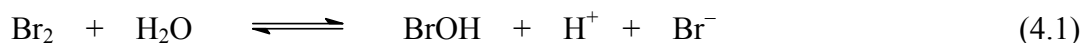


Chapter 4 *Generation and Characterization of Hypobromous Acid in Aqueous Acidic Solutions*

4.1. Introduction

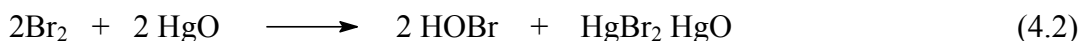
Many non-metal redox reactions take part *via* atom-transfer or ion transfer mechanism, Hypobromous acid is one among several reagents for conducting such reactions. Hypobromous is a weak and unstable acid, and exists only in dilute solutions of concentrations lower than 0.6-0.7 moles per liter.¹ Its aqueous solution appears as pale yellow in color with a jasmine odor. It is known to be decomposed to oxygen and hydrobromic acid in light and/or in the presence of copper or silver salts.¹ Nevertheless, it is a good oxidant as well as an excellent brominating/atom-transferring agent.² Brominations of maleic acid, benzene, benzoic acid and phenols have been known with hypobromous acid.³ Hypobromous acid adds across the olefinic bonds and produce corresponding bromohydrins like 2-bromo-1-phenyl ethanol from styrene, 2-bromo cyclohexanol from cyclohexene,⁴ α -bromo- β -hydroxy cinnamic acid from cinnamic acid³ etc. It is used in trace quantities for bio-fouling control in industrial water systems.⁵ A considerable attention has been made earlier towards the generation and decomposition of hypobromous acid.

4.1.1. Generation of hypobromous acid. Bromine when dissolves (to the extent of maximum 33.6 g/litre at 25°C) in water, the following equilibrium (Eq 4.1) is expected to exist in the solution, acid,



which contains about 0.1% hypobromous (HOBr) acid. Bray⁶ has studied this equilibrium through electrical conductivity measurements on bromine water and

determined it as 5.2×10^{-9} at 25 °C. Jones and Baeckstrom,⁷ and Liebhafsky,⁸ have also studied the equilibrium (Eq 4.1) and obtained the equilibrium constant (5.8×10^{-9}) nearer to it, which microscopically indicate the hopeful formation of hypobromous acid in the absence of bromide ions. Balard⁹ has first time, reported the preparation of hypobromous acid by shaking yellow mercuric oxide with bromine water (Eq 4.2).



Bijlmann *et al*,¹⁰ on the other hand, has used silver oxide as a better method for the preparation of hypobromous acid (Eq 4.3).



The salts of mercury and silver have been used latter,^{11,12} instead of their oxides wherein a mineral acid corresponding to the salt is produced along with hypobromous acid. Kretzschmar¹³ has used silver nitrate for the preparation of hypobromous acid (Eq 4.4) by adding excess bromine to a solution of silver nitrate and distilling at 25°C under 12 mm mercuric pressure. A pale yellow liquid with jasmine odor, containing about 0.1 to 0.25% hypobromous acid was reported to be formed after debromination of trace amounts of bromine present in it by by purging a current of air through the solution. Silver phosphate,¹⁴ silver sulphate¹⁵ and silver acetate^{16,17} have reportedly been used for the production of hypobromous acid from aqueous bromine solution.



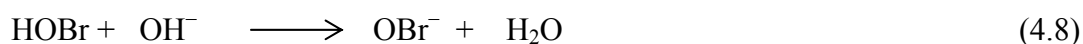
The stability of hypobromous acid depends to some extent on the kind of silver salts used, e. g. Hypobromous acid that produced by using silver acetate decomposes more rapidly than that using silver nitrate.¹⁸ Its acid dissociation constant was determined to be 2×10^{-9} .^{19,20} It is an excellant brominating agent particularly in the presence of silver or lead salts.²¹ Besides the above methods, the hypobromous acid has been observed to be formed during the ozone treatment of bromide containing natural drinking water with

ozone and chlorine.^{22,23} Ozone or chlorine oxidizes bromide to hypobromous acid²⁴⁻²⁷ under various water treatment conditions of natural water containing bromides. Hypobromous acid further reacts with ozone and produces bromate through many intermediate species generation.²³ In France and Spain,²⁸ the sea water is treated with ozone for shellfish depuration and is being considered for use as an alternative to chlorine at coastal power plants for cooling system and biofouling control in the U.S.^{29,30} Hypobromous acid can be generated by using N-bromoamides or imides. N-bromosuccinimide³¹ (NBS) in water is well known and being used since many years to prepare bromohydrins through *in-situ* generation hypobromous acid. In a similar way LeTourneau *et al*³² used N-bromoacetamide-perchloric acid for the preparation of bromohydrins from indazole derivatives.

Schulek, Burger and Pungler³³ have prepared the aqueous BrCl by Eq 4.5. They presumed that Br₂ is first formed in the reaction and oxidized by BrO₃⁻ in subsequent reaction yielding BrCl. Wang et al.³⁴ have suggested the hydrolysis of BrCl to give BrOH (Eq 4.6). They have also investigated and estimated the hydrolysis constant of BrCl as 1.8 x 10⁻⁵ M².

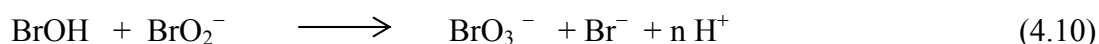
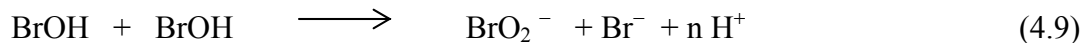


The oxidation of bromide by hypochlorite ion to generate hypobromous acid was studied by Farkas *et al*⁶⁰ in the pH range 10.8-13.2 under second-order conditions. They reported the rate determining step to be the reaction between HOCl and Br⁻ with a rate constant of 2.95 x 10³ M⁻¹ S⁻¹ at 25 °C. They proposed the following mechanism (Eq 4.7 and 4.8) which implies nucleophilic attack by Br⁻ at oxygen, which is equivalent to an OH⁺ transfer between Br⁻ and Cl⁻.



4.1.2. Disproportionation of Hypobromous acid. Chapin,³⁶ Prutton and Maron³⁷ and Liebhaufsky and Makower³⁸ have studied earlier the disproportionation of BrOH in neutral

or weakly alkaline solution and reported a third or mixed-order process for it. Engel *et al.*,³⁹ Lewin and Avrahami,⁴⁰ Shilov⁴¹ have also investigated the decomposition kinetics of hypobromous acid and reported it as a second-order process with the mechanism shown in Eqs 4.9-4.11.



This disagreement could be accounted for varying experimental conditions used in different studies.⁴² The additional complications in these studies may include inadequate titration methods to distinguish BrOH, BrO₂⁻ and BrO₃⁻^{43,44} or use of an inaccurate pK_a values for BrOH.⁷ Metal contamination of reagents may be another source for errors.⁴⁵ The reaction involving BrO₃⁻ in Eq 4.10 is generally regarded as being faster than that of Eq 4.9. The activation energies reported for Eq 4.9 are 58± 3 kJ/mol in 1 M H₂SO₄⁴⁶ and 81.2 kJ/mol⁴⁷⁻⁵⁰ and 95± 2 kJ/mol⁵¹ in basic media. At higher pH, the hypobromous acid dissociates to hypobromite ion with a pK_a of 8.8 at 25 °C and an ionic strength (μ) of 0.5 M.⁵² Eq 4.12 has also been shown as a minor pathway in basic medium, but its contribution is negligible in metal free solutions protected from light.^{42,53}



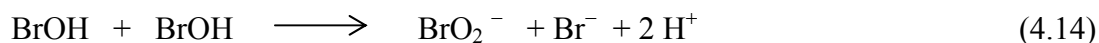
The rate of BrOH disproportionation at high pH is suppressed due to deprotonation of BrOH. Chapin reported that BrOH is least stable at pH 7.3 and most stable at pH 13.4.³⁶ Hamano and Nakamori also showed a similar trend.⁴³ Kulkarni and Nabar⁵⁴ and Gottardi and Bock⁵⁵ monitored BrOH disproportionation at pH 6-10 and observed that the fastest decomposition occurred around pH 7.6. However, without detailed buffer conditions for their work at pH < 7.5, it is not clear whether the trend is due to pH or to decrease buffer assistance. Furthermore, they did not address comproportionation of Br⁻ and BrOH to form Br₂. Only Chapin and Skrabal⁵⁶ mentioned catalysis by buffer. Hypochlorite decomposition is reported to be accelerated by acetate, borate, carbonate, and to a lesser extent by phosphate buffer.³⁶ Fabian *et al.* have observed a small phosphate and carbonate

effect in the decomposition of HOCl.⁵⁷ No buffer dependencies for BrOH decomposition are reported in the literature. Most authors did not attempt a mechanistic explanation of how BrOH is oxidized to BrO₃⁻ and BrO₂⁻.

