Chapter 1

Introduction
Section A
Oxidative halogenations

In the present era, the prime goal for a synthetic organic chemist is to actively engage in the development of efficient and environmentally benign synthetic protocols in response to the increasing pressure to produce the large number of substances required by society in an environmentally benign fashion. Various stringent regulations and stipulations that are placed on the chemical industries, especially in the area of waste management, have inspired the scientists to explore environmentally benign methods to carry out the reactions in an expeditious manner with minimized waste generation.

1.1. Halogen compounds

It is difficult to imagine organic chemistry without organo-halogen compounds. Halogenated organic compounds play a very important role in chemistry, they are essential in organic synthesis as starting compounds and synthetic intermediates, as designer molecules for material science, industrial chemicals and bioactive compounds [1–3].

The past 30 years have witnessed a period of significant expansion in the use of halogenated compounds in the field of agrochemical research and development. There has been a rise in the number of commercial products containing mixed halogens. A survey of new active ingredients used as modern agrochemicals provisionally approved by ISO in the last 10 years shows that around 78.5% of them are halogen substituted. However, the complex structure activity relationships associated with biologically active molecules mean that the introduction of halogens can lead to either an increase or decrease in the efficacy of a compound depending on its change mode of action, physicochemical properties, target interaction or metabolic susceptibility and transformation.
Halogen-containing drugs have entered into usage only since 1820. The incorporation of halogen atoms into a lead results in analogues that are more lipophilic and so less water soluble. Consequently halogen atoms are used to improve the penetration of lipid membranes. However, there is an undesirable tendency for halogenated drugs to accumulate in lipid tissue.

1.2. Naturally occurring organo-halogen compounds

The number of known naturally occurring organo halogen compounds has increased tremendously during the last few decades. Fifty years ago there were less than 30 known examples, whereas today there are more than 4500 documented examples of naturally occurring organo-halogen compounds (ca. 120 iodinated, 2100 brominated, 2300 chlorinated and 30 fluorinated compounds) [4-6].

Among natural organo-halogen compounds, bromophenols are abundant in marine life. These compounds are mostly isolated from red algae of the family Rhodomelaceae [7]. Bromophenols are important compounds in the field of functional food and pharmaceuticals. They also exhibit a wide spectrum of useful biological activities [8] (Fig. 1.1-1.3).
1.3. Halogenation of organic compounds

Generally the halogenation of organic compounds performed by molecular halogens in chlorinated solvents, either in the absence of catalyst or in presence of Lewis acid catalyst [9].

![Chemical structure image]

These methods have several environmental drawbacks like toxic molecular halogen, catalysts and atom efficiency (only half of the halogen atoms react and the remainder are converted into hydrohalic acid, thereby reducing the atom efficiency by 50%). In large scale operations this is an environmental as well as an economic problem. As a result, many industrial halogen compounds are no longer manufactured and are being banned. Therefore direct use of molecular halogens in the reactions is no more recommendable and alternative strategy is required for their use.

Hence, during present thesis work, efforts are being made for development of sustainable halogenations using eco-friendly reagents such as NH₄Br as a brominating agent and oxone as an oxidant.

1.4. Oxidative halogenation

In-situ generation of halonium species via the oxidation of halides using suitable oxidants under moderate reaction conditions.
An increasing environmental concerns and advanced studies on oxidative halogenations, it is desirable for synthetic chemists to study and understand in-depth the oxidative halogenations. Oxidative halogenations is widely used in industry during the preparation of vinyl chloride, where waste HCl generated during the production of isocyanate is regenerated by passing it together with oxygen and ethylene in the gas phase over a Cu (II) catalyst at a temperature of over 200ºC [10].

1.4.1. Oxyhalogenations in nature

Nature has always served as a source of inspiration for those working in diverse areas from creating intelligent systems to discovering new building blocks. In this respect, organic chemistry is no exception, although chemists have yet to match the efficiency by which nature synthesizes complex and chiral molecules. A good example is halogenation: Electrophilic halogenation in nature mainly occurs by oxidative halogenation through the enzyme catalyzed oxidation of the halide ion to form a halogenating reagent (An exception is fluorination, since it is too difficult to oxidize fluoride) [11].

1.4.1.2. Enzymes

Halogenating enzymes are divided into five classes, which are shown in Table 1.1. The first halogenating agent discovered in biological systems was the heme-dependent enzyme chloroperoxidase (isolated from the fungus Caldariomyces fumago) which uses H₂O₂ and chloride anions for “electrophilic” chlorination [12]. To date, chloroperoxidase from
Table 1.1. Classes of halogenating enzymes

<table>
<thead>
<tr>
<th>Entry</th>
<th>Enzyme</th>
<th>Proposed form of activated halogen</th>
<th>Substrate requirements</th>
<th>Cofactor and co substrate requirements</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Heme iron-dependent haloperoxidases</td>
<td>$X^+$</td>
<td>Aromatic and electron-rich</td>
<td>Heme, $H_2O_2$</td>
</tr>
<tr>
<td>2</td>
<td>Vanadium-dependent haloperoxidases</td>
<td>$X^+$</td>
<td>Aromatic and electron-rich</td>
<td>Vanadate, $H_2O_2$</td>
</tr>
<tr>
<td>3</td>
<td>Flavin-dependent halogenases</td>
<td>$X^+$</td>
<td>Aromatic and electron-rich</td>
<td>$FADH_2$, $O_2$</td>
</tr>
<tr>
<td>4</td>
<td>Non-heme iron-dependent halogenases</td>
<td>$X^-$</td>
<td>Aliphatic, unactivated</td>
<td>$Fe(II)$, $O_2$, $R$-ketoglutarate</td>
</tr>
<tr>
<td>5</td>
<td>Nucleophilic halogenases</td>
<td>$X^-$</td>
<td>Electrophilic, good leaving group</td>
<td>$Fe(II)$, $O_2$, $R$-ketoglutarate</td>
</tr>
</tbody>
</table>

Caldariomyces fumago remains the most studied halogenating enzyme. The use of enzymes for halogenation is still potentially the most effective and environmentally friendly route, but so far large scale enzymatic halogenation has not been commercialized because of the low operational stability of the haloperoxidase enzymes (resulting from either inactivation with $H_2O_2$ or the organic solvent) [13]. Consequently, these reactions need to be performed in mixtures of dilute aqueous buffer and organic solvents, thus rendering them economically unattractive.

