SYNTHESIS OF SELECTED FLUOROCOMPOUNDS OF COPPER(I) AND MANGANESE(III)

AND

DEVELOPMENT OF PEROXO-METAL ASSISTED ENVIRONMENTALLY PREFERABLE METHODOLOGIES AND REAGENTS FOR BROMINATION OF ORGANIC SUBSTRATES

By

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to the
DEPARTMENT OF CHEMISTRY
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Certificate

It is certified that the work contained in the thesis entitled " SYNTHESIS OF SELECTED FLUOROCOMPOUNDS OF COPPER(I) AND MANGANESE(III) AND DEVELOPMENT OF PEROXO-METAL ASSISTED ENVIRONMENTALLY PREFERABLE METHODOLOGIES AND REAGENTS FOR BROMINATION OF ORGANIC SUBSTRATES " by Siddhartha Sankar Dhar, a student in the Department of Chemistry, Indian Institute of Technology, Guwahati for the award of degree of Doctor of Philosophy has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

12 July, 2001

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SS Dhar
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(Siddhartha Sankar Dhar)

PREFACE

Transition metal chemistry has contributed tremendously to organic synthesis for several decades and it seems clear that this trend will continue in the future. Transition metal based development of alternate and better routes to reagents, catalysts and methodologies for organic transformations have gained a great momentum in recent times. The synthesis of new organic molecules and the improved synthesis of the known ones has always been a major challenge to the chemists. And to this end inorganic chemists appear to have a significant role to play. Having been motivated by this, the Ph.D. research was oriented to address some of the aspects of topical importance as emphasised above. The thesis entitled " *Synthesis of Selected Fluorocompounds of Copper(I) and Manganese(III) And Development of Peroxo-Metal Assisted Environmentally Preferable Methodologies and Reagents for Bromination of Organic Substrates* " is thus an outcome of our endeavour in this direction. The transition metals have been drawn from copper, manganese, iron, vanadium and molybdenum.

The results of investigation of mixed fluoro complexes of copper(I), viz., $CuF(PPh_3)_3.2ROH$ (R= Me or Et), and a hexafluoromanganate(III), i.e. $(NH_4)_3[MnF_6]$, though constitutes a rather minor part of thesis, is important. While the former not only provides a handle for stabilising fluorocuprate(I) but also likely to exhibit important catalytic activity, the latter demonstrates an example of fluoride assisted stabilisation of manganese(III). The chosen manganese(III) compound is capable of being used as a good source of trifluoromanganese(III), MnF_3, which is an important fluorinating agent. Unlike the synthetic studies made on copper(I) and manganese(III) as stated above, the knowledge of peroxo-chemistry of vanadium(V) and molybdenum(VI) (*cf.* MoO_2^{2+}) has

been utilised to activate the dioxygen (O_2^{2-}) by coordinating with the metal center followed by making use of the activated dioxygen to oxidise bromide (Br^-) in turn to an active bromine species, e.g., tribromide (Br_3^-). This concept-based strategy ultimately led to the development of an environmentally benign route to the synthesis of useful brominating reagent like cetyltrimethylammonium tribromide (CTMATB) and protocols for bromination of organic substrates including aromatics. Indeed, the newer synthesis of reagents as well as the safer methodologies for bromination is expected to be the methods of choice for practicing chemists.

As we go along the line of bromination of organic substrates by a classic brominating agent Br_2, we get to learn that a catalytic amount of iron(III)chloride, $FeCl_3$, facilitates such reactions remarkably. Going by the similarity between Br_2 and our reagents, viz., tetrabutylammonium tribromide (TBATB) or cetyltrimethylammonium tribromide (CTMATB), in so far as the products are concerned, it was quite rational to perceive that $FeCl_3$ might as well catalyse the bromination by TBATB, for example. This possibility has been investigated and what has been observed is that iron(III) chloride indeed catalyses TBATB bromination. The results in conjunction with the isolation of $[Bu_4N][FeCl_3Br]$ from the reaction in addition to the desired bromo-organics, clearly indicates the involvement of "Br^+" as the attacking entity in the process of bromination by TBATB.

ABSTRACT

The results and findings of the research work being presented in this thesis are based on the following aspects of inorganic and coordination chemistry of vanadium(V), molybdenum(VI), copper(I), manganese(III) and iron(III). While the work on copper and manganese involves the synthesis and characterisation of some fluoro compounds of these two metals in the oxidation states mentioned above, the investigation on vanadium and molybdenum includes the ability of their peroxo-intermediates to generate the active bromine species Br_3^- from Br^-, leading to the development of novel synthetic protocols and reagents for bromination of organic substrates. The investigation on iron(III) is concerned with the role of iron(III) chloride, $FeCl_3$ as a catalyst in the bromination by TBATB, and evidence for involvement of "Br^+" in the process.

The text is distributed over seven chapters:

Chapter I: *Introduction and scope of the work*

Chapter II: *Details of elemental analyses and description of the instruments/ equipment used for characterisation and structural evaluation of the compounds*

Chapter III: *Some fluoro compounds of copper(I) and manganese(III): Synthesis of* $CuF(PPh_3)_3.2ROH$ *(R = Me or Et) and* $(NH_4)_3[MnF_6]$

Chapter IV: *An environmentally friendly biomimetic synthetic methodology for the bromination of organic substrates by tetrabutylammonium bromide (TBAB) promoted by* V_2O_5—H_2O_2

Chapter V: *An acid assisted peroxo-molybdate(VI) catalyzed methodology for in situ bromination of organic substrates by tetrabutylammonium bromide (TBAB)*

Chapter VI: *Cetyltrimethylammonium tribromide (CTMATB), $C_{19}H_{42}NBr_3$: A new environmentally favourable synthesis and studies of its reaction profile involving a few selected substrates*

Chapter VII: *Isolation of $[(C_4H_9)_4N][FeCl_3Br]$ from the reaction of $FeCl_3$ with $(C_4H_9)_4NBr_3$ (TBATB) and evidence for $FeCl_3$ as a catalyst in environmentally clean bromination by TBATB*

An outline of the content of each chapter is given below:

I. Introduction and scope of the work

A general introduction to all the topics being included in the thesis has been presented in this chapter along with citation of relevant literature. To begin with a brief report has been presented on the importance of halo, especially the fluoro compounds of copper(I) and manganese(III) emphasising the problems associated with their syntheses. This has been followed by peroxo-chemistry of metals viz., vanadium(V) and molybdenum(VI), particularly in respect of their reactivity to oxidise halide to active halogen species. Mention has been made of the discovery of *V-BrPO*, a vanadium(V) containing enzyme that catalyses the bromide oxidation in marine animals and the consequent biomimetic studies carried out to design the models for *V-BrPO*. Some of the limitations of most of the customary methods of bromination have been identified and the need for development of environmentally cleaner yet highly effective routes to bromoorganic compounds emphasised. The importance of synthesis of such compounds has been underscored. Also highlighted were the advantages of metal assisted bromination over the conventional reagents especially in terms of environmental

compatibility and economic viability in so far as the production of bromoorganics is concerned.

Based on the aforementioned background, scope of the work constituting the basis of the present Ph. D. research was identified.

II. Details of elemental analyses and description of the instruments /equipment used for characterisation and structural evaluation of the compounds

Detailed procedures adopted for the quantitative determination of different constituents and relevant features of the instruments/ equipment used for physico-chemical studies have been provided. Reference has been made to the techniques involved in the structural assessment of the newly synthesized compounds including brominating reagents and bromo-organics.

III. Some fluoro compounds of copper(I) and manganese(III): Synthesis of $CuF(PPh_3)_3.2ROH$ (R = Me or Et) and $(NH_4)_3[MnF_6]$

In this chapter the synthesis and characterization of copper(I)-fluoro complexes viz., $CuF(PPh_3)_3.2ROH$ (R= Me or Et) as well as a manganese (III)-fluoro complex i.e., $(NH_4)_3[MnF_6]$ have been reported. For convenience the results have been divided into two parts (**IIIa** and **IIIb**).

IIIa Fluoro-compounds of copper(I): An easy access to $CuF(PPh_3)_3.2ROH$ (R= Me or Et)

The copper(I) fluoro compounds as well as other halo compounds find wide range of applications in the catalysis of a variety of organic transformations. Some fluoro-copper(I) species are also known to be involved in a few synthetically important transmetallation reactions. Having realized the importance of fluoro-compounds of copper(I) and the challenge associated with their synthesis particularly due to weak interaction of soft acid copper(I) and hard base fluoride, we decided to develop a direct yet efficient synthesis of fluorocuprates(I) containing triphenylphosphine, Ph_3P.