Engel et al. proposed the general rate expression (Eq 4.13) with $k_1 = 8.3 \times 10^{-4} \text{ M}^{-1}\text{s}^{-1}$ and $k_2 = 0.018 \pm 0.003 \text{ M}^{-1} \text{ s}^{-1}$ at pH 8.84 and 25 °C.³⁹

$$d[\text{BrOH}]/dt = 2k_1[\text{BrOH}]^2 + k_2[\text{BrOH}][\text{BrO}_3^-] \quad (4.13)$$

Beckwith and Margerum⁵⁸ have recently investigated the kinetics of hypobromous acid disproportionation at 25 °C in the pH range 0.2-10.2. They have observed a second order decomposition dependence profile in [BrOH] with a maximum rate at pH 3-8 and significantly low rate at above pH 8 as BrOH converts to BrO⁻. They have proposed a more detailed expressions (Eq 4.14-4.16) reflecting a buffer-assisted second-order pathway for the reaction between two BrOH molecules. They have also given a rate expression (Eq 4.17) to encompass the pH range 0-14 and proposed a detailed mechanism and explained the buffer dependent decomposition of BrOH.



$$d[\text{BrOH}]/dt = n \{ (c/c + [\text{H}^+]) k_{1a} [\text{BrOH}]^2 + k_B [\text{B}][\text{BrOH}]^2 + k_{1b} [\text{BrO}^-]^2 \} \quad (4.17)$$

where $k_{1a} = 2 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$, $k_B [\text{B}] =$ is a general base assisted pathway, $k_{1b} = 6 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}$, n is stoichiometric factor that ranges from 2 to 5, and c is a ratio of rate constants that is equal to 0.03M.

4.1.3. Objectives of the present work. It is proposed to study the kinetics of formation in stoichiometric or less quantities of bromide, bromate and protons in sodium sulfate medium ($\mu = 0.1 \text{ N}$) and disproportionation of hypobromous acid in the presence of an externally added mineral acid by spectrophotometry at different temperatures. The objectives and scope of the present work are described as under.

- To study the effect of concentrations of bromide, bromate and hydrogen ions independently on the rates of formation of hypobromous acid.
- To study the rates of formation of hypobromous acid at different temperatures and ionic strength of the medium.
- To investigate the mechanism of formation of hypobromous acid from bromide and bromate salts in stoichiometric or less quantities of hydrogen ion and suggest accordingly the rate law.
- To evaluate the multi order rate constant and the associated thermodynamic parameters for the formation of hypobromous acid.
- To study the rate of disproportionation of hypobromous acid in presence of various concentrations of strong acid.
- To study the rate of disproportionation of hypobromous acid at different temperatures and ionic strength of the medium.
- To investigate the mechanism of disproportionation of hypobromous acid and suggest accordingly the rate law.
- To evaluate the relevant constants and the associated thermodynamic parameters for the disproportionation of hypobromous acid.

4.2. Experimental Section

4.2.1. Materials. The glassware was soaked with chromic acid, washed with detergent and then rinsed with double distilled water. Analytical grade chemicals such as NaBr, NaBrO₃ and Na₂SO₄ (S. D. Fine chemicals, India) and H₂SO₄ (Ranbaxy Fine Chemicals, India) were purchased and used in these investigations. Doubly distilled water was used to prepare all the solutions. The solutions of 0.2 M NaBr and 0.2 M NaBrO₃ were prepared and used as stocks to prepare all the experimental solutions involved in the formation kinetics of hypobromous acid. In these studies a solution of 0.1 N H₂SO₄ was also prepared and used as a stock solution to adjust its composition in all experimental solutions. The stock solutions of 4 N H₂SO₄ and 4 N Na₂SO₄ were prepared and used wherever necessary in the hypobromous acid disproportionation studies.

Hypobromous acid preparation. For the study of disproportionation kinetics, a stock solution hypobromous acid was prepared by mixing 10 ml of 0.2 M NaBr, 5 ml of 0.2 M

NaBrO₃, 2 ml of 1.035 N H₂SO₄ and 12.5 ml of 1 N Na₂SO₄ solutions and diluting to 250 ml with double distilled water. The solution was allowed to react for 5 days for the complete formation of BrOH at room temperature. The formation of hypobromous acid was monitored by spectrophotometry wherein the maximum absorbance at 260 nm was found to reach maximum after 4-5 days. From the maximum absorbance observed at 260 nm and the concentration of BrOH assumed to be equivalent to the concentration H⁺ added, the molar extinction coefficient (ϵ_{260}) for BrOH was calculated to be 447.62 M⁻¹ cm⁻¹.

4.2.2. Instrumentation. Absorption spectra were recorded on Varion 500 Scan UV- Vis spectrophotometer with a built-in thermo stated (± 0.1 °C) cell compartment coupled to a temperature controlling unit. An Adair Dutt digital pH meter sensitive to 0.01 pH was used to measure pH of all experimental solutions.

4.2.3. Spectrophotometric measurements. Absorption spectra of all the samples under investigation were recorded between 200-600 nm in a 10 mm quartz cuvette at 25 °C. Double distilled water was used in all the cases as the reference unless otherwise mentioned.

4.2.4. Experimental procedures. (a) Kinetics of formation of hypobromous acid. In a typical experimental run, the known quantities of 0.2 M bromide, 0.2 M bromate, 1 N Na₂SO₄ solutions diluted to 10 ml was mixed with the known quantity of 1 N H₂SO₄ diluted to 15 ml water and shaken thoroughly. The absorption spectra of the solution was recorded immediately after mixing for about 60-90 min at regular 2 or min intervals. The absorbance at 260 nm was noted and the concentration of BrOH was calculated using the molar extinction coefficient ($\epsilon_{266} = 447.62 \text{ M}^{-1} \text{ cm}^{-1}$) as determined by our present data.

(b) Kinetics of disproportionation hypobromous acid. In a typical experimental run, the aliquot of BrOH from its stock solutions was diluted to 15 ml in a beaker. Similarly the aliquot of H₂SO₄ with or without that of Na₂SO₄ was diluted to 10 ml in a separate beaker. Both the diluted solutions were precooled to the desired temperature for 5-10 min, mixed and shook thoroughly. The absorption spectra of this reaction mixture was recorded immediately after mixing for 60-90 min at a regular 2 or 5 min interval. The absorbance at 260 nm was recorded in each case and converted them into the

concentration of BrOH using the molar extinction coefficient ($\epsilon_{266} = 447.62 \text{ M}^{-1} \text{ cm}^{-1}$) as determined by our present data.

4.3. Results and Discussion

4.3.1. Spectrophotometric characterization of hypobromous acid. 16 mM NaBr, 8 mM NaBrO₃ and 16.56 mM hydrogen ion were mixed in 0.1 N Na₂SO₄ and recorded the absorption spectra between 200-600 nm at every 5 min interval from the time of mixing. The observed data are shown in Figure 4.1. The spectra showed the gradual development

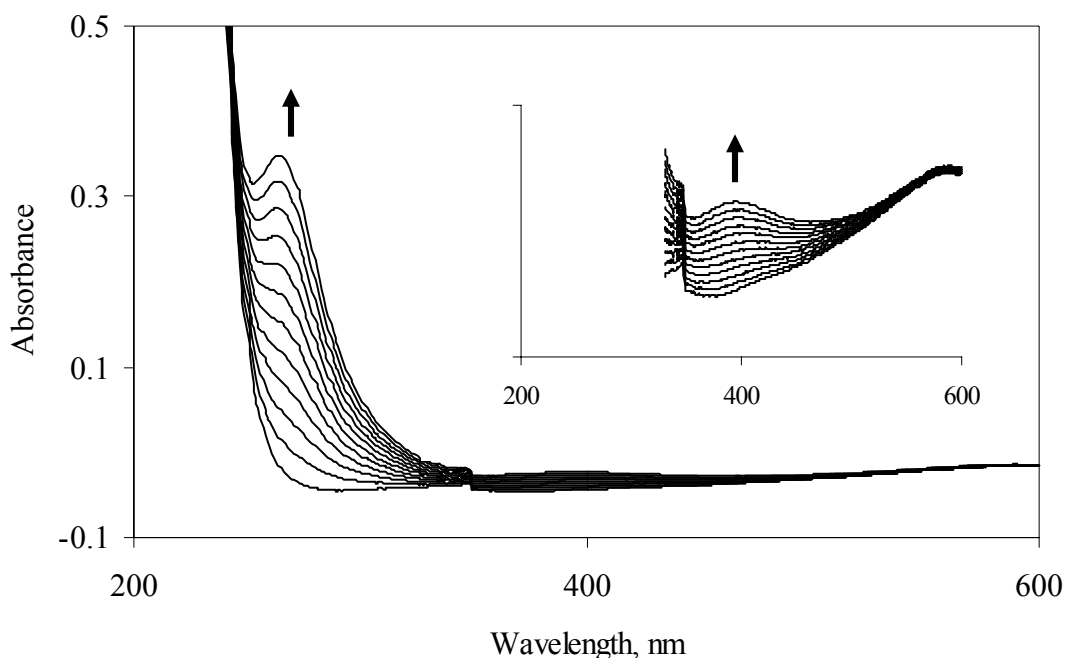


Figure 4.1. Spectral changes recorded during the initial 55 min reaction of 16 mM of Br⁻ with 8 mM BrO₃⁻ in 0.01656 N H₂SO₄ medium at 25 °C.

of a sharp intense band at 260 nm and simultaneously a low intense broad band at 390 nm. Soulard and Bloc,⁵⁹ and Kumar and Margerum⁶⁰ have reported a similar band at 260 nm characteristic for BrOH species. So, the formation and disproportionation of hypobromous acid were studied following the band at 260 nm under variable experimental parameters as outlined in this section.