Nevertheless, research on biological halogenation has boosted the interest in oxidative halogenation and has resulted in the development of several environmentally friendly methods with various catalysts, oxidants and reaction media.

1.4.2. Brominating reagents

Various brominating reagents are reported in the literature. The most classical primary brominating reagent is liquid bromine. Other secondary reagents such as N-bromosuccinimide (NBS), 2,4,4,6-tetrabromo-2,5-cyclohexadien-1-one (TBCD) etc. are also well reported. In the recent years modified oxybrominating reagents are also developed.
1.4.2.1. Liquid bromine

Liquid bromine is very good oxidizing as well as brominating reagent. It adds across unsaturated hydrocarbons (carbon-carbon double and triple bond) to give addition product and incorporated into aromatic nucleus to give nuclear brominated product through electrophilic substitutions. Bromination reactions of organic substrates carried out with liquid bromine are well reported [14]. Bromine combines with other supports such as Br$_2$/NaY zeolite and Br$_2$/alumina are reported for bromination of aromatic substrates [15]. The bromine complex of poly(styrene-co-4-vinylpyridine) [16a], hexamethylenetetramine-bromine/basic alumina [16b] and dioxane–bromide/silica gel [16c] are effective for the conversion of ketones to bromoketones.

1.4.2.2. N-Bromosuccinimide

N-Bromosuccinimide is used in radical bromination reactions and electrophilic addition reactions in organic chemistry. NBS considered as a convenient source of cationic bromine and used for selective oxidations and bromination reactions. The reaction of NBS catalyzed by different catalysts such as Mg(ClO$_4$)$_2$ [17a], Amberlyst-15 [17b], trimethylsilyl trifluoromethanesulphonate (TMSÆOTf) [17c], NaHSO$_4$/Silica [17d], ammonium acetate [17e], photons (light) [17f], Pd(II)/TfOH [17g], (+)-CSA/(DHQD)$_2$PHAL [17h], [Rh(III)Cp*] [17i], isoselenazolone [17j], Pd(OAc)$_2$ [17k] and (S)TRIP/Ph$_3$PS [17l] are effective systems for the bromination of various organic compounds.

1.4.2.3. Other brominating reagents

Many metal centers such as iron, vanadium, molybdenum interact with oxidants having suitable bromide source will react with organic substrate to provide oxybromination products. Due to the better understanding of vanadium role in biological systems, the vanadium and
molybdenum complexes can act as functional mimics of enzyme \textit{vanadium peroxidase}. Oxybromination of various organic compounds can be achieved using aqueous solution of KBr-H$_2$O$_2$ in presence of mineral acid with catalytic amount V$_2$O$_5$ [18]. Also the vanadium catalyzed oxidative bromination of toluene [19a] alkenes and alkynes performed in the aqueous or in a biphasic medium [19b]. A similar reaction has been reported using molybdenum catalyst [20a] as well as in ionic liquids [20b]. Generally, the bromination of sp$^3$ carbon is a challenging task. Reis \textit{et al} observed that salts of synthetic amavidine complex catalyze the bromination of cyclohexane in acetonitrile/water medium in presence of KBr, HNO$_3$ and H$_2$O$_2$ [21]. Schiff base binded and polymer supported vanadium complexes are also effective for oxidative bromination [22]. The reports for the preparation of \(\beta\)-bromoalkenes (Hunds Dicker reaction) from unsaturated carboxylic acids using molybdenium catalyst (Na$_2$MoO$_4$.H$_2$O) is available [23]. Similarly, tungsten catalyst (LDH-WO$_4^2-$) has been used to brominate various alkenes in presence of NH$_4$Br and H$_2$O$_2$ [24]. Methyltrioxorhenium (MTO) used for rapid bromination of phenols and phenyl acetylenes in quantitative yields [25]. The attempts were made to prepare asymmetric \(\alpha\)-bromination of aldehydes and ketones using C$_2$-symmetric diphenylpyrrolidine [26a] and [Pd(CH$_3$CN)$_2$(S)-\textit{Tol}-BINAP](BF$_4$)$_2$ or [Pd(CH$_3$CN)$_2$(S)-\textit{METBOX}](BF$_4$)$_2$ [26b] as catalysts. Masuda \textit{et al} [27] have employed NaBrO$_3$-NaHSO$_3$ reagent combinations for the preparation of bromohydrins. The reaction of the \(N\)-methylpyrrolidin-2-one hydrotribromide complexes (MPHT) with substituted-1-tetralones provided selective \(\alpha,\alpha\)-dibrominated tetralones [28]. The reagents pyridiniumbromide perbromide [29a], quaternary ammonium tribromide [29b], and 2-carboxyethyltriphylphosphonium perbromide [29c] reagents are reported. The reagents 2,4,4,6-tetabromo-2,5-cyclohexadien-1-one (TBCO) [30a] and 2,4,4,6-Tetrabromo-3-\(n\)-pentadecyl-2,5-cyclohexadienone (TBPCO) [30b] are selective and useful brominating reagents.
NaBrO$_2$ in acetic acid [31a] and Selectfluor/KBr [31b] are useful for oxybromination of alkenes to $\alpha$-bromoketones. NaBrO$_3$/H$_2$SO$_4$ has shown to be a promising reagent for bromination of aromatic rings having electron withdrawing substituents [32] NaBrO$_3$/HBr in sulfuric acid or acetic acid medium has been used for bromination of several amides and imides [33], while Ishii et al. have shown that NaBrO$_3$/NaHSO$_3$ is a good reagent for the bromination of alkyl benzenes and for the synthesis of bromohydrins from alkenes [27,34]. BrCl has been used for substitution reactions and the reactions are reported to be faster than those involving bromine alone [35]. Recently, NaBr-H$_2$O$_2$ catalyzed by CeCl$_3$ [36a], H$_2$O/scCO$_2$ [36b], HBr/O$_2$ catalyzed by NaNO$_2$ [36c], KBr-H$_2$O$_2$ catalyzed by polymer anchored Cu(II) [36d], NaBr/O$_2$ catalyzed by palladium-polyoxometalate [36e], LiBr/PhI(OAc)$_2$ [36f], NaBr/NaIO$_4$/H$_2$SO$_4$ [36g], NaBr/H$_2$O$_2$ over ionic catalyst [36h], KBr/H$_2$O$_2$ catalyzed by V-MCM-41 [36i] and trifluoromethanesulphonic anhydride with Grignard reagent or MgBr$_2$ [37] were reported for oxybrominations.

