide ion in this mechanism is quite different from that of a base and therefore one can appropriate that this reaction is not base catalysed. A unique role is played by bromide ion in this mechanism. It is highly significant that where as energy of activation for bromide ion catalysed reaction is distinctly lower than that of the uncatalysed reaction (Scheme 1). The entropy of activation for the two reactions is very nearly same (Tables 2 and 3) and it clearly indicates the formation of same intermediate in both the reactions.

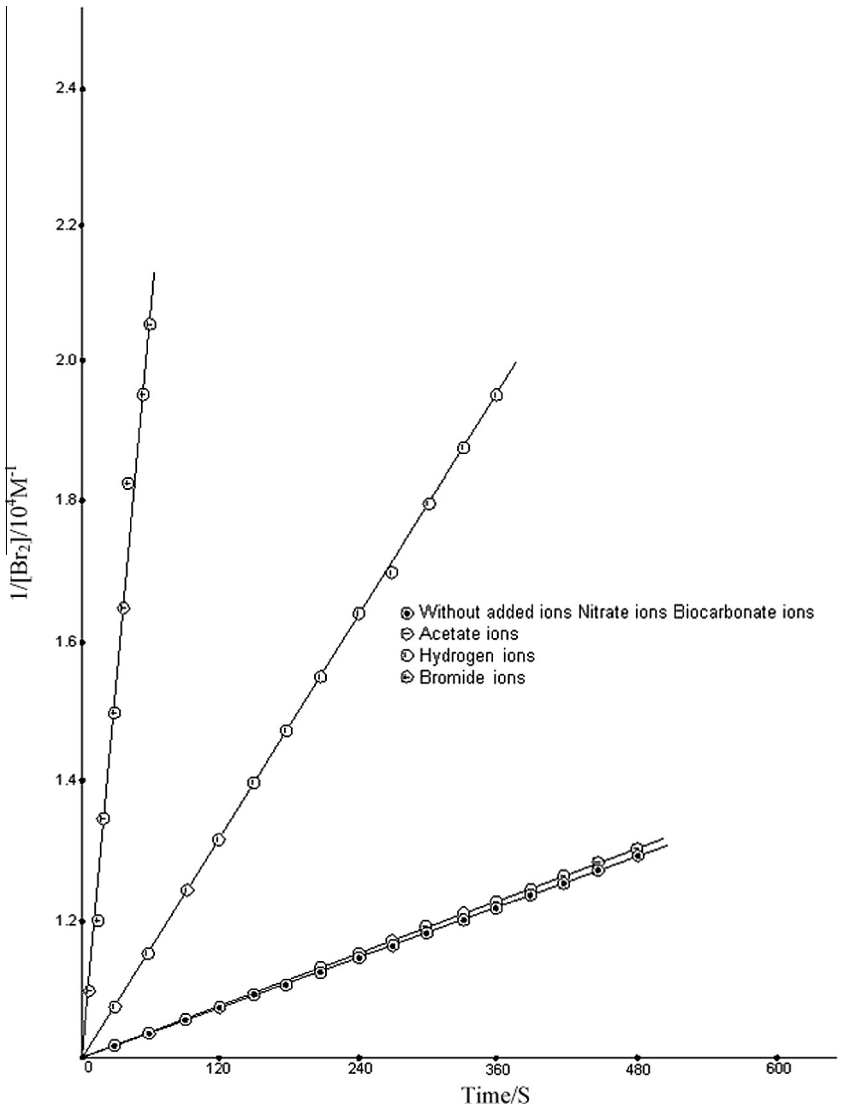
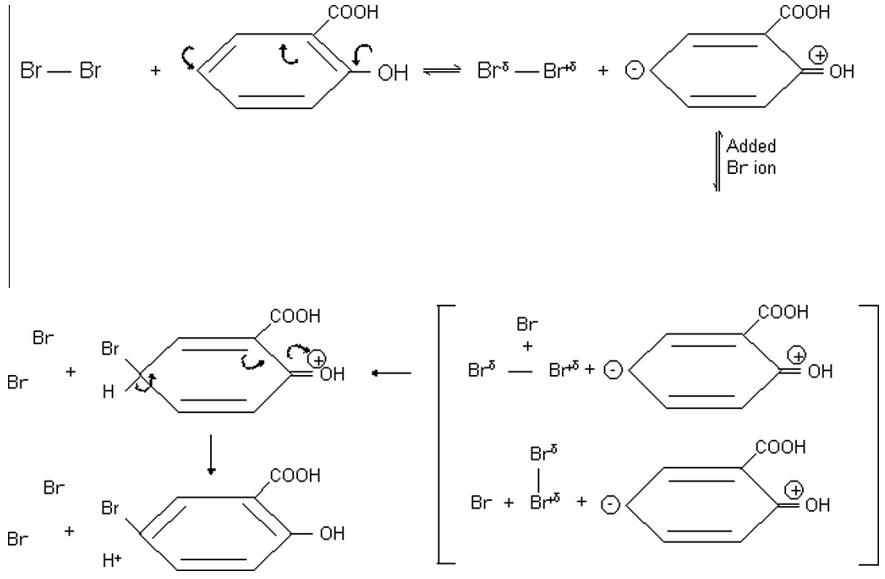