4.3.2. Kinetics of formation of hypobromous acid. (a) Effect of bromide ion concentration. The effect of bromide ion concentration, [Br⁻] on the rate formation of hypobromous acid has been studied by varying its concentration between 3.5 mM and 45

mM. keeping $[\text{BrO}_3^-]$ constant at 8 mM, hydrogen ion concentration $[\text{H}^+]$ at 12.6 mM with H_2SO_4 . In these studies, the ionic strength of the medium was maintained to 0.1 N

Table 4.1. Effect of Br^- ion concentration on the rate formation of BrOH at 25 °C.

$[\text{Br}^-]$ mM	$[\text{BrO}_3^-]$ mM	μ N	pH	$[\text{H}^+]$ mM	$k_{\text{obs}}^f \times 10^{-6}$ M/s	$\log [\text{Br}^-]$	$\log k_{\text{obs}}^f$
4	8	0.1	1.9	12.6	0.572	-2.398	-6.242
8	8	0.1	1.9	12.6	0.645	-2.097	-6.189
12	8	0.1	1.9	12.6	4.895	-1.921	-5.310
16	8	0.1	1.9	12.6	9.770	-1.796	-5.010
40	8	0.1	1.9	12.6	47.700	-1.398	-4.320

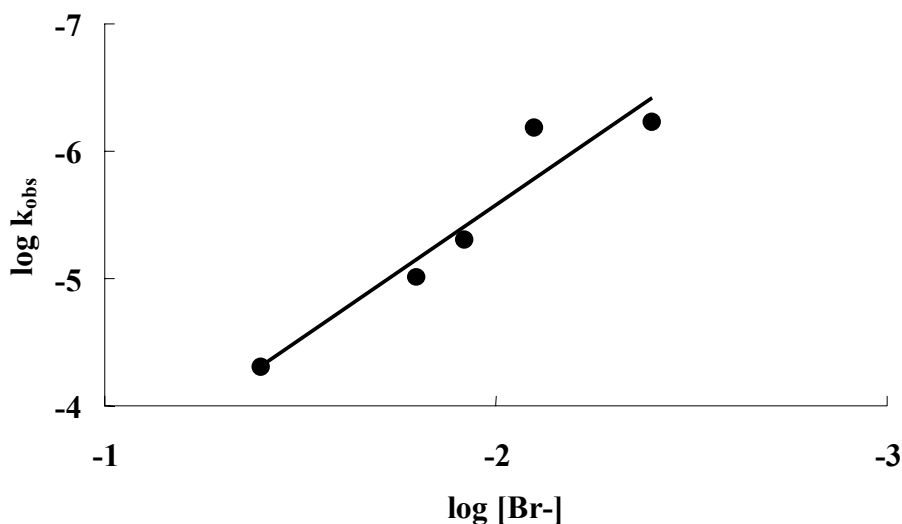


Figure 4.2. Plot of $\log [\text{Br}^-]$ vs $\log k_{\text{obs}}^f$, Satisfies the straight line equation $y = 2.1068x - 1.365$, $R^2 = 0.9152$

with Na_2SO_4 and temperature at 25 °C. The spectra of all these solutions were recorded between 200 nm and 600 nm for 30 min to 60 min at a regular time intervals of 2 or 5 min, depending on $[\text{Br}^-]$. The absorbance at 260 nm, in each case, was recorded, determined the amount of BrOH formed and plotted with time. From the slope of linear portion of these plots, the observed rate (k_{obs}^f) of formation of BrOH was evaluated. The observed rate data thus obtained at different $[\text{Br}^-]$ is depicted in Table 4.1. The plot of $\log [\text{Br}^-]$ vs $\log [k_{\text{obs}}^f]$ is shown in Figure 4.2 which is linear having a slope of two indicating the second order dependence of formation of BrOH with respect to $[\text{Br}^-]$.

(b) *Effect of bromate concentration.* The effect of bromate ion concentration, $[\text{BrO}_3^-]$ on the rate formation of hypobromous acid has been studied spectrophotometrically by varying its concentration between 3 mM and 12 mM keeping $[\text{Br}^-]$ constant at 16 mM, $[\text{H}^+]$ at 12.6 mM with H_2SO_4 while maintaining the ionic strength (μ) of the medium to 0.1 N with Na_2SO_4 and temperature at 25 °C. In these studies, the spectra in each

Table 4.2. Effect of BrO_3^- ion concentration on the rate formation of BrOH at 25 °C.

$[\text{Br}^-]$ mM	$[\text{BrO}_3^-]$ mM	μ N	pH	$[\text{H}^+]$ mM	$k_{\text{obs}}^f \times 10^{-6}$ M/s	$\log [\text{BrO}_3^-]$	$\log k_{\text{obs}}^f$
16	3.2	0.1	1.9	12.6	2.77	-2.495	-5.557
16	4.0	0.1	1.9	12.6	3.86	-2.398	-5.413
16	8.0	0.1	1.9	12.6	9.77	-2.097	-5.010
16	12.0	0.1	1.9	12.6	12.43	-1.921	-4.906

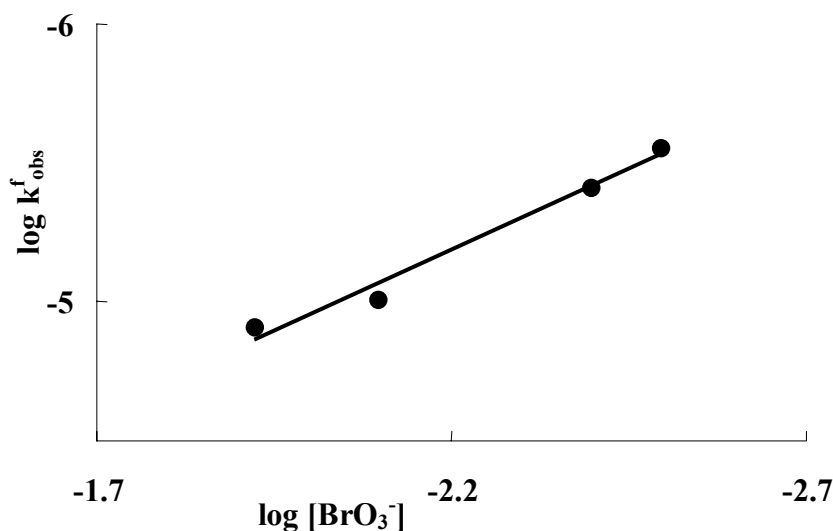


Figure 4.3. Plot of $\log [\text{BrO}_3^-]$ vs $\log k_{\text{obs}}^f$, Satisfies the straight line equation $y = 1.1662x - 2.6237$, $R^2 = 0.9799$

experiment was recorded for 30 min to 60 min at a regular time intervals of 2 or 5 min, depending on the $[\text{BrO}_3^-]$, between 200 nm and 600 nm. The absorbance at 260 nm in each case was recorded, determined the amount of BrOH formed and plotted with time. From the slope of linear portion of these plots, the observed rate (k_{obs}^f) of formation of BrOH was evaluated. The observed rate data thus obtained at different $[\text{BrO}_3^-]$ is depicted in Table 4.2. The plot of $\log [\text{BrO}_3^-]$ vs $\log [k_{\text{obs}}^f]$ is shown in Figure 4.3 which

is a straight line having a slope of one indicating the first order dependence of formation of BrOH in $[\text{BrO}_3^-]$.