In spite of large number of applications of liquid bromine in organic chemistry, it is not recommendable because of its hazardous nature and extreme care for its production, transportation and utilization particularly in graduate and undergraduate levels. Moreover, for bromination reactions half of the bromine atoms end up in the effluent as hydrobromic acid leading to low atom economy and generation of waste. NBS is safe and selective reagent but it also generates succinimide as organic byproduct. Being organic in nature, succinimide creates problems in isolation and purification of desired organic products in some cases. Also liquid bromine is used for its preparation. Some of the handy reagents are prepared for example pyridinium bromideperbromide which is easy to handle but its preparation also requires pyridine as a starting substrate and pyridine is responsible for impotency. In some cases the halogen atom efficiency is improved by using oxidants and transition metal catalysts. In order to minimize
above indicated problems, alternatively safe and environmentally benign brominating reagents and oxidants are utilized for the present research purpose which are described in the following sections.

1.5. Applications of brominated organic compounds

1.5.1. Applications of brominated aromatic compounds

Brominated aromatic compounds are useful synthetic intermediates in the manufacture of pharmaceuticals, fine chemicals, agrochemicals and other specialty chemicals like flame retardants, pesticides, herbicides, etc [38]. They are also useful and important key intermediates for cross coupling reactions [39] and as precursors to organometallic reagents [40]. In addition, several aryl bromides are biologically active and used as potential antitumour, antibacterial, antifungal, antineoplastic antipsycholic, antioxidizing and antiviral agents (Fig. 1-3) [41].

1.5.2. Applications of brominated carbonyl compounds

The α-bromination of ketones is an important transformation in synthetic organic chemistry [42]. α-Bromoketones are among the most versatile intermediates in organic synthesis and their high reactivity makes them prone to react with large number of nucleophiles to provide a variety of biologically active compounds [43] (some of the biologically active compounds which are synthesized from α-bromoketones are shown in Scheme 1.1). α-Bromoacetophenone derivatives have been investigated for their active participation in the inhibition of protein tyrosine phosphatase such as SHP-1 and PTP1B [44]. Bromination at the reactive position in a 1,3-keto compound enhances bioactivity, particularly cytotoxicity against breast cancer 1A9 cells, with respect to the unsubstituted compound [45].
Antibacterial, antitumor agents, pesticides, glucagon receptors, antagonists, p38 mitogen-activated protein kinase inhibitors and B-Raf kinase inhibitors [46].

Antithyroid drugs, anti-inflammatory, inhibition of T-cell antigen receptors, potent CCR2 antagonists as well as antioxidants [47].

Anticancer, antioxidative and anti-inflammatory properties [48].

Antibacterial, phosphatase and aromatase inhibiting, antioxidant, antidepressant and antitumor activities [49].

Antinflammatory, analgesic and kinase (CDK1, CDK5 and GSK3) inhibition, antifungal, melanin-reducing activity (skin whitening agent) and as platelet GPIIb/IIIa receptor antagonists [50].

Antibiotics (echinomycin, leromycin, and actinomycin), wide application in dyes, efficient electroluminescent material, organic semiconductors, dehydroannulenes, and chemically controllable switches [51].

Transthyretin amyloid fibril inhibitors [52].

Antiviral, antitumor, antimicrobial, herbicidal and immunosuppressive agent [53].

**Scheme 1.1.** Biologically active compounds which are synthesized from α-bromoketones
1.5.3. Applications of bromohydrins, bromo ethers and dibromides

Vicinal bromohydrins, bromo ethers and dibromides are versatile intermediates for the synthesis of pharmaceuticals, dyes, flame retardants, agrochemicals, additives, plasticizers and specialty chemicals (Scheme 1.2) [54].

Scheme 1.2. Applications of bromohydrins, bromo ethers and dibromides
1.6. Oxone

Oxone is a white crystalline solid, which contains component of a triple salt with the formula $2\text{KHSO}_5\cdot\text{KHSO}_4\cdot\text{K}_2\text{SO}_4$ [55]. The active component in the triple salt is KHSO$_5$. Oxone is also known as Potassium peroxymonosulfate, potassium monopersulfate and the trade name Caroat. It is the potassium salt of peroxymonosulfuric acid.

Oxone is a cheap commercially available oxidant that easily oxidizes numerous functional groups. It is an efficient single oxygen-atom donor since it contains a nonsymmetrical O–O bond which is heterolytically cleaved during the oxidation cycle. It is an inexpensive reagent ($0.02–0.04/g$), which compares favorably with hydrogen peroxide and bleach. It is about one-half as expensive as $m$-chloroperoxybenzoic acid ($m$CPBA). Its byproducts do not pose an immediate threat to aquatic life upon disposal, and unlike chromium trioxide and bleach, it does not emit pungent vapors or pose a serious inhalation risk. Its main advantage over hydrogen peroxide is easier handling. HSO$_5^-$ is proposed to be an intermediate in the atmospheric oxidation of sulfur and it is hypothesized that 35% of the total sulfur species in clouds exist as HSO$_5^-$.