Figure 4 Kinetics of the bromination of *o*-hydroxybenzoic acid: in the presence of hundred fold added ions.



Scheme 2

The studies carried out to probe into effect of added bromide ion hardly indicate any mechanism, the proposed one explains the best catalytic effect and is consistent with all the observed features.

4. Conclusion

On careful consideration of the observations, it is concluded that different mechanism operates for the bromination of *o*-hydroxy benzoic acid by bromine in aqueous solution in the presence of bromide ions. The reaction is of second order with respect to bromine and *o*-hydroxy benzoic acid. This is observed irrespective of the relative concentration of the added bromide ion. Therefore bromine and *o*-hydroxy benzoic acid are involved in the rate determining step. The fact bromide ion catalyses the bromination by bromine, suggests that in the rate determining step the bromide ion is also involved. The suggested mechanism satisfactorily explains all the observed features of the reaction.

References

Allen, A.H., 1914. Commercial Organic Analysis, vol. II, part-III, Blakistan, p. 75.
Beletskaya, I.P., Chepraker, A.V., 2000. Chem. Rev. 100, 3009.
Butler, A., Walker, J.V., 1993. Chem. Rev. 93, 1937.
Cabri, W., Candiani, I., 1995. Acc. Chem. Res. 28, 2.
Cannon, K.C., Krow, G.R., 1996. Handbook of Grignard Reagents. Dekker, New York.
Davies, S.G., 1982. 'Organotransition Metal Chemistry', Application to Organic Synthesis. Pergamon Press, Oxford.
De la Mare, P.B.D., Ridd, J.H., 1959. Aromatic Substitution. Butterworths, London, 133.
Eigen, M., Kustin, K., 1962. J. Am. Chem. Soc. 84, 1355.
Fresenius, W., 1900. Analyst 19.
Gribble, G.W., 1998a. Acc. Chem. Rev. 31, 141.
Gribble, G.W., 1998b. Chem. Soc. Rev. 28, 335.
Mc Kinnic, Bonnic, G., 1999. US Patent 6,002,050 to Albemarle Corporation.
Kirk-Othmar, 1997, fourth ed.. In: Encyclopedia of Chemical Technology, vol. 10 Wiley, New York.
Kolthoff, I.M., Lingane, J.J., 1952, second ed.. In: Polarography, vol. 1 Interscience, New York.
Maijere, A., Mayor, F.E., 1994. Angew Chem., Int. Ed. 33, 2379.
Rao, T.S., Mali, S.I., Naturforsch, Z., 1976. 3lA, 1735.
Rao, T.S., Mali, S.I., Dangat, V.T., 1978. Tetrahedron 34, 205.
Weissberger, A., 1956. In: Techniques of Organic Chemistry, vol. IX. Interscience, New York.
Wilson, W.J., Soper, F.G., 1949. J. Am. Chem. Soc., 3376.