(c) *Effect of hydrogen ion concentration:* The effect of hydrogen ion concentration $[\text{H}^+]$, on the rate of formation of hypobromous acid has been studied by varying its concentration between 8 mM and 60 mM keeping $[\text{Br}^-]$ constant at 16 mM, $[\text{BrO}_3^-]$ at 8

Table 4.3 : Effect of $[\text{H}^+]$ ion concentration on the rate formation of BrOH at 25 °C.

$[\text{Br}^-]$ mM	$[\text{BrO}_3^-]$ mM	μ N	pH	$[\text{H}^+]$ mM	$k^f_{\text{obs}} \times 10^{-6}$ M/s	$\log [\text{H}^+]$	$\log k^f_{\text{obs}}$
16	8	0.1	2.08	8.32	0.437	-2.080	-6.359
16	8	0.1	1.78	16.64	2.322	-1.779	-5.634
16	8	0.1	1.60	25.00	7.322	-1.602	-5.135
16	8	0.1	1.38	41.60	20.541	-1.381	-4.687
16	8	0.1	1.24	58.24	46.406	-1.235	-4.333

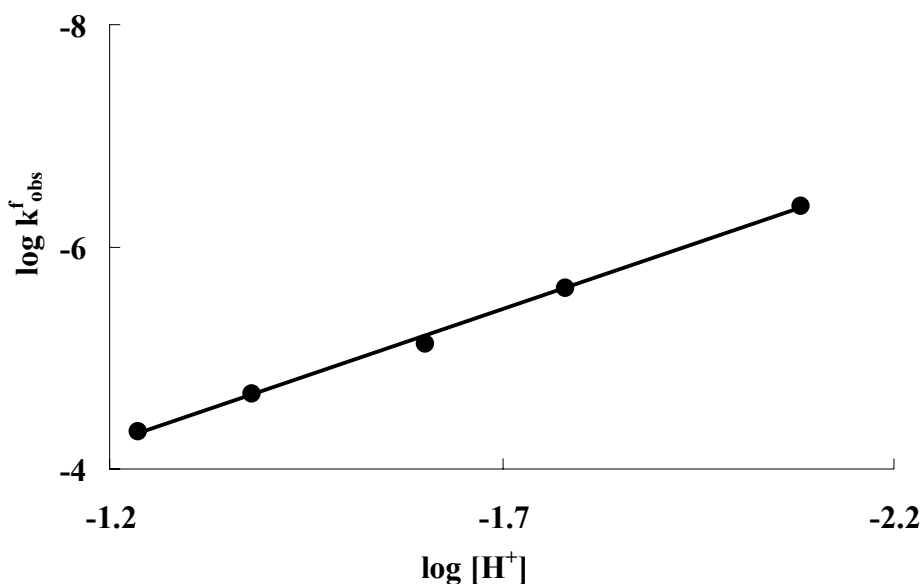


Figure 4.4. Plot of $\log [\text{H}^+]$ vs $\log k^f_{\text{obs}}$. Satisfies the straight line equation $y = 2.3967x - 1.358$, $R^2 = 0.9981$

while maintaining the ionic strength (μ) of the medium to 0.1 N with Na_2SO_4 and temperature at 25 °C. In these studies, the spectra in each experiment was recorded between 200 nm and 600 nm for 30 min to 60 min at regular time intervals of 2 or 5 min depending on the $[\text{H}^+]$ value. The absorbance at 260 nm, in each case, was recorded, determined the amount of BrOH formed and plotted against time. From the slope of linear portion of these plots, the observed rates (k^f_{obs}) of formation of BrOH were

evaluated. The observed rate data thus obtained at different $[H^+]$ is depicted in Table 4.3. The plot of $\log [H^+]$ vs $\log [k_{obs}^f]$ is shown in Figure 4.4 which is a straight line having a slope of 2.4 indicating nearly third order dependence of formation of BrOH with respect to $[H^+]$.

(d) *Effect of ionic strength.* The effect of ionic strength (μ) of the medium on the rate

Table 4.4 : Effect of ionic strength of the medium on the rate formation of BrOH at 25 °C.

[Na ₂ SO ₄] N	[Br ⁻] mM	[BrO ₃ ⁻] mM	[H ⁺] mM	μ	$k_{obs}^f \times 10^{-5}$ M/s	$\mu^{1/2}/(1+\mu^{1/2})$	$\log k_{obs}^f$
0.005	16	8	20.8	0.089	6.373	0.2293	-4.1960
0.030	16	8	20.8	0.151	1.180	0.2798	-4.3812
0.025	16	8	20.8	0.139	4.193	0.2716	-4.3780
0.080	16	8	20.8	0.276	0.780	0.3444	-4.8979
0.050	16	8	20.8	0.201	2.054	0.3095	-4.6880
0.120	16	8	20.8	0.376	1.270	0.3801	-4.9962
0.075	16	8	20.8	0.264	1.378	0.3392	-4.8610
0.100	16	8	20.8	0.326	0.972	0.3634	-5.0120

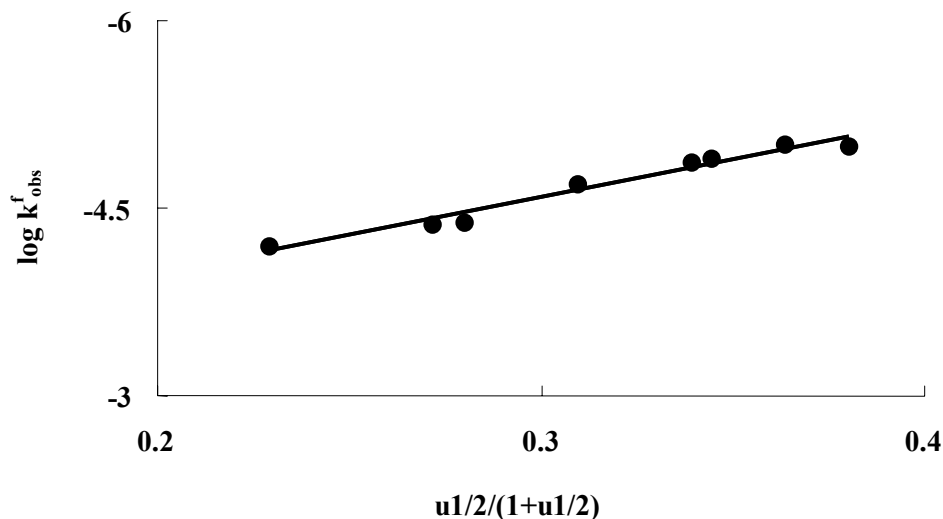


Figure 4.5. Plot of $\mu^{1/2}/(1+\mu^{1/2})$ vs $\log k_{obs}^f$. Satisfies the straight line equation $y = -6.0717x - 2.7658$, $R^2 = 0.9686$

formation of hypobromous acid has been studied by varying the concentration of Na₂SO₄ between 0.005 N and 0.1 N. In these studies, the [Br⁻] is kept constant at 16 mM, [BrO₃⁻] at 8 mM and [H⁺] at 20.8 mM with H₂SO₄ temperature at 25 °C. In these studies, the spectra in each experiment was recorded between 200 nm and 600 nm for 30 min to 60 min at a regular time intervals of 2 or 5 min, depending on the (μ). The absorbance at

260 nm in each case was recorded, determined the amount of BrOH formed and plotted with time. From the slope of linear portion of these plots, the observed rate (k_{obs}^f) of formation of BrOH was evaluated. The observed rate data thus obtained at different total ionic strength (μ) of the medium is depicted in Table 4.4. The plot of $\log \mu^{1/2}/(1+\mu^{1/2})$ vs $\log [k_{\text{obs}}^f]$ is shown in Figure 4.5 which is a straight line having a negative slope of six indicating the product of ionic charges on all species is -6 in the rate determining step of formation of BrOH from bromide, bromate and hydrogen ions in their stoichiometric or less quantities.