A solution of $CuSO_4.5H_2O$ when treated with $NH_2OH.HCl$ produced Cu_2O, which on being reacted with Ph_3P and aqueous HF (48%) in MeOH or EtOH afforded $CuF(PPh_3)_3.2ROH$ (R= Me or Et) in good yield. The compounds were

$$CuSO_4.5H_2O + NH_2OH.HCl \xrightarrow{\text{dil. NaOH}} Cu_2O$$

$$Cu_2O + \text{aq. HF} + Ph_3P \xrightarrow{\text{MeOH}} CuF(PPh_3)_3.2MeOH$$

$$Cu_2O + \text{aq. HF} + Ph_3P \xrightarrow{\text{EtOH}} CuF(PPh_3)_3.2EtOH$$

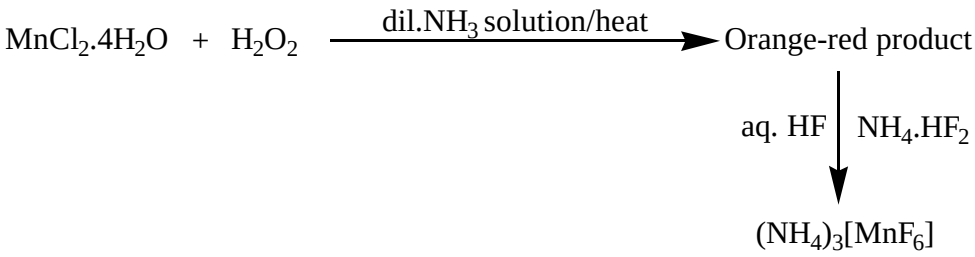
characterised by different spectroscopic techniques in addition to chemical analyses and solution electrical conductance measurements. The advantages of the present work over the earlier methods have been highlighted. In order to assess the thermal stability of fluorocuprates(I), TG analysis on $CuF(Ph_3P)_3.2MeOH$ as a typical example was carried out. TG profile reveals that the compound loses the solvent molecules and triphenylphosphines in the temperature range of 118 – 274 °C, yielding 'CuF' at 274°C.

Results emerged out of the present studies on fluorocopper(I) compounds provide an easy access to the title compounds and reveal an interesting thermal property of the compounds.

IIIb. Hexafluoromanganate(III): A new synthetic route to $(NH_4)_3[MnF_6]$

In view of the biological and chemical importance of fluorine containing organic molecules, rapid development of new reagents and methods for fluorofunctionalization of organic molecules has taken place in the last few decades. Fluoro compounds of manganese(III) are known to be potential sources of fluorinating agents. Moreover, Mn(III) compounds draw special attention not only because it is difficult to stabilize in aqueous medium but also many of its complexes demonstrate unusual magnetic properties and structural features. We have developed a direct and easy method of synthesis of $(NH_4)_3[MnF_6]$. Reported in a part of this chapter are its synthesis and characterisation by physico-chemical techniques.

The treatment of an aqueous solution of $MnCl_2.4H_2O$ with H_2O_2 and dil. NH_3 solution resulted in the formation of a brown flocculent precipitate, which upon heating at *ca*. 70°C produced an orange-red product. The isolated product on being reacted with NH_4HF_2 and aqueous HF (48%) followed by concentration of the reaction solution yielded the title compound in good yield. The compound is insoluble in most of the common solvents and in water it undergoes hydrolysis to give hydrated manganese(III) oxide. The compound was characterised by IR and reflectance spectroscopies, magnetic susceptibility measurements and TG analysis in addition to chemical determination of



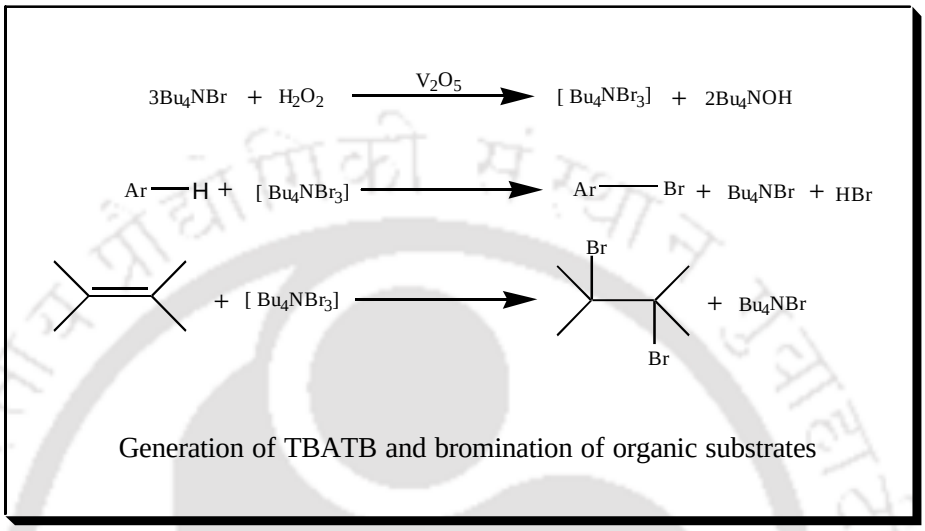
manganese and fluoride. The chemical determination of oxidation state of manganese, which is considered to be important, supported the occurrence of Mn(III) in the compound. In order to gain knowledge of thermal behaviour of the compound, thermogravimetric analysis (TGA) was conducted. The thermogram revealed that the compound is stable up to 250°C and thereafter it loses NH_4F between 250 and 315°C affording MnF_3 at 315°C.

IV. An environmentally friendly biomimetic synthetic methodology for bromination of organic substrates by tetrabutylammonium bromide (TBAB) promoted by V_2O_5—H_2O_2

This chapter reports the development of a new biomimetic synthetic protocol for bromination of a variety of organic substrates by TBAB and H_2O_2 promoted by vanadium(V). Coordination to the metal center activates the peroxide towards oxidation of bromide, generating *in-situ* the active bromine species tribromide, Br_3^- (a "Br^+" equivalent), in the reaction solution. The Br_3^- thus formed then brings about bromination of the chosen organic substrates.

A typical reaction involved the addition of TBAB to an aqueous-acetonitrile suspension of vanadium pentoxide, V_2O_5, and hydrogen peroxide followed by the addition of the organic substrate. The resulting mixture when stirred for a specific

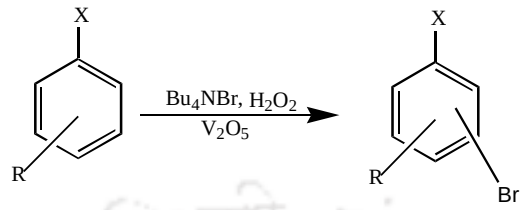
period of time afforded bromo derivative of the substrate in a very high yield. The reactions were monitored by TLC and GC.



Generation of TBATB and bromination of organic substrates

A variety of substrates were brominated by this methodology with yields generally varying between 70 and 90%. The products were characterized by comparison with authentic compounds, while for a few samples IR and ^{1}H NMR spectroscopic techniques were also used. Included in this chapter are the substrates drawn from activated aromatic compounds, namely, aniline, phenol, and 2-naphthol, polycyclic aromatic compound, viz., anthracene, cyclic alkene, viz., cyclohexene, α,β-unsaturated alcohol, i.e., crotyl alcohol and a ketone i.e., cyclohexanone. The environmental compatibility stems from the choice of V_2O_5 to be the metal promoter and H_2O_2 as the oxidant. Incidentally H_2O_2 is regarded as a green oxidant. The other notable feature is the regioselectivity of the protocol. Majority of the substrates gave a single regioisomer. As for example, anthracene, aniline, and 2-naphthol, afforded exclusively 9,10-

dibromoanthracene, 4-bromoaniline and 1-bromo-2-naphthol, respectively. A remarkable aspect of the methodology is the redundancy of the use of acid.



X = H, CH_3

R = OH, NH_2

The high to very high yields of most of the products obtained under mild reaction conditions with the other advantages mentioned above make the methodology a desirable alternative to traditional reagents and protocols for bromination.

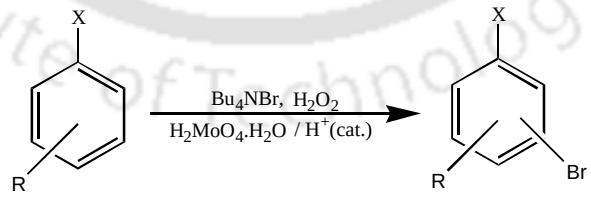
V. An Acid assisted peroxo-molybdate(VI) catalyzed *in situ* bromination of organic substrates by tetrabutylammonium bromide (TBAB) and H_2O_2

In the methodology reported earlier the amount of V_2O_5 was used in considerable excess to generate sufficient acidity to afford products in high yields. Consequent upon this and taking into consideration the requirement of a reasonably strong acidic medium in the metal mediated *in situ* bromination of organic substrates, development of a metal catalyzed bromination protocol was considered to be a worthwhile exercise. Accordingly, we designed an acid assisted bromination protocol for organic substrates using MoO_4^{2-} as the catalyst. There is a striking resemblance between various aspects of peroxo-chemistry of vanadium and molybdenum. Molybdenum(VI) (*c.f.* vanadium(V)) is also known to activate hydrogen peroxide through its coordination to the dioxygen. These led to the selection of molybdenum(VI) as the catalyst for O_2^{2-} activation to bring about *in situ* oxidation of Br^- to Br_3^- (an 'Br^+'

equivalent) in the presence of a catalytic amount of an acid. This in turn gave rise to a protocol for bromination of organics substrates. The reactions were monitored by GC and TLC.