As long as oxone is stored under dry and cool conditions, it loses about 1% activity per month under release of oxygen and heat. Decomposition to SO$_2$ and SO$_3$ takes place under the influence of heat (starting at $300^\circ\text{C}$). Acidic, aqueous solutions of the pure reagent in distilled water are relatively stable. The stability reaches a minimum at pH 9, where the mono anion (HSO$_5^-$) has the same concentration as the dianion (SO$_5^{2-}$). Iron, cobalt, nickel, copper, manganese and further transition metals can catalyze the decay of oxone in solution.

Oxone is also an environmentally friendly oxidant with no toxic by-products, and thus is an attractive green reagent. These features make oxone attractive for large-scale applications.
Uses of other oxidizing agents lack the desired ingredients to attract the interest of industry because of tedious purification processes from their deoxygenated counterparts.

1.7. Applications of oxone

Owing to its high stability simple manipulation, non-toxic nature and efficiency, oxone has found many applications in the oxidation of organic compounds, primary oxidant for water oxidation catalyst and shock oxidizer.

1.7.1. Oxidation of organic compounds using oxone

Oxone has found many applications in the oxidation of functional groups such as alkanes, alkenes, alkynes, alcohols, carbonyl compounds, carboxylic acids, amines, amides, nitro compounds, boron, sulphur and phosphorus compounds (Scheme 1.3-1.9) [55].

Scheme 1.3. Oxidation of alkanes using oxone

Scheme 1.4. Oxidation of alkenes using oxone
Scheme 1.5. Oxidation of alkynes using oxone

Scheme 1.6. Oxidation of alcohols using oxone

Scheme 1.7. Oxidation of carbonyl compounds and carboxylic acids using oxone
Scheme 1.8. Oxidation of amines, amides and nitro compounds using oxone

\[(\text{R}_3\text{B}) \rightarrow (\text{RO})_3\text{B}\]

\[
\begin{align*}
\text{R-S-R} & \rightarrow \text{R-SR} \\
(\text{R})_3\text{P} & \rightarrow (\text{R})_3\text{P} = \text{O}
\end{align*}
\]

Scheme 1.9. Oxidation of boron, sulphur and phosphorus compounds using oxone

1.7.2. Oxone as a primary oxidant for water-oxidation catalyst

Increased global attention to the effects of releasing carbon dioxide into the atmosphere by burning fossil fuels has led to investigation of alternative fuel sources. One of the most promising of such methods is artificial photosynthesis. In an artificial photosynthetic cell, solar energy is collected and passed to a water-oxidation catalyst (WOC) that splits water into dioxygen, protons and electrons. The electrons produced can then reduce protons to form...
dihydrogen or may be used to reduce other organic molecules or CO₂ to products that can serve as fuels.

Oxone, is a powerful two-electron oxidant that has seen success in characterizing WOCs [56]. The reduction potential of oxone is 1.82 V vs. NHE, comparable to that of Ce(IV). Oxone has seen extensive use in the study of the Mn terpyridine dimer, and has since been used with a number of other first row transition metal complexes. In addition to being a two electron oxidant, oxone also has the ability to behave as an oxo-transfer reagent, leading to the possibility that oxygen produced by WOCs driven by oxone is unrelated to water oxidation.

As a two-electron oxidant, oxone can drive WOCs that form unstable complexes when they undergo one-electron oxidation. This is the primary reason that oxone has been useful in characterizing WOCs based on first row transition metals, which have a tendency to be more labile than their second and third row counterparts. Oxone is also stable up to a pH of about 5.5, allowing for characterization of WOCs at pH values close to neutral where an ‘artificial leaf’ might function. Additionally, the reduction product of oxone is sulfate, a relatively benign by-product.

1.7.3. **Oxone as a shock oxidizer**

Oxone can be used in swimming pools to keep the water clear, thus allowing chlorine in pools to work to sanitize the water rather than clarify the water, resulting in less chlorine needed to keep pools clean. The benefits of using oxone in pools are given below [57].

1) Keeps the water crystal clear

2) Reduces eye, nose and skin irritation

3) Eliminates the strong chlorine smell

4) Keeps pool surface and bathing suits looking newer
5) Very less time (15 minutes) is required to dissolve and spread through the water

1.8. Organic transformations using oxone in the present work

Oxidation of various organic compounds using oxone in the present thesis is shown in Scheme 1.10 and which are deeply discussed in chapters 4 and 5.

Scheme 1.10. Organic transformations in the present work using oxone
1.9. References


Section B
Zeolites

1.10. Zeolite molecular sieves

Zeolites are defined as crystalline microporous aluminosilicates with pore structures consisting of a three dimensional network of \([\text{SiO}_4]\) and \([\text{AlO}_4]\) tetrahedra linked by corner sharing of oxygen ions. The term Zeolites (Greek, zeo,"to boil", lithos, "a stone") was originally coined in the 18th century by a Swedish mineralogist named Axel Fredrik Cronstedt who observed, upon rapidly heating a natural mineral (Stilbite) that the stones began to dance about as the water evaporated. Using the Greek words which mean "stone that boils", he called this material as zeolite [1]. The first reported synthetic zeolite was Linde A. This was synthesized in 1949 by Milton, working at Union Carbide. Zeolites can be described with the following empirical formula [2]:

\[
\text{M}_{2/n} \cdot \text{Al}_2\text{O}_3 \cdot \text{XSiO}_2 \cdot \text{YH}_2\text{O}
\]

Where M represents the exchangeable cations, n represents the cation valency and, X can assume a value equal or greater than 2 as no two Al\(^{3+}\) can occupy the adjacent tetrahedral position (Lowenstein rule) [3] and Y is the number of H\(_2\)O molecules present in the channel or cavities of the three dimensional network.

The porous materials may be divided into three types based on their pore dimensions, namely, microporous (< 2 nm), mesoporous (2-50 nm) and macroporous (> 50 nm). The pores of the zeolites are of molecular dimensions ranging between 0.5 and 1.0 nm in diameter. Hence, zeolites are also known as molecular sieves because of their ability to discriminate the molecules
of different size and shape. The characteristics, which make molecular sieves useful as catalysts are:

- Generation of highly acidic sites when exchanged with protons.
- Shape selective catalytic properties.
- High surface area and thermal stability.
- Ease of regeneration of the initial activity.