(e) *Mechanism of hypobromous acid formation.* On the basis of above experimental data which revealed a second order dependence on $[\text{Br}^-]$ (Figure 4.2), first order dependence on $[\text{BrO}_3^-]$ (Figure 4.3) and a third order dependence on $[\text{H}^+]$ (Figure 4.4) together with the ionic strength dependence (Figure 4.5) of observed rate (k_{obs}^f) of formation of BrOH, the following reaction (Eq 4.18) is suggested as the rate controlling step.



where $K_{\text{ass}}^f = [\text{HOBr}]/[\text{BrO}^-][\text{H}^+]$, $k_f = k_f' K_{\text{ass}}^f$. It is presumed that the two Br^- ions are activated in acidic medium leading to react with bromate ion to give three moles of hypobromite (BrO^-) ion (Eq. 4.19) which in turn produce a weak hypobromous acid (BrOH) in its subsequent reaction at equilibrium with equal number of protons H^+ in the medium (Eq 4.20). The observed rate (k_{obs}^f) data at different acid concentrations are summarised in Table 4.5. A proton dependent rate expression to explain the multi order rate of formation BrOH (Eq 4.18) is given as Eq 4.21.

$$\begin{aligned} k_{\text{obs}}^f &= d[\text{OBr}^-]/dt + K_{\text{ass}}^f [\text{OBr}^-][\text{H}^+]^3 \\ k_{\text{obs}}^f / [\text{Br}^-]^2 [\text{BrO}_3^-] &= k_f' + k_f' K_{\text{ass}}^f [\text{H}^+]^3 \quad \text{OR} \\ k_{\text{obs}}^f / [\text{Br}^-]^2 [\text{BrO}_3^-] &= k_f' + k_f [\text{H}^+]^3 \end{aligned} \quad (4.21)$$

The plot $k_{obs}^f / [Br^-]^2 [BrO_3^-]$ vs $[H^+]^3$ depicted in Figure 4.6 is straight line indicating the validity of the rate expression Eq 4.19. From the values of slope and intercept of the

Table 4.5. Observed rate (k_{obs}) data at different hydrogen ion concentrations. $[Br^-] = 16 \text{ mM}$; $[BrO_3^-] = 8 \text{ mM}$;

$[H^+]$, mM	$k_{obs}^f \times 10^{-6}$	$[H^+]^3 \times 10^{-5}$	$k_{obs}^f / [Br^-]^2 \times [BrO_3^-]$	k_f'	K_{ass}^f	pK_{dis}^f
0.0083	0.437	0.0576	0.2134	1.0546	1.0561×10^5	5.024
0.0166	2.322	0.4607	1.1338			
0.0250	7.322	1.5625	3.5752			
0.0416	20.540	7.1991	10.0293			
0.0582	46.406	19.7544	22.6592			

Note: Slope = $k_f = k_f' K_{ass} = 1.1138 \times 10^5$; Intercept = $k_f' = 1.0546$.

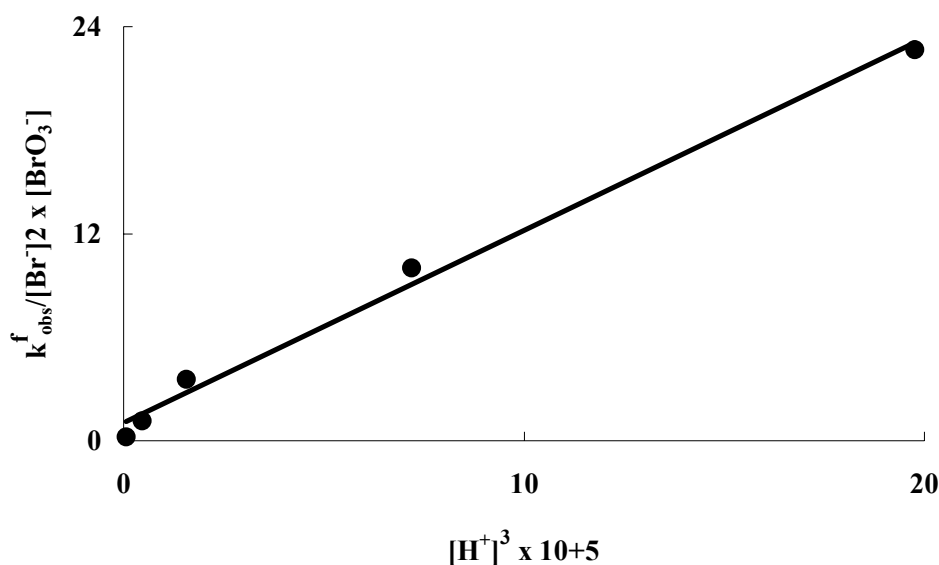


Figure 4.6. Plot of $k_{obs}^f / [Br^-]^2 [BrO_3^-]$ vs $[H^+]^3$. Satisfies the linear equation $y = 1.1138 \times 10^5 x + 1.0546$, $R^2 = 0.9922$.

plot Figure 4.6, the values of multiple order rate constant, k_f , the third order rate constant (k_f') and the proton association constant (K_{ass}^f) are evaluated to be 1.1138×10^5 , $1.0546 \text{ M}^{-2} \text{ s}^{-1}$ and $1.056 \times 10^5 \text{ M}^{-1}$ respectively. From the value of K_{ass}^f , the acid dissociation constant (pK_a) is evaluated as 5.024 which is close to 5.013 reported in the literature⁶¹ but less than that of the value (8.8 at 25 °C in 0.5 M ionic strength) reported by Troy and Margerum.⁵²

(f) *Evaluation of thermodynamic parameters.* The rate formation of hypobromous acid has been monitored by spectrophotometry at different temperatures between 15-45°C. In these studies, the $[\text{Br}^-]$ was kept constant at 16 mM, $[\text{BrO}_3^-]$ at 8 mM and $[\text{H}^+]$ at 12.6 mM with H_2SO_4 in 0.1 N Na_2SO_4 solutions. The spectra of each of these solutions was recorded for 30 min to 60 min at a regular time intervals of 2 or 5 min, depending on the temperature, between 200 nm and 600 nm. The absorbance at 260 nm in each case was recorded, determined the amount of BrOH formed and plotted against time. From the slope of linear portion of these plots, the observed rates (k_{obs}^f) of formation of BrOH were evaluated. The observed rate data thus obtained at four different temperatures are depicted in Table 4.6.

$$\log k = -E_a/2.303R[1/T] + \log C, \quad (4.22)$$

$$\Delta H^\ddagger = E_a - RT \quad (4.23)$$

$$\Delta S^\ddagger = 2.303 R \log [hk/k_bT] + \Delta H/T \quad (4.24)$$

$$\Delta G^\ddagger = \Delta H - T \Delta S \quad (4.25)$$

where E_a = activation energy; C = frequency factor; h (Planks constant) = 6.6256×10^{-27} ergs/sec; k_b (Boltzman's constant) = 1.38054×10^{-16} ergs/deg; R = 1.987 cal/deg/mol, k = absolute rate constant.

Table 4.6. Effect of temperature on k_{obs} . $[\text{Br}^-] = 16$ mM; $[\text{BrO}_3^-] = 8$ mM; $[\text{H}^+] = 0.0126$ N; $\mu = 0.1$ N with Na_2SO_4 ; temp. = 25 °C.

T °K	$[\text{Br}^-]$ mM	$[\text{BrO}_3^-]$ mM	$[\text{Na}_2\text{SO}_4]$ mM	$[\text{H}^+]$, N	$k_{\text{obs}}^f \times 10^{-6}$	$k_f \times 10^7$	1/T °K	log k_f
288	16	8	100	0.0126	5.052	1.160	0.003472	7.064
298	16	8	100	0.0126	9.791	2.297	0.003355	7.361
308	16	8	100	0.0126	13.96	3.298	0.003247	7.518
318	16	8	100	0.0126	18.00	4.267	0.003145	7.630

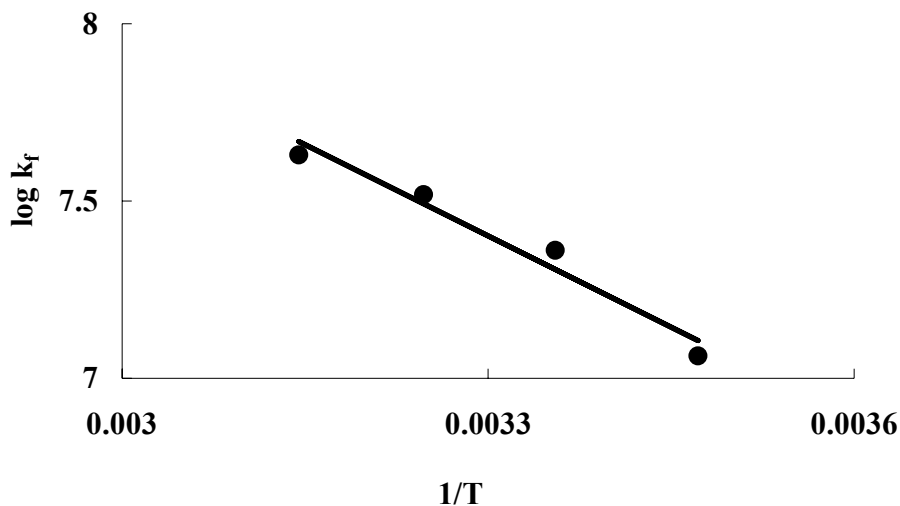


Figure 4.7. Plot of $1/T$ vs $\log k_f$. Satisfies the straight line equation $y = -1713.7x + 13.057$, $R^2 = 0.9627$

The plot $\log 1/T$ vs $\log k_f$ (Figure 4.7) is linear indicating the validity of Arrhenius equation Eq 4.20.⁶² From the slope of the plot $\log 1/T$ vs $\log k_f$, (Figure 4.7) the energy of activation E_a of the reaction Eq 4.18 is calculated to be 7.842 Kcal/deg/mol. The other relevant thermodynamic parameters such as ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger for this reaction are evaluated by substituting E_a value and other parameters those described in equations Eqs 4.23 – 4.25. They are found to be 7250 cal/deg/mol for ΔH^\ddagger , -0.527 cal/deg/mol for ΔS^\ddagger and 7.47 Kcal/deg/mol for ΔG^\ddagger , respectively. The thermodynamic data thus obtained for the reaction in Eq 4.18 indicate that it the BrOH formation is purely controlled by enthalpy of formation and free energy change. The change in entropy value of this reaction is negligible but its negative value supports the association mechanism rather than the dissociation.