A typical reaction involved the activation of peroxide through its coordination to the molybdenum(VI). The activated peroxide then oxidizes the bromide to tribromide in presence of an acid. The tribromide thus formed brominates the chosen organic substrates.

The results of this methodology are quite similar to those of the previous methodology reported in **chapter IV**. The points of difference are the use of molybdenum(VI) as the catalyst and the requirement of catalytic amount of an acid. The environmental friendliness, high yield and selectivity and the other advantageous features of this methodology over the conventional protocols and reagents are reported in details in this chapter. One of the notable aspects of this methodology is that the product selectivity observed in the present case is different from that of earlier methodology. It has been shown with the help of the results obtained by other collaborators that for some of the substrates namely anthracene and phenol, the products



X = H, CH_3

R = OH, NH_2

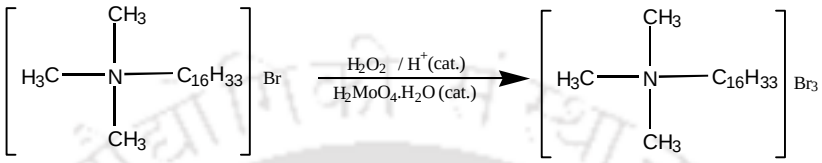
are different from what were obtained by peroxo-vanadium(V) promoted methodology, suggesting a distinct difference in regioselectivity with the change of the metal activator.

VI. Cetyltrimethylammonium tribromide (CTMATB), $C_{19}H_{42}NBr_3$: A new environmentally favourable synthesis and studies of its reaction profiles involving a few selected substrates

In our continued effort to develop new and improved methodologies for reagents and protocols for bromination, we embarked on to develop an environmentally safe synthetic route to an organic ammonium tribromide, cetyltrimethylammonium tribromide, $C_{19}H_{42}NBr_3$ (CTMATB). Organic ammonium tribromides have been proved to be extremely versatile brominating reagents in recent times. A number of tribromides are known and their efficacy as brominating agents have been appreciated. Cetyltrimethylammonium tribromide (CTMATB), $C_{19}H_{42}NBr_3$, appears to be mentioned in the literature but its preparation as reported only in a patent involves the use of molecular bromine whose use is rather hazardous from safety point of view. Interestingly, the usefulness of CTMATB as a brominating reagent was not reported to the best of our knowledge. The present study is based on the ability of a peroxo-molybdenum system to oxidize bromide to tribromide. Taking a cue from this cetyltrimethylammonium tribromide (CTMATB) was prepared from the corresponding bromide and its reaction profile was investigated.

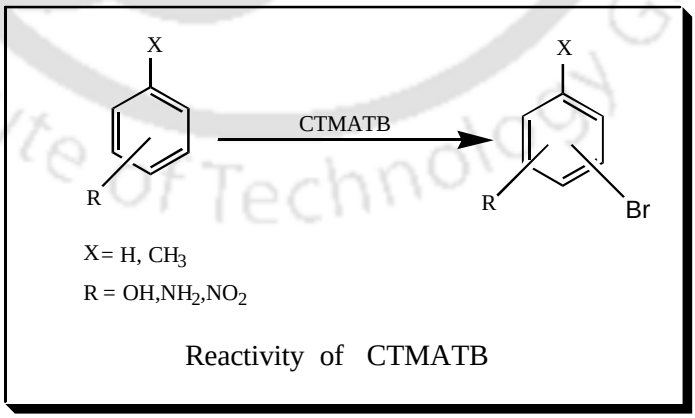
The preparation involved the oxidation of CTMAB to the corresponding tribromide by H_2O_2, catalyzed by $H_2MoO_4.H_2O$, in the presence of a catalytic amount of H_2SO_4. The use of two molar equivalents of potassium bromide (ostensibly to increase

the yield), as the consumable source, afforded the product in 93% yield. The product thus obtained was recrystallised from acetonitrile. The recrystallised product registered a sharp melting point at 94°C. The product has been found to be stable for a prolong period.



Formation of CTMATB from CTMAB

The efficacy of CTMATB as a brominating reagent was established by conducting bromination of a few selected substrates. The substrates chosen were mostly moderately activated aromatic compounds like phenol, cresols, aniline and phluroglucinol. The yields of majority of the products were high to very high (60-85%). Environmental implication of the preparation of the reagent has been highlighted. One of the inherent advantages of the reagent is its phase transfer property. Thus, it can be used very effectively in a biphasic reaction condition thereby enlarging the scope of bromination of a wide variety of substrates.



Reactivity of CTMATB

Moreover, the reagent is highly selective, as exemplified by the formation of 4-bromophenol and 2,4-dibromoanilne from phenol and aniline, respectively, as the major

isomers. Similarly *o*-cresol and *m*-cresol afforded selectively 2-bromo and 4-bromo derivatives, respectively. For *o*-nitroaniline and phluroglucinol (1,3,5-trihydroxy benzene) the products obtained were 4-bromo *o*-nitroaniline and 2,4-dibromophluroglucinol. Additionally, the reagent is cost-effective and capable of brominating a wide range of substrates. These features together with its safer might be good enough reasons to render it a sought-after reagent for bromination for organic substrates.

VII. Isolation of $[(C_4H_9)_4N][FeCl_3Br]$ from the reaction of $FeCl_3$ with $(C_4H_9)_4NBr_3$ (TBATB) and evidence for $FeCl_3$ as a catalyst in environmentally clean bromination by TBATB

Taking into consideration of the similarity of products profile of the bromination of aromatics by Br_2 and TBATB, it was conjectured that both the reagents might involve similar attacking species in their reactions. Recollecting the catalytic role of iron(III) chloride, $FeCl_3$, in the bromination of aromatics in which Br_2 is activated by the salt to generate 'Br^+' as the active species with the formation of $[FeCl_3Br]^-$, it was thought to react $FeCl_3$ with TBATB in acetonitrile and then to ascertain the product obtained thereof. If the reaction would lead to the formation of a salt of $[FeCl_3Br]^-$ then it would be quite logical to believe that 'Br^+' was also formed in the reaction in the bromination by TBATB. Assuming a positive outcome, it was logical to believe that $FeCl_3$ would be able to catalyse the bromination by TBATB. To this end, $FeCl_3$ catalyzed brominations of a few aromatic substrates including chalcone were conducted.

Brominations of aniline, phenol and chalcone were conducted by TBATB in acetonitrile in presence of catalytic amount of $FeCl_3$. The reaction times, ratio of substrates to catalyst, products and yields along with the results of the control reactions have been summarized in **Table 1**.

Table 1

Substrate	Amount of catalyst	Reaction time (min)	Product [a]	Yield (%) [b]
Chalcone	5 mol%	30	Threo-dibromochalcone	70
Chalcone	0	30	Threo-dibromochalcone	10
Aniline	5 mol%	2 or 3	2,4,6-tribromoaniline	65
Aniline	0	5	2,4,6-tribromoaniline	20
Phenol	5 mol%	10	2,4,6-tribromophenol	73
Phenol	0	10	2,4,6-tribromophenol	15

[a] products were characterized by comparison with the authentic samples, [b] isolated yields

A comparison of the results of the catalytic reactions (**Table 1**) with those of uncatalysed reactions clearly suggests that $FeCl_3$ catalyses the bromination reactions by TBATB.

These results along with the isolation of $[FeCl_3Br]^-$ provides an evidence for the involvement of Br^+ in the bromination by TBATB.

The characterization of synthesised compounds including bromo-organics being reported in different chapters were made by a combination of variety of physical techniques, viz., IR and electronic spectroscopies, solution electrical conductance and magnetic susceptibility measurements, ^1H NMR spectroscopy, thermal analyses, and gas chromatography. In addition to the physical techniques mentioned above, microanalyses of carbon, hydrogen and nitrogen and chemical determination of a few other constituents were made by standard chemical procedures.