1.11. Nomenclature of zeolite molecular sieves

Milton, Breck and coworkers at Union Carbide employed Arabic alphabets, viz., zeolites A, B, X, Y, L. Mobil and Union Carbide later used the Greek alphabets alpha, beta and omega. Many of the synthetic zeolites have the structural topology of mineral, for example, synthetic mordenite, chabazite, erionite and offretite.

The IUPAC nomenclature was evolved in 1979, with acronyms viz., ZSM-5, ZSM-11, ZK-4 (Mobil); EU-1, FU-1, NU-1 (ICI); LZ-210, ALPO, SAPO, MeAPO, UOP (Union Carbide), ECR-1 (Exxon) [4] etc. and is limited to the known zeolite type material. The IZA Atlas of zeolite structure types published by the International Zeolite Association [5] assigns a three-letter code to be used for a known framework topology irrespective of their chemical composition. Table 1.2 provides the typical IZA Atlas nomenclature of various zeolites.

1.12. Classification

Several attempts have been made to classify the families of zeolites on the basis of their morphological characteristics [6], crystal structure [7], chemical composition [8], effective pore diameter [9] and natural occurrence.
<table>
<thead>
<tr>
<th>Pore size</th>
<th>Structure type (IUPAC)</th>
<th>Trivial names</th>
<th>Pore diameter (Å)</th>
<th>Dimensionality</th>
<th>Adsorbed molecules</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small</td>
<td>LTA</td>
<td>Zeolite A</td>
<td>4.1</td>
<td>3</td>
<td>n-hexane</td>
</tr>
<tr>
<td>Medium</td>
<td>MFI</td>
<td>ZSM-5, TS-1, VS-1</td>
<td>5.3X5.6, 5.1X5.5</td>
<td>3</td>
<td>Cyclohexane</td>
</tr>
<tr>
<td></td>
<td>MEL</td>
<td>ZSM-11, TS-2 VS-2</td>
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<td></td>
<td>TON</td>
<td>Theta-1, ZSM-22</td>
<td>4.4X5.5</td>
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<td>MOR</td>
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<td>Zeolite X or Y</td>
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<td>3</td>
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<td>-</td>
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<tr>
<td></td>
<td>VFI</td>
<td>VPI-5</td>
<td>12.1</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Meso-</td>
<td>MCM-41</td>
<td>15.0-100</td>
<td>1</td>
<td>-</td>
<td>porous</td>
</tr>
</tbody>
</table>
1.12.1. Chemical composition

According to chemical composition zeolites can be classified on the basis of their silica to alumina ratio [8] as low silica zeolites, medium silica zeolites, high silica zeolites and silicalites (Table 1.3).

Table 1.3. Classification of zeolites on the basis of their Si/Al molar ratio

<table>
<thead>
<tr>
<th>Type</th>
<th>Si/Al ratio</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low silica</td>
<td>1 to 1.5</td>
<td>LTA, FAU (Y), LTL, etc</td>
</tr>
<tr>
<td>Intermediate</td>
<td>~ 2 to 5</td>
<td>Natural zeolites: erionite, clinoptilolite, mordenite Synthetic zeolites: Y, large pore mordenite, omega</td>
</tr>
<tr>
<td>High</td>
<td>5 to 500</td>
<td>MFI, BEA, NCL-1, etc</td>
</tr>
<tr>
<td>All silica</td>
<td>α</td>
<td>Si-MFI, Si-UTD-1, etc</td>
</tr>
</tbody>
</table>

1.12.2. Pore opening size

All zeolites have been classified by the number of T atoms, where T = Si or Al, that define the pore opening. Zeolites containing these pore openings are also referred to as: small pore (6 or 8 member ring), medium pore (10-member ring), large pore (12-member ring) and ultra large pore (14-or more member ring). Some examples on the basis of pore size classification are given below in Table 1.4.

On the basis of their morphology, zeolites are classified as fibrous, lamellar etc. Structural classification of zeolites has been proposed depending on differences in secondary building units. With the addition of new synthetic and natural zeolites, they are grouped into ten classes: Analcime, Natrolite, Chabazite, Philipsite, Heulandite, Mordenite, Faujasite, Laumontite, Pentasil and Clatharate.
### Table 1.4. Classification of zeolites based on pore size (pore diameter <2 nm)

<table>
<thead>
<tr>
<th>Zeolite type</th>
<th>Pore opening</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small pore</td>
<td>8-membered ring</td>
<td>MTN, NU-1, etc</td>
</tr>
<tr>
<td>Medium pore</td>
<td>10-membered ring</td>
<td>MFI, MEL, etc</td>
</tr>
<tr>
<td>Large pore</td>
<td>12-membered ring</td>
<td>FAU, MTW, BEA, NCL-1, etc</td>
</tr>
<tr>
<td>Extra large pore</td>
<td>14-membered ring</td>
<td>UTD-1</td>
</tr>
</tbody>
</table>

#### 1.13. Structural details of zeolite molecular sieves

Zeolites are crystalline aluminosilicates with an open lattice framework and contain silica and alumina tetrahedra joined through oxygen bridges to form a three dimensional structure. The primary building units of tetrahedra can arrange themselves in different ways to form different rings of various dimensions. These rings are joined together to form complex secondary building units [10].

The secondary building unit (SBU) consists of selected geometric groupings of primary tetrahedra. There are nine such building units, which can be used to describe all of the known zeolite structures. These secondary building units consist of 4, 6 and 8-membered single rings, 4-4, 6-6 and 8-8 member double rings, and 4-1, 5-1 and 4-4-1 branched rings [11]. The topologies of these units are shown in Fig. 1.4.
Fig. 1.4. Secondary building units and their symbols. Number in parenthesis indicates frequency of occurrence

1.13.1. Zeolite β: structure and properties

Zeolite Beta is a high silica and large pore crystalline material. It is an old zeolite discovered before Mobil began the "ZSM" naming sequence. As the name implies, it was the second in an earlier sequence. Zeolite beta consists of an intergrowth of two distinct structures termed Polymorphs A (tetragonal) and polymorph B (monoclinic). The polymorphs grow as two-dimensional sheets and the sheets randomly alternate between the two. Both polymorphs have a three dimensional network of 12-ring pores. The intergrowth of the polymorphs does not significantly affect the pores in two of the dimensions, but in the direction of the faulting, the
pore becomes tortuous, but not blocked. The two hypothetical polymorphs are depicted in Fig. 1.5 & 1.6 and bond distances and bond angles in zeolite beta are shown in Table 1.5.

