Chapter 6 Conclusions

Organo bromine compounds find many applications in various fields. They are commonly prepared by using liquid bromine through addition and substitution reactions. However, the liquid bromine is highly fuming corrosive liquid and hence hazardous by nature. Thus, extreme care is required not only during the preparation of organo bromine compounds but also in the production and transportation of liquid bromine. Moreover, the bromine atom efficiency of liquid bromine in all its substitution reactions is only 50% as the remaining half ends up in the effluent as hydrobromic acid which demands either neutralization for its safe discharge or further processing for its reuse. Thus a need to develop a safe and an efficient brominating reagent alternate to the use of liquid bromine is highly essential. The present thesis work is therefore, dedicated to systematically develop i) spectrophotometric methods of estimations of bromide and bromate ions in acidic chloride and chloride-free media, ii) the preparation of non-hazardous brominating reagents enabling to carry out bromination of various organic substrates *via* substitution and addition mechanisms, iii) the generation and characterization of hypobromous acid in aqueous acidic solutions and iv) the preparation and characterization of organo bromine compounds with the help brominating reagents developed here. The study is further, extended to the selective dehalogenation of halo phenols as it is an important and intermediate step for obtaining several value added organic compounds.

As a part of the present study, the facile, quick, reliable and precise analytical procedures for the estimation of bromide and bromate ions both in the presence and absence of excess chloride by spectrophotometry, are meticulously described. The bromide ion estimation is based on its reaction with excess bromate in acid medium and the resultant absorption band i) at 390 nm for aq–Br_2 in the absence and ii) at 335 nm for

$BrCl_2^-$ in the presence of excess chloride ion. In contravention, the bromate ion determination is based on its rapid reaction in acidic medium with i) excess chloride and the resultant absorption band at 335 nm for $BrCl_2^-$ or ii) excess (chloride–free) bromide ion and the resultant absorption band at 390 nm for Br_3^-. Calibration graphs for Br^- ion estimation in 0.25% $KBrO_3$ – 4% H_2SO_4 and 0.1% $KBrO_3$ – 3 and 5% NaCl – 4% H_2SO_4, media and BrO_3^- ion in 4% KBr – 4% H_2SO_4 and 5% NaCl – 4% H_2SO_4 media were determined. The redox reaction between BrO_3^- and Cl^- in absence and presence of two equivalents of Br^- giving BrCl and the reaction stoichiometry in each case was established by spectrophotometric titration. With the help of present methods, the inorganic bromide present in industrial mixtures, sea water samples from different places of varied density, and soil or plant extracts, while, the bromate concentration in industrial alkaline bromine samples and de-brominated effluents were estimated. Further, the effects of sulfuric acid as well as chloride, bromide and bromate ions on the absorption spectra of aq-Br_2 were reinvestigated. Detection limits for Br^- in 0.25% $KBrO_3$ – 4% H_2SO_4 and 0.1% $KBrO_3$ – 3-10% NaCl – 4% H_2SO_4 media, and BrO_3^- in 4% NaBr – 4% H_2SO_4 and 5% NaCl – 4% H_2SO_4 media were measured.

Two kinds of brominating reagents BR(S) and BR(A) are developed for bromination of organic compounds through addition and substitution mechanism. They are obtained in environmentally benign ways by utilizing the industrial alkaline bromine mixture produced as an intermediate in the bromine recovery plants working on the Cold Process. The brominating reagent BR(A) possessing bromide and bromate in 5:1 stoichiometry is a substitute for liquid bromine in bromine addition reactions. The brominating reagent BR(S) having bromide to bromate in 2:1 ratio obtained by partial oxidation of alkaline bromine mixture with Cl_2 gas is especially suitable for aromatic bromine substitution reactions with maximum bromine atom efficiency and negligible formation of hydrobromic acid. Both the brominating reagents are conveniently activated by simple addition of a calculated/stoichiometric quantity of a mineral acid.

The likely benefits and usefulness of the brominating reagents BR(S) and BR(A) are summarized as

- They dispense the use of corrosive liquid bromine in a large number of reactions.

- They are prepared economically by environmentally benign routes using alkaline bromine intermediate mixture and easily available oxidizing agents.
- They can be obtained either in solution form or in the solid form for users convenience.
- They are safe to handle and easily transportable.
- They are non-hazardous materials and thus do not require any special equipment or handling skills.
- They are useful in common aromatic brominations and olefinic bromine addition reactions relatively at faster rates in absence of catalysts.
- They assure high yields of brominated products with maximum bromine atom efficiency.
- They do not generate any hazardous byproducts or wastes in discharges.
- They generate highly reactive intermediate BrOH or Br_2 during their reaction with a mineral acid for further reaction with organic substrates.
- The left out materials of these brominating reagents are simple water-soluble inorganic salts that are safe to discharge.