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CHAPTER I

Introduction and scope of the work

The studies involving metal complexes containing fluoride, F^-, as the ligand has been one of the highly active areas of research in inorganic chemistry for a long time. [1-79] Much of these interests have been fuelled by wide range of applicability of fluorometallates in diverse areas.[37-40, 47-52] Metals drawn from transition elements [2-14, 31-46], main group elements [15-18, 47-52], lanthanides and actinides [26-30] form a wide variety of compounds with fluoride in different oxidation states. A number of fluorometallates are known to have high material values [80] which make them useful for industrial applications, as for example, in microelectronics, in the manufacture of pure metals by thermal reduction, in laser technology, in the manufacture of optical instruments and in electrochemical cells with solid electrolytes. [49,50] There has been a reported use of a few main group metal fluorides in the production of III-V semiconductors [73], a class of well known electronic and optoelectronic materials. A number of metal fluorides as well as metal complexes with fluorine substituted organic ligands are used as precursors for the chemical vapor deposition (CVD) of inorganic materials. [25, 47] Apart from the material values of fluorometallates highlighted above many transition metal fluorides are also known to be good fluorinating agents. [81] Indeed, biological and chemical importance of fluorine containing organic molecules have resulted in the rapid development of reagents and methods for fluorofunctionalisation of organic molecules [79], with transition metal fluorides have their own share of contribution towards this development. [47, 81]

Significantly, the chemistry of fluorine is quite different from that of other halogens. [63] The three main possible reasons are (i) low dissociation energy of fluorine

molecule [D (F_2) = 37.7 KCal\mol], (ii) relatively stronger bonds formed by fluorine with metallic and non-metallic elements, and (iii) the relatively small ionic size of the fluorine atom and fluoride which gives rise to the most electronegative and ionic ligand. The above properties make fluoride one of the hardest bases known.

Transition metals in their lower oxidation states behave as soft acids and in compliance with the Pearson's HSAB principle most of these metals tend to form weaker bonds with fluoride. This poses a difficulty in synthesizing fluoro-metal compounds with metals in their relatively lower oxidation states.

The group, in which the present Ph. D. research has been carried out, has been involved in the investigation of various aspects of fluoro-metal chemistry for over two decades. [3-19, 26-46] The different aspects being addressed include the synthesis, characterisation and reactivity studies of both binary as well as mixed fluoro compounds of a variety of metals in different oxidation states. Indeed this endeavour afforded a notable dividend by way of introducing newer reagents like Pyridinium Fluorochromate(VI) (**PFC**) [37-39] , Quinolinium Fluorochromate(VI) (**QFC**) [40] and 3,5-Dimethylpyrazolium Fluorochromate(VI) (**DmpzHFC**) [46] and demonstrating the possibility of stabilising Mn(III) in aqueous solution. [36] Attention of the present worker was drawn to a few very selected aspects of fluoro chemistry of copper(I) and manganese(III).

Incidentally, the chemistry of copper(I) is less extensive than copper(II) and coordination chemistry of copper(I) is comparatively more restricted. The first clear description of co-ordination chemistry of copper(I) compounds by F. H. Jardine [82] was published in 1975. Copper(I) can form complexes in which the cation acts as a Lewis

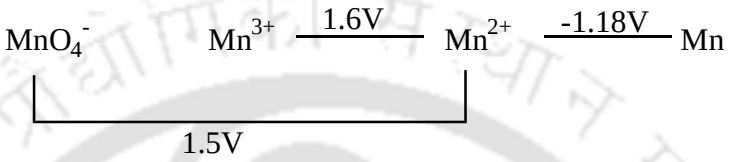
acid and the ligands as Lewis bases. However, while copper(II) is generally considered as a borderline hard acid, copper(I) clearly behaves as a soft acid and the order of stability of the ligands to metal is that of a soft base class b behaviour. Though copper(I) forms a host of complexes with halides like Cl^-, Br^- and I^-, similar examples with F^- happen to be far fewer. [83] One of the most important domains in which copper(I) halo compounds find extensive use is in the development of organocopper reagents. [84] A vast majority of organocopper reagents are prepared by transmetallation reactions involving an organometallic reagent and copper(I) salt of a halide including fluoride. [84-95] It is worth mentioning that organocopper reagents are an indispensable part of synthetic organic chemists' tool kit. [84] They can be employed to prepare alkanes, alkenes, alkynes and aromatics and the transformations are usually characterised by high chemo-, regio- and stereo- selectivity. Organocopper reagents have been employed to prepare innumerable novel and natural products. Copper(I) halides with I^-, Br^-, and Cl^- are very commonly employed as starting materials for organocopper reagents presumably due to their easy accessibility but fluorocuprate(I) is less frequently used for this purpose. However, of late there has been a noticeable increase on the use of fluorocuprate(I) as mediators in a variety of transformations including a few useful transmetallation reactions. [94,95] A few examples of copper(I) halides that are commonly used as precursors for organocopper reagents are listed below:

Copper(I) bromide, CuBr, copper(I) bromide-bis(dibutylsulfide) complex, $CuBr.(SBu_2)_2$, copper(I) chloride, CuCl, copper(I) iodide-bis(dibutylsulfide) complex , $CuI.(SBu_2)_2$, copper(I) iodide-tetramethylethylenediamine complex, CuI.TMEDA etc.

Although there seems to be a growing demand for fluorocuprates(I) in view of their increasing uses as promoters or catalysts in a variety of organic transformations, the accessibility to such compounds has always been rather tricky. [83] This is primarily due to very weak interaction of soft acid copper(I) and hard base fluoride. Therefore, in order to sustain the demand of fluorocuprates(I) it becomes imperative to get easy and safe access to these compounds in a cost effective manner. Incidentally, our attention was drawn to the mixed ligand fluorocompounds of the type $CuF(PPh_3)_3.2ROH$ (R= Et or Me) due, in part, to their use in a few synthetically important transmetallation reactions. [94] The literature synthesis [83] of these compounds, especially that of $CuF(PPh_3)_3.2EtOH$ has a few limitations in scope. For instance, (i) it is rather indirect, (ii) the process of purification is relatively long and (iii) the yield is low. In view of this, it was considered worthwhile to develop an easy and direct synthesis of $CuF(PPh_3)_3.2ROH$ (R= Et or Me) followed by an investigation of its thermogravimetric (TG) profile. The latter is expected to provide the temperature for the formation of 'CuF' in addition to its stability at least within the range of temperature involved.

As far as our present endeavour on fluorometal chemistry is concerned, apart from the fluorocopper(I) mentioned above, we also sought to address some related aspects of fluoromanganate(III) chemistry. Manganese exhibits the widest spectrum of oxidation states, for example –III to +VII. Interestingly, in biological systems [96-98] the metal in II-IV oxidation states performs a variety of functions including water splitting by photosynthetic enzymes, disproportion of H_2O_2 in microorganisms and reduction of ribo to deoxyribonucleotides in caryneform bacteria. [36] Manganese(III) also draws special attention not only because of the unusual magnetic properties and structural

features of many of its complexes but also due to difficulty in stabilizing it [Mn(III)] in an aqueous medium. As a result a lot of attention has been focused on Mn(III) compounds over the years. [6, 8-11, 36, 99-105] Importantly, manganese(III) is strongly oxidising in aqueous solution with a marked tendency to disproportionate to Mn(IV) (i.e. MnO_2) and manganese(II).



Consequently the aqueous chemistry of Mn(III) was relatively slow to develop. Significantly, the coordination chemistry of Mn(III) with the halides is more limited than that of Mn(II) and the only binary compound that is stable at room temperature is MnF_3.[81]

Our group's sustained effort on the development of binary and mixed ligand fluoromanganates(III) has resulted to of some very interesting results [4-6, 8-11,36] which not only provided an easy way to stabilise Mn(III) in aqueous medium but also led to the observance of unusual magnetic properties for such compounds. Although quite a lot of studies on the fluoromangantes(III) has been made by our group leading to a clear understanding of some aspects of fluoromanganate(III), yet there remains a number of gaps to be filled up. As for example, one of the important concerns was to develop a facile and direct synthetic protocol for the ammonium salt of hexafluoromanganates(III) since such species could become an useful source for MnF_3, a highly sought after fluorinating agent. Several attempts in this endeavour were apparently met with failure. As a part of the present Ph. D. program we have chosen to address this particular problem. The reported synthesis of this compound has a few drawbacks with the

prominent one being the involvement of multiple steps in its synthesis. Thus, in view of the limitations of the literature synthesis of $(NH_4)_3[MnF_6]$ and also for its anticipated usefulness as a precursor for MnF_3, it would be of practical utility to develop an easy preparative route to this compound. The TG analysis of this compound would constitute an important part of the investigation for it is anticipated that such experiments would provide a lead to obtain the MnF_3 in a safer way.

While the selected aspects of fluorometal chemistry of copper(I) and manganese(III) form a rather small yet important part of the present Ph. D. research, the major theme of the present thesis has been based on some chosen aspects of peroxo chemistry of vanadium and molybdenum.