![Structure of zeolite Beta (poly type A)](image)

**Fig. 1.5. Structure of zeolite Beta (poly type A)**

**Table 1.5. Bond distance and bond angles in zeolite Beta**

<table>
<thead>
<tr>
<th>Type</th>
<th>Bond distance Si – O (Å)</th>
<th>Bond angle O – Si – O (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly type A</td>
<td>1.616</td>
<td>109.47</td>
</tr>
<tr>
<td>Poly type B</td>
<td>1.616</td>
<td>109.47</td>
</tr>
</tbody>
</table>

![Structure of zeolite Beta (poly type B)](image)

**Fig. 1.6. Structure of zeolite Beta (poly type B)**

Zeolite Beta have several unique and interesting features. It is the only high silica zeolite to have fully three dimensional 12-membered ring pore system and also the only large pore zeolite to posses chiral pore intersections. It has high catalytic potential compared to the faujasite.
type zeolite by virtue of its high silica content, acid site distribution and stacking faults [12]. In addition, the comparatively smaller dimension of one of the two types of pores (5.5 Å) offers a certain level of the shape selectivity similar to that observed in medium pore zeolites.

1.13.2. ZSM-5 (Zeolite Scony Mobile Number 5) structure and properties

ZSM-5 (Fig. 1.7) is the parent zeolite of the Mobile Five (MFI) group, patented by Argauer and Landolt using Na-TPA system in 1972 [13]. The molar oxide composition of the mixtures from which ZSM-5 is crystallized is as follows:

$$(R_4N)^+_2O, M_{2n}, Al_2O_3, XSiO_2, H_2O$$

Where $(R_4N)^+$ is a quaternary ammonium ion and $M$ is the alkali metal cation of valency ‘n’. A wide range of Silica-Alumina contents ($Si/Al = 10-\infty$) in the reaction mixture yields ZSM-5 phase.

Zeolite ZSM-5 is a member of shape-selective catalysts with unique medium pores between large-pore faujasite and small pore zeolites such as Linde type A and erionite. The framework structure is built up of pentasil blocks (Five membered SBUs) and so called pentasil chains. These chains can similarly be connected to form sheets. The three dimensional network is built up by cross linkage of the sheets. The framework contains two types of intersecting channels. One type is straight and has elliptical opening of 10 membered rings of 5.2 X 5.8 Å internal diameter and runs parallel to the b-axis of the orthorhombic unit cell. Nearly circular 10 membered rings of 5.4 X 5.6 Å internal diameter circumscribe another kind of channel. It is sinusoidal (zig-zag) and directed along the a–axis. The maximum diameter at the intersections is about 0.9 nm. The composition of the unit cell in Na form is Na$_n$ [Al$_n$ Si$_{96-n}$ O$_{192}$]16 H$_2$O. (n <27 and typically equal to 3) [14]. The number of atoms obtained from the unit cell is from relation

$$N_{Al} = \left[\frac{96}{1+R}\right],$$
Where $R = \frac{N_{\text{Si/Al}}}{N_{\text{Si}}}$, $N_{\text{Si}}$ and $N_{\text{Al}}$ are grams of atoms of Si and Al, respectively.

**Fig. 1.7.** Structure of MFI Zeolite (ZSM-5): (A) Mode of interconnection of pentasil chains (B) with emphasized chain system.

### 1.14. Characteristic properties of zeolite molecular sieves

#### 1.14.1. Shape selectivity of zeolites

The capability of molecular sieves to organize and to discriminate molecules with high precision is responsible for their shape selective properties [15]. Shape selectivity has been studied in reversible and acid catalyzed processes [16]. Csicsery [17] defined the three well-known categories of shape selectivity (Fig. 1.8).

- **Reactant shape selectivity:** Only molecules that are able to enter the zeolite channels will react.
- **Product shape selectivity:** Only molecules that are able to diffuse out of the zeolite channels are found in the product mixture.
- **Restricted transition-state shape selectivity:** Reactions occurs only when the required transition state can be formed in the zeolite cavities.
1.14.2. Zeolite molecular sieves as acids and bases

*Zeolite molecular sieves as acids:* There are two types of acid catalytic activity associated with zeolites namely, Bronsted acidity (H⁺) and Lewis acidity. In zeolites the centers of the TO₄ tetrahedra are occupied by silicon and aluminum atoms in a Si/Al ratio from 1 to ∞. The difference in valencies of Si (tetravalent) and Al (trivalent) produce an overall negative charge for each incorporated aluminum atom. These negative charges are balanced by alkali and/or alkali earth cations. Bronsted acid site in catalyst arises when cations (often Na, K or Cs) are replaced by proton (H⁺, from ammonium ion exchange, followed by the thermal decomposition of the ammonium form to H⁺ form of the zeolites).
Lewis acid sites arise at the defect sites where triagonal Al is present either in the framework or at charge compensating ions. The Lewis acidity can also be formed by high temperature (>500°C) dehydroxylation of the Si (OH) Al (i.e. Bronsted) sites (Fig. 1.9).

![Image](image.png)

**Fig. 1.9.** Schematic showing Lewis and Brønsted acid sites on an aluminosilicate surface.

The strength of these acid sites is found to vary with (i) zeolite structure (ii) Si/Al ratio and (iii) isomorphously substituted metal ions in the zeolite framework [18]. The acid strength increases with decreasing aluminum content and the number of acid sites decreases. The strength of acidic sites is also influenced by the nature of the trivalent atom in the framework. Chu and Chang [19] showed that substitution of Al by B, Fe or Ga in framework of MFI zeolite decreases the strength of the Bronsted acid sites in the order Al-MFI > Ga-MFI > Fe-MFI > B-MFI.