4.3.3. Spectrophotometric behavior of hypobromous acid in the presence of externally added mineral acid. The absorption spectra of 4.97 mM BrOH in 0.03 N Na₂SO₄ was recorded the between 200 nm 600 nm at regular 5 min interval after mixing it with 0.16 N H₂SO₄. The observed data are depicted in Figure 4.8 which showed a gradual decrease in the intensity of 260nm band with concomitant enhancement in the band intensity at 390 nm indicating the disappearance of BrOH with time in the solution. Simultaneously, the solution slowly turned to a thick yellow in color confirming the disproportionation of BrOH leading to the formation of bromine and bromate in the solution. Two isobestic

points at 240 nm and 340 nm which also were observed further confirm the transformation of BrOH to Br₂ and BrO₃⁻ ion. The kinetics of disproportionation of BrOH was thus, studied in an externally added mineral acid by following the characteristic band at 260 nm under variable experimental conditions as outlined in this section.

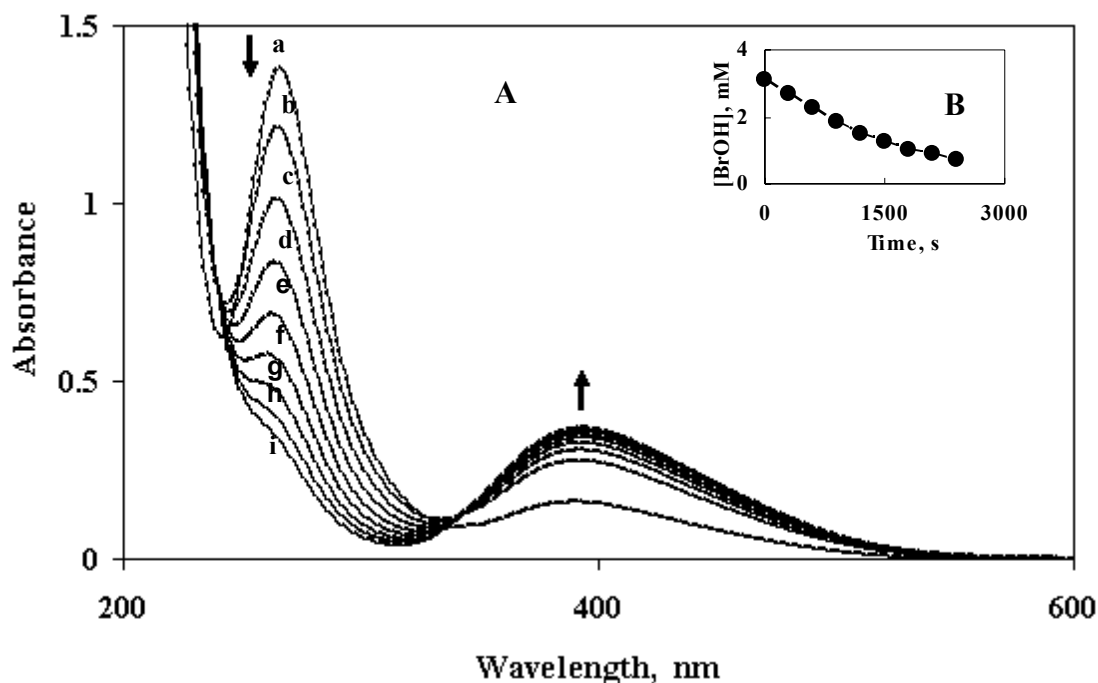


Figure 4.8. (A) Absorption spectra of 4.97 mM of BrOH in 0.16 N H₂SO₄ and 0.03 N Na₂SO₄ with time. (a) 0 min, (b) 5 min, (c) 10 min, (d) 15 min, (e) 20 min, (f) 25 min, (g) 30 min, (h) 35 min, (i) 40 min, (B) Plot of [BrOH] vs time.

4.3.4. *Kinetics of disproportionation of hypobromous acid. (a) Effect of hypobromous acid concentration.* The effect of hypobromous acid concentration [BrOH] on its rate of

Table 4.7. Effect of [BrOH] on k^d_{obs} .

S. No.	[BrOH], mM	k^d_{obs} , M/s $\times 10^6$	log [BrOH]	log k^d_{obs}
1.	0.414	0.00085	-3.383	-9.0708
2.	0.828	0.00582	-3.0819	-8.2532
3.	1.656	0.06100	-2.7809	-7.2146
4.	3.312	0.15325	-2.4799	-6.8146
5.	4.968	1.09170	-2.3038	-5.9619
6.	6.624	1.34900	-2.2048	-5.8700

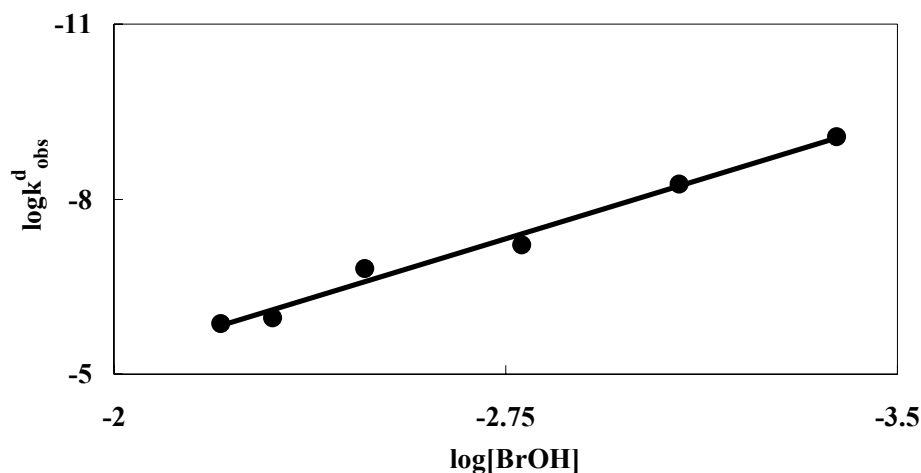


Figure 4.9 Plot of $\log [\text{BrOH}]$ vs $\log k_{\text{obs}}^{\text{d}}$. Satisfies the straight line equation $y = 2.7262x + 0.1788$, $R^2 = 0.9861$.

disproportionation was studied by varying its concentration between 0.4 and 0.70 mM, keeping hydrogen ion concentration $[\text{H}^+]$ at 0.6 N, while maintaining the $[\text{Na}_2\text{SO}_4]$ to 0.03 N with and temperature at 25 °C. The absorption spectra of each one of the experimental solutions were recorded for initial 60 min between 200 nm and 600 nm at regular 5 min interval. The absorbance at 260 nm, in each case, was recorded, determined the amount of BrOH disproportionated and plotted with time. From the slope of linear portion of these plots, the observed rate of disproportionation ($k_{\text{obs}}^{\text{d}}$) of BrOH was evaluated. The observed rate data thus obtained at different $[\text{BrOH}]$ is depicted in the Table 4.7. The plot of $\log [\text{BrOH}]$ vs $\log [k_{\text{obs}}^{\text{d}}]$ is shown in Figure 4.9 which is linear having a slope of 2.73 indicating nearly a third order dependence of BrOH disproportionation with respect to its concentration.