Transition metals in their higher oxidation states give rise to highly varied reactions with hydrogen peroxide, H_2O_2, leading to the formation of flamboyant complexes in solution. [106-121] For example, vanadium(V) reacts with H_2O_2 to form mono- (red), [112] di- (yellow), [109] tri- (blue) [110] and tetra- peroxovanadates(V) (violet).[111] Significantly, the reactions of transition metals with hydrogen peroxide have often been found to be fairly complicated resulting in the formation of a number of complex species with varying compositions.[112] This notwithstanding, peroxo-metal chemistry has registered marvelous growth over the years. One of the major contributions for this development has come from the outcome of research work devoted to find synthetic, structural and functional analogues of biological oxygen carriers. [112] This has led to the creation of numerous novel substances containing transition metals that either bind to or react with dioxygen. A host of such products have been isolated and characterized at the crystallographic level. In such compounds peroxide has been found to bind the metal in

one or more of the following modes of coordination (**Fig.1**). Importantly, many of these compounds find use as materials or as industrial catalysts.

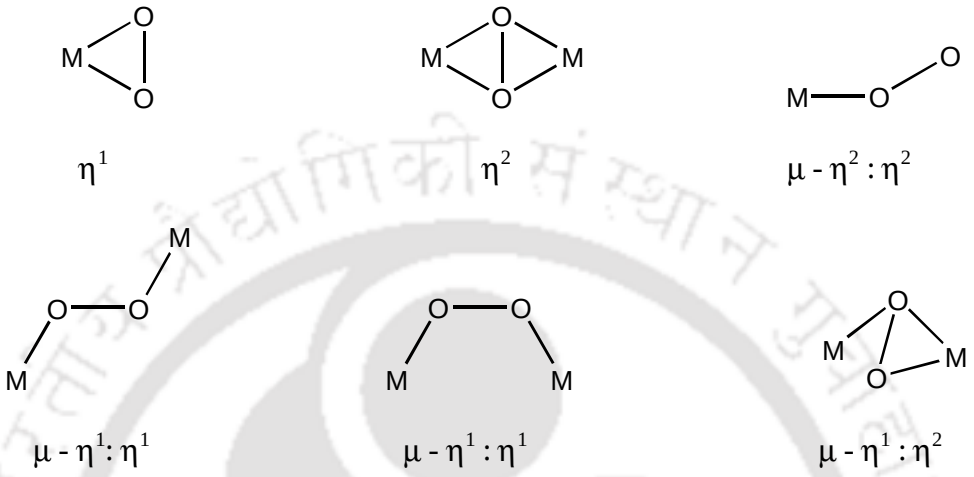


Fig. 1

A perusal of relatively recent developments in peroxometal chemistry reveals that this area has attracted renewed interest some years ago presumably because of an intrinsic biological interest [122-126] and catalytic activity [127-135] in some important organic transformations. [122-135] It was during the late seventies through early eighties when several workers in this field started conducting solution studies [136-140] of peroxo-metal species that our group began its research work on the syntheses of peroxo compounds of metals like Ti, V, Zr and UO_2^{2+}, for instance. This endeavour led to the successful syntheses of several binary as well as heteroligand peroxo compounds of these metals.[141-149] The attention of our group had gradually shifted to a great extent towards peroxo-vanadium chemistry leading to creation of a good number of simple and heteroligand di- and triperoxovanadates. [31,45,118] In this process the importance of pH in the synthesis of such compounds and scope of their reactivity were realised. Inspired by

the growing knowledge of the formation and transformation of peroxo complexes of vanadium, several reactivity studies were conducted by our group [148, 149] as well as by others. [112] Such studies with peroxovanadates conducted by our group, included bromide among a host of other inorganic substrates.

In the meantime, there was a breakthrough in the peroxovanadium chemistry following the discovery and isolation of vanadium dependent haloperoxidase (VHPO). [126] VHPOs are a class of enzymes that catalyse halide oxidations in marine animals leading to biosynthesis of haloorganics. [150] Indeed, there are evidences that haloperoxidases are responsible for creation of a major part of a striking array of halogenated products [151, 152] produced by natural sources in the biosphere. The detailed mechanism by which haloperoxidases catalyse the halogenation of an organic molecule is still a moot point.[152] However, for some of the enzymes, viz., vanadium bromoperoxidase (*V-BrPO*), the reaction mechanism appears to be simple and involves two-electron oxidation of electron donor (Cl^-, Br^-, I^-) by H_2O_2 to form hypohalous acid or its equivalent. The oxidized halogen species can halogenate selected organic compounds or oxidize a second equivalent of H_2O_2 producing singlet oxygen [153] ($^1O_2$) (**Fig.2**). Vanadium occurs in the enzyme in the pentavalent oxidation state that activates hydrogen peroxide through coordination with the result that the activated peroxide functions as the oxidant for the halide.[150] The metal does not undergo redox cycling as the reduced vanadium has been observed to deactivate the enzyme catalyst. [150]

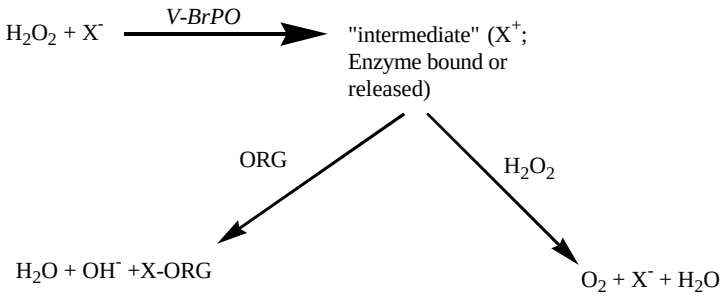


Fig. 2

While continuing with the investigation of reactivity of peroxovanadates(V), an interesting observation was made. It was found that peroxovanadium(V) system reacted with Br^- to oxidize it to Br_3^- (λ = 266 nm) rather easily. Subsequently, the tribromide was isolated as tetrabutylammonium tribromide (TBATB). The TBATB thus isolated was characterized by a variety of spectral analyses, while the structural delineation was made by X-ray crystallography (**Fig. 3**).

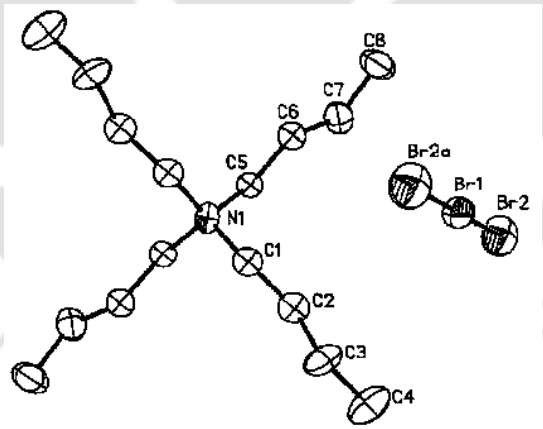


Fig. 3 Crystal structure of Tetrabutylammonium tribromide, TBATB

The IR and laser Raman spectral features observed for TBATB are characteristics of Br_3^-. [154] The IR bands for the TBATB occur at 171 and 191cm^{-1}, while the laser Raman spectrum of the compound shows two bands at 146 and 164 cm^{-1}. The X-ray structure

of TBATB [155] shows that the compound crystallizes in monoclinic space group C2/c, and the Br-Br-Br is totally symmetrical with Br2a-Br1-Br2 angle being 180 °. The two Br-Br distances are identical (2.533(3) °). The synthesis of TBATB and investigation of its reaction profiles have been carried out by other co-workers of our laboratory. [156] Taking cues from the results of ours as well as those of others, it became quite convincing that an active bromine species tribromide (Br_3^-), could be generated *in situ* and used for bromination of organic substrates including aromatics. In the meanwhile our attention was drawn to the importance of bromoorganics, in particular bromoaromatics, and the role that inorganic chemists could play to make important contributions to this field.

It is noteworthy that bromination of organic substrates has drawn a special attention in recent years. [156-165] This is because of the growing industrial and commercial importance of bromoorganics. Indeed, a great number of bromoaromatics are considered to be important [150] as potent antitumor, antibacterial, antifungal, antineoplastic, antiviral and antioxidizing agents. They are also used as industrial intermediates [164] for the manufacture of speciality chemicals, pharmaceuticals and agrochemicals. Apart from these, bromination is an important intermediate step in synthesis of numerous target-oriented natural products. [166-168] A specific example that can be cited is the ortho-bromination of phenol in the synthesis of mycophenolic acid, [166] an antibiotic having anti tumor properties.

A few naturally occurring organobromine compounds that exhibit important biochemical activities are exemplified below:

Organobromine metabolites viz., aeroplysinin-1 (a) [169], 14-debromopriaraplysillil (b) [170], 2-(2′-bromophenoxy)-3,4,5,6-tetrabromophenol (c) [171] exhibit antimicrobial activities thus serving in a chemical protection role for the organisms. A few brominated indoles (d) [173] are known to display potent antioxidant activities as well. Thelepin (e) [173] is another bromo-compound, which displays antifungal activity. A diterpene compound solenolide E [172] exhibits anti-inflammatory and antiviral properties. The chemical structures of a few of these naturally occurring organobromine compounds are shown in **Fig. 4**.