The effects discussed above allow tailoring of basicity and acidity from weakly basic to strongly acidic [20]. A metal cation or a proton that constitutes a Lewis- or a Brönsted- acid site, respectively [21] balances the negative charge in the zeolite framework. In solid acid catalysts the number of potential Bronsted acid sites is equal to the number of trivalent atoms present in the silica framework. For zeolites it can be stated that the concentration of aluminum in the lattice is directly proportional to the concentration of acid sites and the polarity of the lattice is indirectly proportional to the strength of acid sites [22]. For a given chemical composition of the zeolite, the polarity of the lattice increases with decreasing framework density [23]. Thus, by changing the framework Si/Al ratio, either during synthesis or post-synthesis, it is possible to change not only the total number but also the acid strength of the Bronsted acid sites.
Extra-framework aluminum also creates the acidity in zeolites. When zeolites are dealuminated by steam-calcination part of the framework Al is extracted and generates extra-framework species (EFAL) that can be cationic, anionic or neutral. Some of these EFAL species can act as Lewis acid sites [24] or can influence the Bronsted acidity, by either neutralizing Bronsted Acid sites by cation exchange or by increasing the acidity by a polarization effect and/or by withdrawing electron density from lattice oxygens [25]. This opens the way to Lewis acid catalysis by the Al [26].

**Zeolite molecular sieves as bases:** According to Barthomeuf and Kazansky, the extra framework protons and cations in zeolites are the Bronsted and Lewis acid sites, respectively, while the framework oxygens are their conjugated basic sites [27]. Except for non-oxide catalysts among various heterogeneous basic catalysts the basic sites are believed to be surface oxygen atoms. Oxygen atoms existing on any materials may act as basic sites because any oxygen atom would be able to interact with a proton.

### 1.14.3. Hydrophobicity of zeolite molecular sieves

In zeolites, the hydrophilicity and hydrophobicity can be easily manipulated. Siliceous and high SiO₂/Al₂O₃ ratio zeolites are less hydrophilic and more organophilic, which are well suited for chemical transformations. Hydrophobicity of the titanium silicate framework is held responsible for the high activity of these materials in the heterogeneous catalytic oxidation of organic compounds with aqueous hydrogen peroxide solutions compared to an amorphous Titania-silica mixture [28].

### 1.14.4. The physico-chemical properties of zeolite related to its SiO₂/Al₂O₃ ratio

An important variable in the main group of zeolites is the Si/Al ratio, which has a bearing on several properties as shown in Scheme 1.3 [29]. In the case of zeolites from type A to silicate...
as Si/Al ratio increases, thermal stability and acidity increases. According to Olson [30], ion exchange capacity and catalytic activity increases with increasing Al content, while hydrophobicity increases with decreasing Al in the framework.

![Scheme 1.11](image)

**Scheme 1.11.** Various properties depending on Si/Al ratio

**1.15. Concepts of zeolite synthesis**

**1.15.1. Natural zeolites**

Zeolites occur in nature in vugs and vesicles of basic lava, in specific kinds of rocks subjected to moderate geological temperature and pressure. The formation of such zeolites with volcanic glass and saline water as reactants must have occurred in temperature range 300-350 K and pH > 13, requiring several years of crystallization [31]. Many of these natural zeolites have been commercialized for purification of natural gas (chabazite), radioactive waste disposal (clinoptilolites), ammonia recovery from sewage effluents (clinoptilolite) and various petroleum and petrochemical catalyst applications (eronite, mordenite).

**1.15.2. Concept of zeolitization**

The hydrothermal synthesis of aluminosilicate zeolites, in a broad sense, corresponds to the transformation of a mixture of silica and alumina compounds, inorganic bases like sodium hydroxide, organic quaternary ammonium salts either in the form of hydroxides or halide and
water in the form of an alkaline super saturated solution into micro or mesoporous crystalline aluminosilicates. The complex chemical processes involved in this transformation are schematically presented in Fig 1.10.

![Figure 1.10](image)

**Fig. 1.10.** A schematic representation of zeolite formation process in an autoclave. (SDA = Structure Directing Agent)

### 1.15.3. Zeolitization process sequence

The important steps involved in the zeolitization process are:

- Rapid formation of an aluminosilicate hydro-gel.
- Solid phase dissolution mediated by mineralizing agents to provide a solution of silicate and aluminate monomer and oligomer.
- Ageing of the hydrogel for specific period of time at predetermined temperature to achieve desired crystalline characteristics [32].
- Simultaneous dissolution or depolymerization of the silica sol particles, which is catalyzed by alkaline conditions [33].
- Copolymerization of the monomeric silicate anions in solution to yield negatively charged oligomeric species.
- Rapid intra and intermolecular exchange of silicate monomers [34].
Reaction of oligomeric silicate species with monomeric \([\text{Al(OH)}_4]^-\) to produce aluminosilicate structures [35]. They are more stable in the ring and cage like structures than in the linear chains [36] and are called “secondary building units (SBU)”, which are essential for both the nucleation and crystal growth processes.

Ageing and heating of hydrogel to crystallization temperature in the range of 60 to 200°C [33].

1.16. Factors influencing zeolitization

The parameters such as molar composition, alkalinity, temperature, time of heating and nature of template play a major role in the zeolitization process.

1.16.1. Molar composition of gel

The chemical composition of the hydrogel can be expressed in terms of: \(a\ \text{SiO}_2 : b\ \text{Al}_2\text{O}_3 : c\ \text{MxO} : d\ \text{NyO} : e\ R : f\ H_2\text{O}\) in which M and N stand for (alkali) metal ions, R for organic template and ‘a’-‘f’ are molar ratios. The relative amounts of Si, Al, M, N and R are key factors in deciding the outcome of crystallization process. Their molar ratio can influence nucleation and crystallization processes, nature of the crystalline material, lattice Al content and its distribution and the crystal size and its morphology [37].