On the way to have a insight into the reaction of BR(S) with a mineral acid and identification of the possible intermediate species produced during bromination reactions of various organic substrates, the studies on the generation, charactarization and the kinetics of formation of hypobromous acid (BrOH) have been conducted. BrOH is found to be generated when two equivalents of bromide and one equivalent of bromate are reacted with three equivalents or less of hydrogen ions. The effects of concentration of bromide, bromate, hydrogen ion concentration and ionic strength on the observed rate of formation of hypobromous acid are investigated. Relevant mechanism for the formation of BrOH is suggested. A proton dependent rate expression is suggested and the sixth order rate constant is evaluated. Further, the energy of activation and relevant thermodynamic parameters are evaluated.

The disproportionation kinetics of hypobromous acid in the presence of externally added mineral acid are also investigated. The effect of concentration of hypobromous acid [BrOH], hydrogen ion concentration [H^+], total ionic strength [μ] and temperature on

the kinetics of disproportionation of BrOH have been determined. A suitable proton dependent rate determining step is suggested and the third order rate and equilibrium constants are evaluated. The thermodynamic parameters pertaining to the rate controlling step have been measured.

Some selected aromatic substrates such as phenols, amines, amides (acetanilide), imides (succinimide), ethers, and hydrocarbons through substitution are brominated as paradigms to BR(S) applications by adding stoichiometric amounts of a mineral acid in the presence of substrate. The monobromination of phenol the 82:18 ratio of *para* to *ortho* selectivity has been observed with present brominating reagent BR(S) system without the use of any catalyst. The bromination of unsubstituted phenols is carried out in water to 1-4 degree of bromination and obtained 91-94% yield The substituted phenols also gave 82-99% yields of bromo derivatives when carried out in 20% aqueous methanol medium. In the case of 2-naphthol, 66% during monobromination and 86% during dibromination of products are obtained. Tetrabromobisphenol-A is obtained to the extent of 94% in dichloromethane-water medium.

Mono/di/tri-bromo derivatives are obtained to the extent of 84-98.5% with substituted anilines in dichloromethane-water and aniline in 20% aqueous-methanol. Anisole gives 96% *p*-bromoanisole while 1,4-dimethoxy benzene give 96% dibromoderivative in dichloromethane-water system. 4-Bromoacetanilide is obtained in 93% yield in 20% aqueous methanol and N-bromosuccinimide 91% in water.

Similarly, the addition reactions of BR(A) and BR(S) with some selected olefins are conducted by adding required quantity of mineral acids. The addition reactions using BR(A) are carried out in two different media, carbon tetrachloride-water and dichloromethane-water systems. The later system offers a better medium for obtaining dibromo derivatives from the corresponding olefins with BR(A). The yield of dibromo derivative increases as the olefin ring size or carbon chain increases.

Bromohydrins have been prepared from olefins with BR(S) by employing two different solvent biphasic (carbon tetrachloride-water at 65°C) and homogeneous (dioxane-water at room temperature) systems. Better yields of bromohydrin are obtained in dioxane-water with an increasing trend with the increase in carbon chain of straight

chain olefin. The addition of BrOH across olefinic bond resulted a maximum product following the Markovnikov's rule and negligible amount of anti-Markovnikov's product.

The present studies have also been extended to selective dehalogenation of polyhalophenols. These studies are conducted in two heterogeneous catalytic media *viz*. Hβ–Zeolite-sodium sulfite and $KHSO_4$–sodium sulfite. Dehalogenation of 1-bromo-2-naphthol and 1-iodo -2-naphthols using Hβ–Zeolite-sodium sulfite give lower yields compared to those obtained in $KHSO_4$–sodium sulfite medium. The studies further revealed that the selective dehalogenation of 2,4,6-tribromophenols and 2,4,6-triiodophenols occurs at *para* (C_4) position and give higher yields of corresponding 2,6-dihalophenols in Hβ–Zeolite-sodium sulfite medium than that in $KHSO_4$–sodium sulfite medium. In the Hβ–Zeolite medium the catalyst is regenerated which can be reused for the successive experiments with comparable results. Chlorophenols are reluctant to undergo dechlorination under both the media. Poly halophenols are selectively dehalogenated at *para* position. The ease of dehalogentaion is observed to decrease in the order of I > Br > Cl substituted phenol.