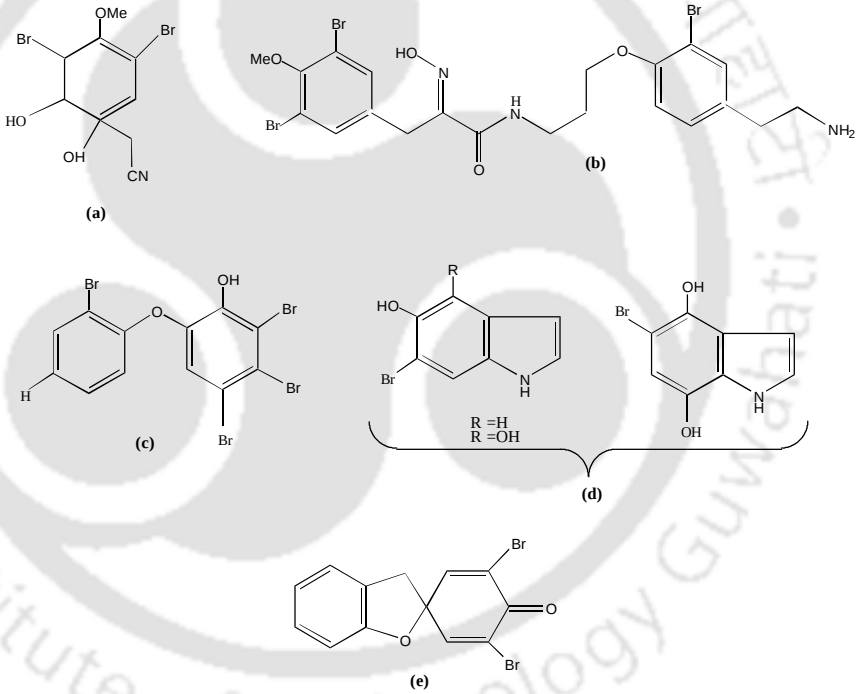


Fig. 4

Thus, in view of such a wide range of uses of bromoorganics, there has been an ever-growing demand for newer and more efficient reagents and methodologies for bromination of organics. Vis-à-vis this development, there has been growing ecological awareness in recent years that have resulted in the implementation of increasingly

stringent environmental restrictions on both industrial as well as laboratory scale chemical processes. Indeed, such restrictions have forced the chemical industry worldwide to redefine some production lines in order to comply with the protection of the environment.[174, 175] Thus, it has become imperative to develop reagents and methodologies that are not only highly efficient but also capable of conforming to the stringent environmental restrictions. However, most of the traditional methods for bromination use elemental bromine, metal bromides and some other hazardous chemicals that from the environmental viewpoints [156,164] cause grave concerns. A few examples of commonly used brominating agents along with their associated hazards are given below:

(i) Br_2, it is an extremely corrosive and toxic reagent in both liquid and vapor form and as a liquid it produces painful burns and blisters in the skin,

(ii) HBr, it is corrosive and cause severe skin burns,

(iii) DBH (1, 3-dibromo-5, 5-dimethylhydantoin) is an irritating solid, and

(iii) NBS (N-Bromosuccinimide) liberates considerable Br_2 vapor during its use

Thus, in order to comply with the safety requirements and also realising the increasing value of bromoaromatics, several groups have endeavoured into developing newer environmentally compatible reagents and methodologies for bromination of organic substrates. A few examples cited below (**Fig. 5**) bear a testimony to this assertion.

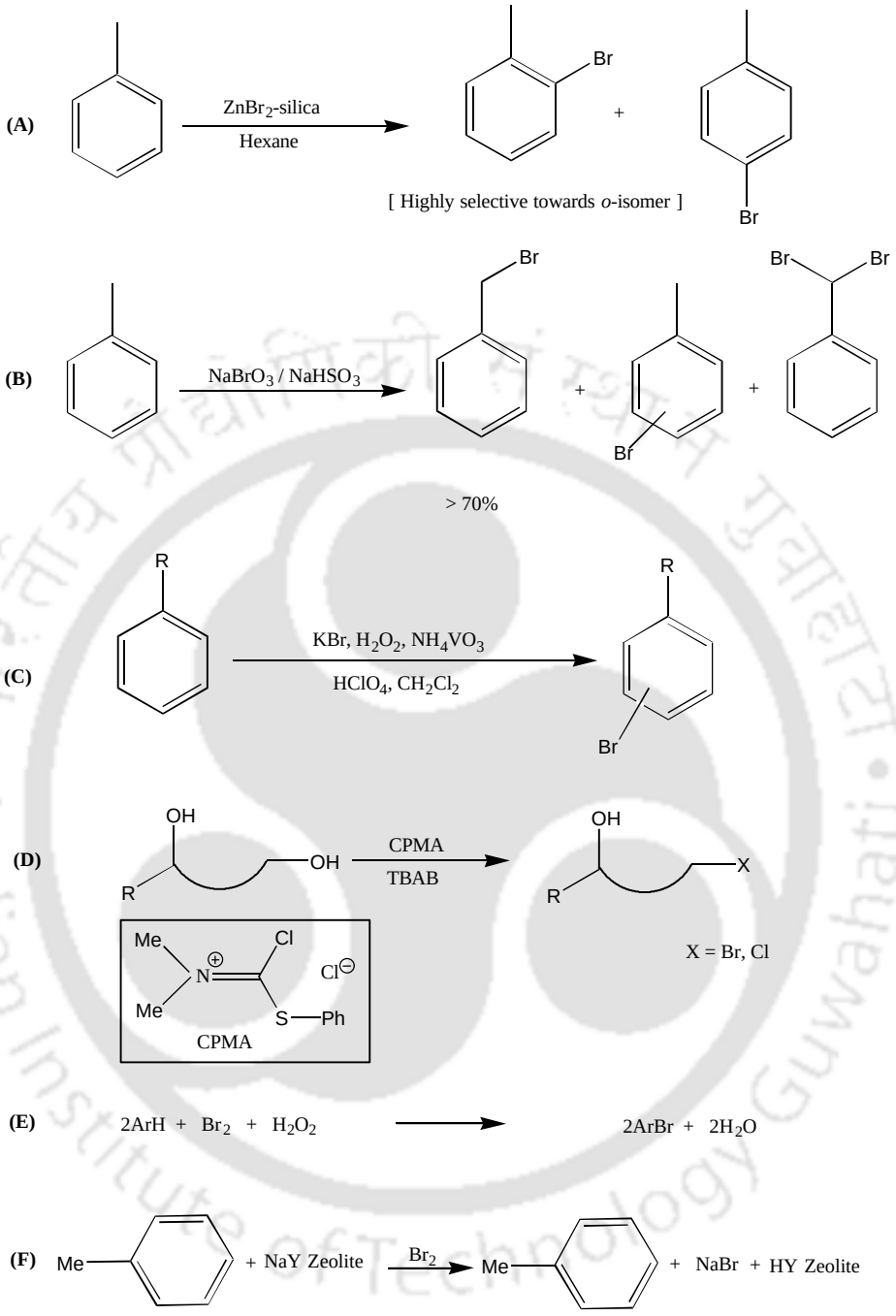


Fig.5

Thus, for instance: Clark et al. have recently reported an efficient and selective bromination (**A**) [164] of substituted benzenes using metal-bromide catalysts. A procedure for selective bromination (**B**) [176] of alkylbenzenes using $NaBrO_3$ / $NaHSO_3$ has been

reported by Ishii and his co-workers. This reagent is believed to generate HOBr *in situ* that acts as a bromohydroxylating species. However, the clear assessment of the actual nature of the brominating species could not be made owing to the difficulty in its isolation. A biomimetic methodology (**C**) [160] for bromination of organic substrates in a biphasic (H_2O/ CH_2Cl_2) system was reported by Di Furia et al. in which ammonium metavanadate (NH_4VO_3), hydrogen peroxide (H_2O_2) and KBr were used as alternative reagents for this purpose. The use of CH_2Cl_2 is, however, not preferred from environmental point of view. [177-180] Yet another methodology for bromination of aromatic substrates reported by Pandey et al. [161] involved KBr, NH_4VO_3 and H_2O_2, in presence of tetraisopropyl ammonium bromide (TPAB), which serves as a phase transfer catalyst as well as a source of bromide. Selective bromination of primary alcohols using (chloro-phenylthio-methylene)dimethylammonium chloride (CPMA) in presence of tetrabutylammonium bromide (TBAB) has also been reported (**D**) [181] recently as an efficient procedure for bromination of such substrates. The use of Br_2 in presence of H_2O_2 in the bromination (**E**) [182] of substituted benzenes has been shown to be economically viable and environmentally acceptable as the harmful HBr generated in the process of bromination is oxidized by H_2O_2 to give bromoaromatics. Notwithstanding the environmental constraints *per se* two more citations are quite relevant in the context of bromination of organic compounds. The one that involves the use of HBr-Me_2SO [163] in the regiospecific bromination of aromatics and the other (**F**) [162] is based on the zeolite assisted highly efficient para-selective bromination of simple aromatic substrates by bromine.