1.16.2. Alkalinity

The alkalinity of the synthesis solution (which is generally between 9.0 and 13.0) is a key factor in zeolite formation. The \(\text{OH}^-\) ions play a crucial role in the mineralization process for bringing Si and Al oxides into solution at optimum rate. Increased pH can accelerate the crystal growth, and shorten the induction period (the period before the formation of viable nuclei) by enhancing the precursor concentration.
1.16.3. Temperature and time of heating

Temperature and time of heating have positive influence over zeolite formation. At higher temperature, both the nucleation and the linear growth rates are increased. Zeolite synthesis is governed by the occurrence of successive phase transformations with thermodynamically least favorable phase crystallizing first. As time progresses, more stable phases are formed. The precise effect of temperature and time parameters largely depends on the type of the zeolite synthesis.

1.16.4. Nature of templates

Templates, which are also called as structure-directing agents, contribute both thermodynamically and chemically to the formation of the zeolite lattices. Generally the templates are cationic, anionic or neutral forms of organic / inorganic entities. The present knowledge is not yet adequate to pre assess the type of template needed for obtaining a specific zeolite with a required structure and composition. However, it is well established that the factors like solubility, stability under synthesis conditions and steric compatibility are important for template design [38]. The method of removing the template without destroying the zeolite framework has also been standardized [39].

1.17. Applications of zeolite molecular sieves

Due to the diverse properties of zeolite molecular sieves, these materials are finding applicability in a broad range of industrial processes that are environmentally sensitive. Zeolites have been explored as catalysts in petrochemical [40] and to some extent in fine chemical synthesis [41]. The industrial use of zeolites started at the beginning of 1960’s with replacement of cracking catalysts based on the amorphous alumino silicates [42]. Number of reviews have
documented the applications of zeolite molecular sieves [43]. Few important applications are discussed here.

1.17.1: Zeolites in petrochemical processes

The use of silicon rich zeolites as highly acidic, extremely shape selective and thermally stable catalysts led to new industrial petrochemical processes [44] selectoforming [45], olefin oligomerizations [46], Dewaxing [47] and MTG (Methane to Gasoline) [48]. Zeolites are much more active than silica-alumina in cracking of small molecules such as light alkanes. In the petrochemistry, a major isomerization process based on zeolites is the xylene isomerization process. The process essentially converts the less desired m-xylene into an equilibrium mixture of xylenes. Both mordenite and ZSM-5 have been used as catalysts for this purpose.

1.17.2: Zeolites in fine chemical process improvements

The fine chemical industry is generally defined as the selective production of organic compounds containing functional groups. Traditionally, many of these processes have been homogeneous, liquid phase catalyzed systems that generate large quantities of waste during the neutralization processes including contaminated water streams, salts and heavy metals. These materials make the work up costly and can lead to corrosion problems and increased costs. Zeolites are being extensively studied as heterogeneous catalysts that can be recovered and recycled more easily and cheaply leading to less waste and fewer by-products [49]. The cost of the materials is cheaper and the processes are more efficient, frequently combining all of the reactants in one pot. Zeolites are also more selective in comparison to classic synthetic paths. One such example is the use of microporous Titanium silicalite-1 [50] catalyst for selective oxidation of a variety of organic substrates by aqueous H₂O₂ under milder conditions [51].

1.17.3: Zeolites in acid catalysis
Alkylation reactions are the major source of petrochemicals/bulk chemicals such as ethylbenzene, cumene and xylenes. The earlier processes used mineral acids such as H₂SO₄, HF, AlCl₃ and BF₃. The recent processes use zeolites (safe solid acids) as catalysts. An added benefit of zeolites is their shape selective property, which results in the production of a specific isomer. Examples of shape selective alkylations using zeolites practiced in the industry are the production of p-diethyl benzene (modified ZSM-5), 2,6-dialkyl naphthalene and 4,4’-dialkyl biphenyls (dealuminated mordenite) [52]. Synthesis of 4-Methyl thiazole (4-MT) over Cesium loaded zeolites is a first example of commercially useful basic zeolites [53].

1.17.4: Zeolites in rearrangement and cyclization reactions

Kulkarni et al. [54] have reported extensively in the cyclization and macro cyclization reactions using zeolites or meso porous molecular sieves such as MCM-41 as catalysts. The products of these reactions have resulted in very important organic intermediates, which are used in the preparation of agro chemicals, drugs, and in host-guest chemistry.
1.18. Objectives and scope of the present work

- To develop eco-friendly process for the oxybromination of aromatic compounds using simple inorganic salt like NH₄Br as bromine source and oxone as an oxidant.
- To develop eco-friendly process for the α-bromination of ketones, 1,3-dicarbonyl compounds and β-keto esters and α,α-dibromination of 1,3-dicarbonyl compounds and β-keto esters using NH₄Br/Oxone.
- To develop eco-friendly process for the hydroxybromination, dibromination and alkoxybromination of olefins using NH₄Br/Oxone.
- To develop eco-friendly process for the synthesis of cyclic acetics and esters from olefins using I₂ as a catalyst and oxone as a terminal oxidant.
- To develop metal modified zeolites for the cyclization reactions in vapour phase for the synthesis of annelated pyridines.
- To develop metal modified zeolites for the tetrahydropyranulation of alcohols.

The scope of this thesis to develop a simple, economic and environmentally safe processes for bromination of aromatic compounds, carbonyl compounds and olefins using NH₄Br as brominating agent and oxone as an oxidant. To develop eco-friendly process for the synthesis of cyclic acetics and esters from olefins using I₂ as a catalyst and oxone as a terminal oxidant. To study the modification of zeolite Beta with Ni, Cu, Pb, La, Ce, Cr, Fe, W, Zn, Co, Mo, Zr and Sn metal cations and characterize them by XRD, IR, and Elemental analysis. To use above prepared metal modified zeolites as catalysts for the synthesis of various annelated pyridines in vapour phase. To use metal modified zeolite Beta as catalysts for tetrahydropyranulation of alcohols. The organic products were characterized by using GC, ¹H NMR, ¹³C NMR, MASS, IR and CHNS elemental analyzer.
1.19. References

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