(b) *Effect of hydrogen ion concentration.* The effect of hydrogen ion concentration, $[\text{H}^+]$ on the rate of disproportionation of hypobromous acid, $k_{\text{obs}}^{\text{d}}$, has been studied by varying its concentration between 0.05 N and 0.75 N with H_2SO_4 keeping $[\text{BrOH}]$ constant at 4.97 mM, while maintaining the $[\text{Na}_2\text{SO}_4]$ in the medium to 0.03 N and temperature at 25 °C. The spectra in each experiment was recorded for initial 60 min between 200 nm and 600 nm at regular 5 min interval. The absorbance at 260 nm, in each case, was recorded,

Table 4.8. Effect of $[\text{H}^+]$ on $k_{\text{obs}}^{\text{d}}$

S. No	[H ⁺], N	k ^d _{obs} x 10 ⁶ M/s	log [H]	log k ^d _{obs}
1	0.08	0.2787	-1.0969	-5.8351
2	0.16	1.345	-0.7958	-5.8213
3	0.32	1.345	-0.4948	-5.7213
4	0.48	1.893	-0.3187	-5.6828
5	0.64	1.731	-0.1938	-5.6617
6	0.72	2.1476	-0.1427	-5.621

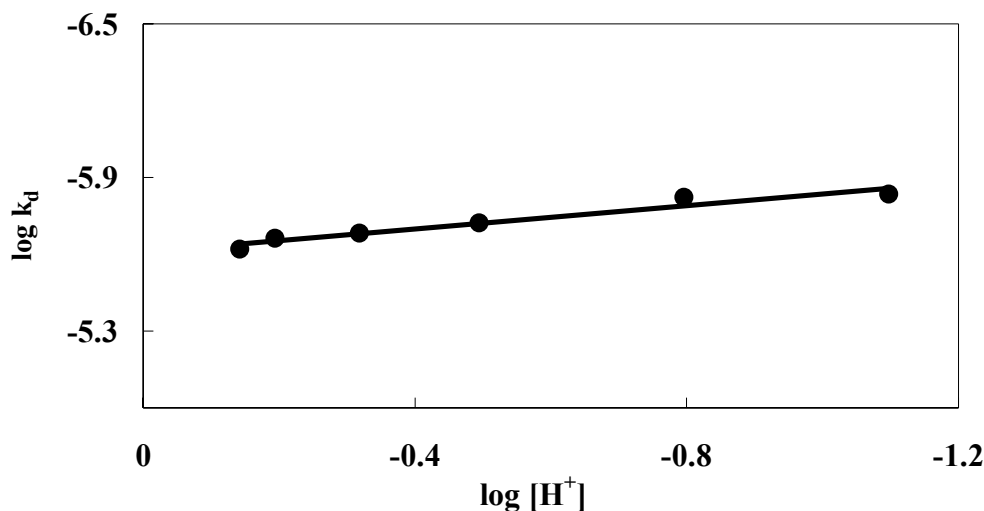


Figure 4.10. Plot of log [H⁺] vs log k_d. Satisfies the straight line equation $y = 0.2271x - 5.6087$, $R^2 = 0.9469$ determined the amount of BrOH disproportionated and plotted with time. From the slope of linear portion of these plots, the observed rate (k^d_{obs}) of disproportionation of BrOH was evaluated. The observed rate data thus obtained at different [H⁺] is depicted in Table 4.8. The plot of log [H⁺] vs log [k^d_{obs}] is shown in Figure 4.10 which is linear having a slope of 0.227 indicating partial order dependent disproportionation of BrOH in [H⁺].

(c) *Effect of ionic strength.* The effect of ionic strength (μ) of the medium on the observed rate of disproportionation (k^d_{obs}) of hypobromous acid has been studied by varying the Na₂SO₄ concentration between 0.0 N and 0.1 N keeping [BrOH] constant at 4.97 mM, [H⁺] at 8.28 mM and temperature at 25 °C In these studies, the spectra in each experiment was recorded for initial 60 min between 200 nm and 600 nm at regular 5 min

Table 4.9. Effect of ionic strength on k^d_{obs}, [BrOH] = 4.97 mM, [H⁺] = 8.28 mM at 25 °C.

[Na ₂ SO ₄] M	NaBr M	NaBrO ₃ M	H ₂ SO ₄ , N	μ	k ^d _{obs} x 10 ⁶	$\mu^{1/2}/(1+\mu^{1/2})$	log k ^d _{obs}
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0	0.008	0.004	0.00828	0.0327	0.7962	0.15314	-6.099
0.01	0.008	0.004	0.00828	0.0577	0.8609	0.19368	-6.0650
0.05	0.008	0.004	0.00828	0.1577	1.0313	0.28424	-5.9866
0.08	0.008	0.004	0.00828	0.2327	1.1308	0.32541	-5.9466
0.1	0.008	0.004	0.00828	0.2827	1.1811	0.34712	-5.9277

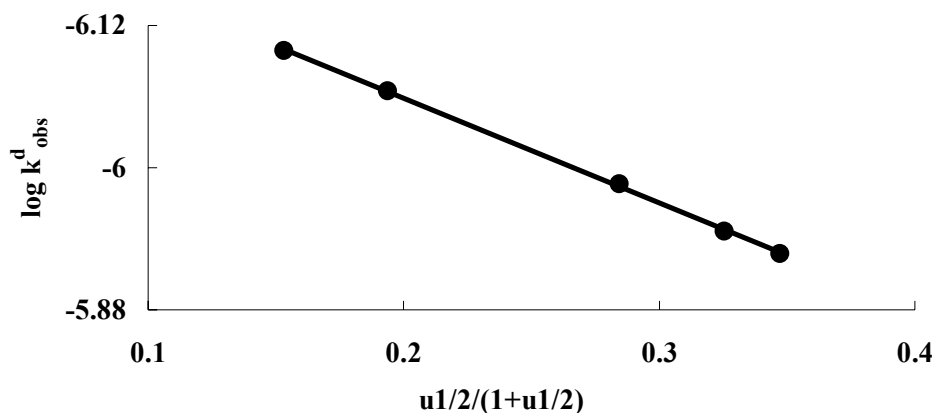
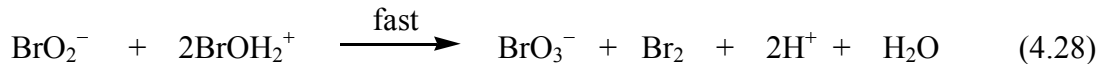
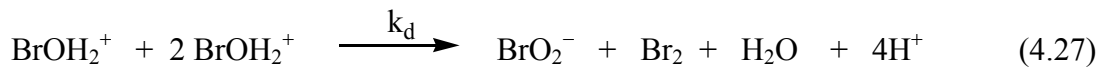
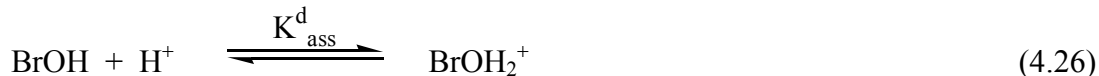


Figure 4.11. Plot of $\mu^{1/2}/(1+\mu^{1/2})$ vs $\log k_{\text{obs}}^{\text{d}}$; The data satisfy the linear equation $y = 0.8853x - 6.2358$, $R^2 = 0.9996$]

interval. The absorbance at 260 nm, in each case, was recorded, determined the amount of BrOH disproportionated and plotted with time. From the slope of linear portion of these plots, the observed rate ($k_{\text{obs}}^{\text{d}}$) of disproportionation of BrOH was evaluated. The observed rate data thus obtained at different μ is depicted in Table 4.9. The plot of $\mu^{1/2}/(1+\mu^{1/2})$ vs $\log k_{\text{obs}}^{\text{d}}$ is shown in Figure 4.11 which is linear having a positive slope of 0.885 indicating that the product of ionic charges on all species in the rate determining step of BrOH disproportionation in the presence of externally added mineral acid is around +1 with respect to total ionic strength $[\mu]$.