A comprehension of the available literature on brominations and brominating agents pin points an enormous scope of work in this area that could lead to better and improved routes to bromoorganics. Considering this and also taking cues from the previous experience [156] with TBATB it appeared worthwhile to investigate the possibilities of V_2O_5-H_2O_2 promoted *in situ* generation of Br_3^- followed by bromination of organic substrates. Importantly, it was expected that the methodology would work very efficiently without the addition of any acid. Since the bromide oxidation requires the medium to be acidic, the V_2O_5 may be required in more than a catalytic amount in this protocol.

It may be relevant to mention in passing that there is a striking similarity in the chemistries of vanadium, molybdenum and uranium in that all the three metals are found to exist as oxo-species, viz., VO_2^+, MoO_2^{2+} and UO_2^{2+} in solution. [183] This apart, peroxo-molybdate(VI) chemistry also resembles that of vanadium(V) in a number of ways. Molybdenum(VI) forms binary compounds [184] with peroxide in all the four metal to peroxide ratios, viz., 1:4, 1:3, 1:2 and 1:1 (*cf.* vanadium(V)) in pH sensitive reactions. Molybdenum is known to form a host of oxo mono- and di- peroxo binary and hetero-ligand complexes [184] some of which have been shown to be important stoichiometric reagents e.g., $[MoO(O_2)_2(pic)]^-$ and $[MoO(O_2)(H_2O)(dipic)]$, $[MoO(O_2)_2(ox)]^{2-}$ and $[MoO(O_2)_2(phen)]$ for the epoxidation of alkenes. [185] In view of the close resemblance of peroxochemistry of molybdenum(VI) to that of vanadium(V), it is quite logical to assume that an acid assisted MoO_4^{2-}-H_2O_2 catalysed bromination protocol should as well be possible. It is also likely that the product selectivity of this protocol may have some notable differences from the one proposed earlier in this

section. The use of safe and cost-effective chemicals, operational simplicity, mild reaction conditions, high yield and selectivity are expected to be major strengths of the protocol.

In keeping with our sustained efforts on the development of newer reagents and methodologies [13,37,38,40,46,156,186] (apart from the aforementioned synthetic protocols for bromination for organic substrates), one of the important items that figured in our agenda was the exploration of the possibilities of working out a clean and facile synthesis of cetyltrimethylammonium tribromide (CTMATB) and studies of its reaction profiles. Incidentally, there is a literature precedence for the preparation of CTMATB as described in a patent [187] which included some of its pharmacological properties. But the reported method used elemental bromine and aqueous HBr that are considered to be ecologically incompatible. Significantly, cetyltrimethylammonium ion is known [188] to facilitate the oxidation of bromide to tribromide by forming an ion pair with bromide ion. It may be noted that such a cation assisted halide oxidation in a softer manner underscores the importance of the role of quaternary ammonium ion in facilitating certain type of reactions like the one just mentioned. In view of the aforementioned rationales as well as the consideration of cost effectiveness of CTMAB, it was considered to be quite rewarding to synthesise the CTMATB from CTMAB and ascertain its efficacy as a brominating reagent.

Taking into account of the properties of tetrabutylammonium tribromide (TBATB) [156] and their similarities with Br_2 [189, 190] as a brominating agent it was conjectured that both of these might involve similar attacking species in the bromination reactions. Interestingly, in the bromination of organics by molecular bromine, iron(III)

chloride has been shown to act as a catalyst and in the process 'Br^+' is generated as the actual attacking species with the formation of $[FeCl_3Br]^-$ [189, 190] (**Fig. 6**).

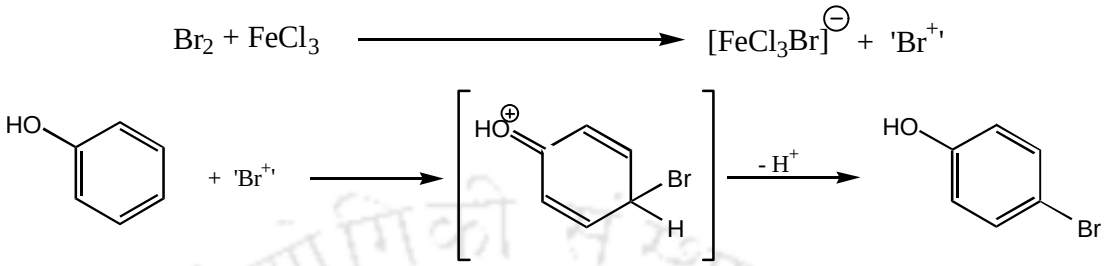


Fig. 6

In order to gain support to this contention it may be necessary to carry out the reaction of $FeCl_3$ with TBATB and to probe the product formed in the process. Additionally, in order to ascertain the effect of $FeCl_3$ as a catalyst, it might be necessary to conduct separate bromination reactions by TBATB involving catalytic amount of $FeCl_3$.

What therefore emerges out of the foregoing overview on the fluorometal and peroxometal chemistries is that though these areas have matured quite considerably yet there remains a lot of scope for important works. Accordingly, the following problems have been identified to be important for the present Ph. D. research:

I. Easy and direct synthesis of $CuF(PPh_3)_3.2ROH$ (R = Et or Me) and $(NH_4)_3[MnF_6]$, their characterisation by physico-chemical techniques. The other prime concern in this investigation was to probe TG profiles of these compounds. The results obtained from our efforts addressing these problems are compiled in **chapter III.**

II. Development of a biomimetic, environmentally safe synthetic protocol for *in situ* bromination of organic substrates including aromatics by

tetrabutylammnium bromide (TBAB) promoted by V_2O_5-H_2O_2. The results of these studies are presented in **chapter IV**.

III. An acid assisted MoO_4^{2-} catalyzed bromination protocol for organic substrates using TBAB and H_2O_2. The details of this investigation are reported in **chapter V**.

IV. An environmentally favourable synthesis of CTMATB and studies of its reactivity. An account of this investigation is put forward in **Chapter VI**.

And finally,

V. Studies of $FeCl_3$ catalyzed bromination of organics by TBATB and reactions of TBATB with $FeCl_3$ to provide evidence for the involvement of 'Br^+' in the TBATB bromination. The outcome of this investigation is incorporated in **chapter VII**.

In summary, the **present chapter** gives an overview of the relevant background of the problems identified for the present Ph. D. research. **Chapter II** presents the details of chemical procedures for the estimation of different constituents of various compounds and the relevant features of the instruments/ equipment used for physical studies and structural characterisation while **chapters III** through **VIII** contain several newer information/ results obtained during the Ph. D. research. Each chapter has been so designed as to make it a self-contained one with a brief introduction, sections on experimental and results and discussion followed by bibliography. Care has been taken to avoid repetitions as far as possible. However, some of the pertinent points considered essential in the context of the information and results presented in various chapters have been retained.

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CHAPTER II

Details of elemental analysis and description of instruments/equipment used for characterization and structural assessment of the compound

Detailed procedures adopted for the quantitative determination of different constituents and relevant features of the instruments /equipment used for physico-chemical studies including structural evaluation of metal compounds, newer brominating reagents as well as for the assessment of regioselectivity of bromo-organics are reported in this chapter. All the chemicals used were of reagent grade and obtained from E. Merck, BDH, Fluka, Loba Chemie Industries, Glaxo Laboratories (India) Ltd., S. D. Fine Chemicals and Ranbaxy Laboratories (India) Ltd.

MEASUREMENTS

INFRARED SPECTRA

Infrared spectra were recorded as KBr pellets (for solid samples) or as neat (for liquid samples) on a Nicolet- 201 Fourier Transform Infrared Spectrometer, FTIR. For a few samples IR spectra in low frequency region were recorded as Nujol mulls on a Perkin-Elmer model 983 Infrared Spectrometer as well.

ELECTRONIC ABSORPTION SPECTRA

Electronic absorption spectra were recorded on a Hitachi-U2001 spectrophotometer.

REFLECTANCE SPECTRUM

Reflectance spectrum was recorded against MgO by using a Carl-Zeis Jena VSU 2-P instrument.

MAGNETIC SUSCEPTILBILITY MEASUREMENTS

Magnetic susceptibility measurements were made on a MSB-1, magnetic susceptibility balance manufactured by Sherwood Scientific Ltd., Cambridge, and on a PAR vibrating sample magnetometer model 155 fitted with a scientific magnet model L75 FBAL using $Hg[Co(NCS)_4]$ as the calibrant.