(d) *Mechanism of disproportionation of hypobromous acid.* On the basis of above experimental data which revealed a third order dependence on $[\text{BrOH}]$ (Figure 4.9) and negligible dependence on $[\text{H}^+]$ (Figure 4.10) together with the ionic strength dependence (Figure 4.11) of observed rate ($k_{\text{obs}}^{\text{d}}$) of disproportionation of BrOH, the following reaction mechanism (Eq 4.26) is suggested.



where $K_{\text{ass}}^{\text{d}} = [\text{BrOH}_2^+]/[\text{BrOH}][\text{H}^+]$. It is presumed that upon addition of a mineral acid, the BrOH immediately undergoes protonation (Eq 4.26) to give a protonated hypobromous acid (BrOH_2^+) causing for its destabilisation. The less stable BrOH_2^+ disproportionates in a rate control step to BrO_2^- and Br_2 ions (Eq 4.27). The BrO_2^- is rapidly oxidized in the following step (Eq 4.28) by BrOH_2^+ to give stable BrO_3^- and Br_2 . (Eq 4.20). A proton dependent rate expression is therefore suggested as Eq 4.29 to explain the third order disproportionation of BrOH as shown in Eqs 4.26-4.28.

$$k_{\text{obs}}^{\text{d}} = k_{\text{d}} [\text{BrOH}_2^+]^3 = k_{\text{d}} (K_{\text{ass}}^{\text{d}})^3 [\text{BrOH}]^3 [\text{H}^+]^3 = k_{\text{d}} (K_{\text{ass}}^{\text{d}})^3 [\text{BrOH}]^3 [\text{H}^+]^3 / \{1 + K_{\text{ass}}^{\text{d}} [\text{H}^+]\}^3$$

OR

$$\begin{aligned} [\text{BrOH}]^3 / k_{\text{obs}}^{\text{d}} &= 1 / \{ [\text{H}^+]^3 k_{\text{d}} (K_{\text{ass}}^{\text{d}})^3 \} + 3 / \{ [\text{H}^+]^2 k_{\text{d}} (K_{\text{ass}}^{\text{d}})^2 \} + 3 / \{ [\text{H}^+] k_{\text{d}} (K_{\text{ass}}^{\text{d}}) \} + 1 / k_{\text{d}} \text{ OR} \\ [\text{BrOH}]^3 / k_{\text{obs}}^{\text{d}} &= 1 / \{ [\text{H}^+]^3 k_{\text{d}} (K_{\text{ass}}^{\text{d}})^3 \} + 1 / k_{\text{d}} \text{ when } [\text{H}^+] < 1 \text{ N} \end{aligned} \quad (4.29)$$

The plot of $[\text{BrOH}]^3 / K_{\text{obs}}^{\text{d}}$ vs $1/[\text{H}^+]^3$ ($[\text{H}^+] < 1$) is depicted in Figure 4.12. It showed a straight line indicating the validity of the rate expression Eq 4.29. From the values of slope and intercept of the plot Figure 4.12, the values of third order rate constant, k_{d} , and the proton association constant ($K_{\text{ass}}^{\text{d}}$) are evaluated to be 15.524 and .0546 $\text{M}^{-2} \text{s}^{-1}$ and 6.96, respectively. Beckwith and Margerum⁵⁸ have studied spectrophotometrically the disproportionation of 2.3 mM of BrOH in 0.09 and 0.63 M HClO_4 and reported a second order rate constant as $2.2 \pm 0.2 \times 10^{-3} \text{M}^{-1} \text{s}^{-1}$ which were significantly larger than the previously reported values in 1.67 M HClO_4 and 1 M H_2SO_4 .⁶³

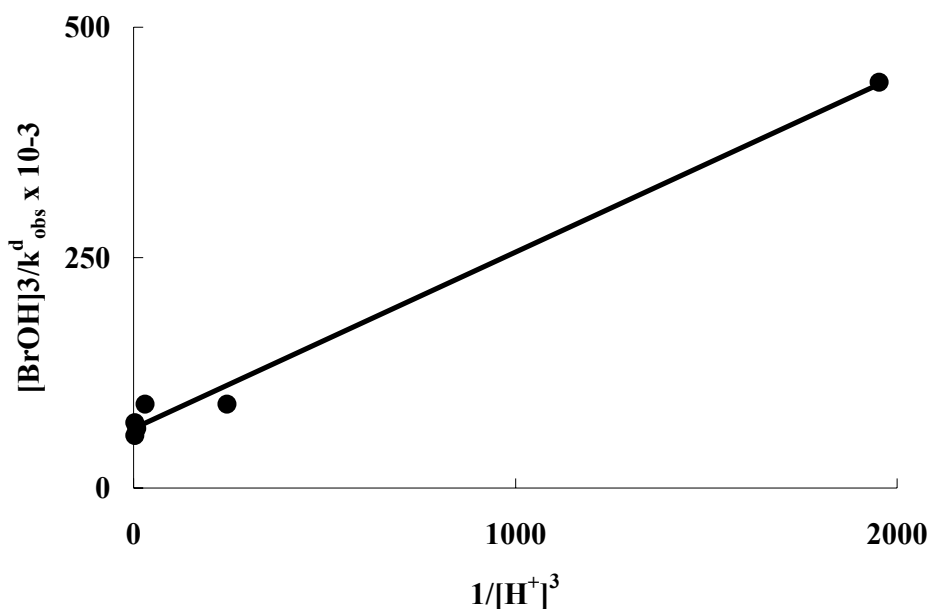


Figure 4.12. Plot of $1/[H^+]^3$ vs $[BrOH]^3/k_{obs}^d \times 10^3$ The data satisfy the linear equation $y = 1.914 \times 10^{-4} x + 0.06442$; $R^2 = 0.9917$)

(e) *Evaluation of thermodynamic parameter.* The effect of temperature on the decomposition of hypobromous acid has been studied by keeping BrOH (4,28 M) and H₂SO₄ (0.8N) constant and recording the spectra from 200 nm to 600 nm in regular 5 min interval for 60 min at different temperatures 15 °C, 25 °C and 35 °C. The absorbance at 260 nm in each case was recorded, determined the amount of BrOH disproportionated and plotted against time. From the slope of linear portion of these plots, the observed rates (k_{obs}^d) of BrOH disproportionation were evaluated. The observed rate data thus obtained at three different temperatures are depicted in Table 4.10.

Table 4.10. Effect of temperature on BrOH decomposition $[BrOH] = 4.97mM$; $[H^+] = 8 mM$

T °K	k_{obs}^d $\times 10^{-6}$	k_d $\times 10^4$	1/T $\times 10^{-3}$	log k_d	Ea Kcal/deg/mol	ΔH Cal/deg/mol	ΔS^\ddagger Cal/deg/mol	ΔG KCal/deg/mol
288	0.500	2.403	3.472	4.3808	5.491	4899	-21.33	11.26
298	0.719	3.456	3.355	4.5385				
308	0.930	4.470	3.247	4.6503				

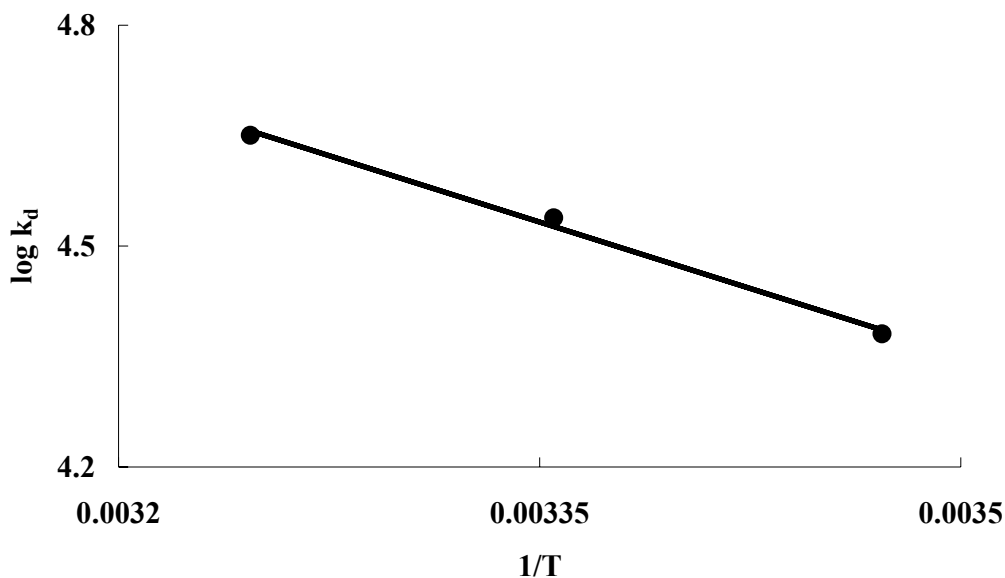


Figure 4.13. Plot of $1/T$ vs $\log k_d$ Satisfies the straight line equation $y = -1199.9 x + 8.5523$, $R^2 = 0.9944$

The plot $\log 1/T$ vs $\log k_d$ (Figure 4.13) is straight line indicating the validity of Arrhenius equation Eq 4.22.⁶² From the slope of the plot $\log 1/T$ vs $\log k_d$, (Figure 4.13), the energy of activation E_a of the reaction Eq 4.27 is calculated to be 5.491 Kcal/deg/mol. The other relevant parameters such as ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger for this reaction are evaluated by substituting E_a value and other known parameters those described in the equations (Eqs 4.23 – 4.25). They are found to be 4899 cal/deg/mol for ΔH^\ddagger , -21.33 cal/deg/mol for ΔS^\ddagger and 11.26 Kcal/deg/mol for ΔG^\ddagger , respectively. The thermodynamic data thus obtained for the reaction in Eq 4.27 indicate that the BrOH disproportionation is purely controlled by enthalpy of formation and free energy change. The change in entropy value of this reaction is negligible but its negative value supports the association mechanism rather than the dissociation.

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