THERMAL ANALYSIS

Thermogravimetric experiments were conducted on a Mettler Toledo TGA\SDTA 851 analyzer and on a Perkin-Elmer model Delta Series TGA 7 under pure nitrogen gas with a heating rate of either10 °C/min or 5 °C/min.

SOLUTION ELECTRICAL CONDUCTANCE MEASUREMENTS

Electrical conductance measurements of 10^{-3} M solutions of different compounds in appropriate solvents were recorded using Systronics Model 306 direct reading conductivity meter.

CARBON, HYDROGEN AND NITROGEN MICROANALYSIS

Carbon, hydrogen and nitrogen microanalyses were carried out on a Perkin-Elmer PE 2400 series II CHN analyzer in the analytical laboratory of IIT Guwahati. For a few samples C, H and N analysis results were obtained from Indian Association for the Cultivation of Science, IACS, Calcutta.

^{1}H NMR SPECTROSCOPY

^{1}H NMR spectra were recorded on a Bruker 200 MHz FT-NMR spectrometer as well as on a 90 MHz Varian EM 390 CW spectrometer using TMS as an internal standard.

GC ANALYSIS

Gas chromatographic analyses were made on a Hewlett-Packard HP 6890 Series chromatograph using SE 30 capillary column.

ELEMENTAL ANALYSES

Copper from fluoro compounds of copper(I)

Gravimetry [1]

An accurately weighed amount of the copper(I) compound was digested three times with 3 mL of 1:1 (v/v) mixture of conc. HNO_3 and conc. $HClO_4$ each time and then heated on a steam bath for 30 min. A colourless solution with a little amount of suspended oily mass (insoluble oxidized Ph_3P) was obtained at this stage. The oily mass was removed by filtration and to the filtrate 10 mL of 0.25 M H_2SO_4 was added followed by 25 mL of 5% sodium bisulfite solution and the mixture was diluted to *ca*. 100 mL. The mixture was then heated to boiling for *ca*. 15 min and to this 20 mL of freshly prepared dilute NH_4SCN solution was added with constant stirring. The white precipitate of cuprous thiocyanate (CuSCN) thus obtained was allowed to stand for nearly 2h and then filtered through a previously weighed sintered glass crucible (G-4), washed 3 or 4 times with dilute NH_4SCN solution and finally with 20% ethanol solution to remove excess of NH_4SCN. The precipitate was dried at 110-120 °C to a constant weight.

1 g of CuSCN= 0.5226 g of copper

Iodometry [2]

An accurately weighed amount of copper(I) compound was digested with 3 mL of conc. HNO_3 for three times. In this process the compound was decomposed and copper(I) was oxidized to copper(II). To it 25 mL of water was added to obtain a colourless solution with a little amount of suspended oily mass (insoluble Ph_3PO). This was filtered and to the filtrate 1 g of urea was added and the mixture was heated to boiling for 15 min. The solution was allowed to cool and to this 1 g of $NaHCO_3$ was added until a permanent turbidity was observed. The turbidity was removed by adding a few drops of acetic acid. An appropriate amount of KI (2 g) was added to this with constant stirring. The mixture was then kept in dark for approximately 15 min and the amount of liberated I_2 was titrated with standard sodium thiosulphate solution using starch as the indicator.

$$1 \text{ mL of } 1M\ Na_2S_2O_3 \equiv 0.0635 \text{ g of copper}$$

Fluoride from fluoro compounds of copper(I)

Gravimetric [3]

An accurately weighed amount of the fluoro compound of copper(I) was digested three times with 3 mL each of conc. HNO_3 to ensure the complete decomposition of the compound as well as oxidation of copper(I) to copper(II). To this was added 10 mL of water to obtain a faint blue solution with a little amount of oily suspension. The suspension was removed by filtration, the filtrate was diluted to *ca*. 25 mL and the copper(II) was precipitated as hydrated copper(II) oxide by adding 10% NaOH solution with constant stirring, followed by heating on a steam-bath for 15 min. The hydrated oxide was removed by filtration and the residue was washed thoroughly with water. The

combined filtrate and washings was first neutralized and then made slightly alkaline with dilute NaOH solution. To this was then added 3 mL of 10% NaCl solution followed by 2 drops of bromophenol blue indicator. The resulting blue solution was diluted to *ca.* 250 mL. To this was added dilute HNO_3 in small portions until the color of the solution turned yellow and then again a few drops of NaOH were added to turn the color back to blue. This was then treated with 1 mL of conc. HCl and the resulting yellow solution was heated at *ca*. 70 °C for 15 min. To this was added an amount of 5 g of $Pb(NO_3)_2$ and the mixture was stirred until all the nitrate had dissolved. This was followed by the addition of 5 g of sodium acetate (CH_3COONa) with continuous agitation for 3 min. This led to the formation of a white granular precipitate of leadchlorofluoride, PbClF. The whole was heated on a steam bath for half-an-hour. The precipitate was filtered through a previously weighed sintered crucible (G-4), washed with water (3 mL × 2) and then with saturated solution of PbClF (3 mL × 2). The precipitate was dried at 140-150 °C to a constant weight.

1 g of PbClF ≡ 0.0726 g of Fluoride

Volumetric [4]

For the estimation of fluoride by volumetric method, the compound was decomposed and fluoride was quantitatively precipitated as PbClF by the procedure described above. The whole was heated on a steam bath for half-an-hour and allowed to stand for overnight. The precipitate was filtered through quantitative filter paper and washed with water (3 mL × 2) and then with saturated solution of PbClF (3 mL × 2). The PbClF was then dissolved in 100 mL of 5% HNO_3 solution by boiling the solution for 30 min. To this was added an excess of known amount of 0.1 M $AgNO_3$ solution

and the mixture was digested on a steam bath for 30 min to coagulate the AgCl precipitate. The precipitate was filtered and washed with water several times. The combined filtrate and the washings was titrated with 0.1 M NH_4SCN solution using $Fe(NO_3)_3$ as an indicator till the faint red-brown precipitate of $Fe(SCN)_3$ was detected. The volume of $AgNO_3$ thus found in the filtrate was subtracted from the original volume and the fluoride content was calculated from the volume $AgNO_3$ solution consumed.

Fluoride from $(NH_4)_3[MnF_6]$ [4]

For the estimation of fluoride from $(NH_4)_3[MnF_6]$, the compound was decomposed by the treatment of a known amount of the compound with 100 mL of 5% NaOH solution. This alkali treatment resulted in precipitation of hydrated oxide of manganese(III). The mixture was boiled for 15 min to ensure complete precipitation as well as the coagulation of the precipitate. The precipitate was removed by filtration and washed thoroughly. The amount of fluoride in the filtrate was then estimated by following the procedure described above.

Chloride and bromide from mixed halo compound of iron(III)

Gravimetric [5]

The amount of chloride and bromide was determined as follows:

An accurately weighed amount of the mixed halo compound of the iron(III) was dissolved in 25 mL of water under slightly acidic condition. The solution was first neutralized and then made alkaline with 20% NaOH solution to precipitate iron(III) as its hydrated oxide. The precipitate was removed by filtration and washed several times with water. The combined filtrate and washings was diluted to *ca*. 100 mL. This was

then neutralized and then acidified with 5 mL of 6M HNO_3 followed by addition of an excess of $AgNO_3$ solution. The precipitate of silver halides thus obtained was filtered on a previously weighed sintered-glass crucible. The precipitate was washed with water. This was then washed thoroughly with 2 M ammonia solution in order to dissolve the precipitate of AgCl leaving only the precipitate of AgBr in the crucible. The residual AgBr was then washed 2 or 3 times with very dilute HNO_3. The precipitate was dried at 130-140 °C to constant weight.

1 g of AgBr ≡ 0.4252 of bromide

The washings of the ammonia solution, which contain the dissolved AgCl was rendered sufficiently acidic by 6 M HNO_3 upon which the precipitate of AgCl was reformed. The precipitate was filtered on a previously weighed sintered-glass crucible. This was then washed with water and then with very dilute HNO3. The precipitate was dried at 130-140 °C to a constant weight.

1 g of AgBr ≡ 0.2473 g of bromide

Iron from mixed halo compound of iron(III)

Volumetric [6]

An accurately weighed amount of the iron(III) compound was dissolved in 25 mL of water under slightly acidic condition. The solution was first neutralized and then made alkaline with 20% NaOH solution to precipitate iron(III) as its hydrated oxide. The precipitate was washed free of halides and was dissolved in 30 mL of 6 M HCl. The iron(III) in the solution was then reduced with moderately conc. $SnCl_2$ solution added dropwise from a burrette with stirring until the yellow colour of the solution had nearly disappeared. The reduction was then completed by diluting the solution of $SnCl_2$

with 2 volumes of dil. HCl and adding the dilute solution dropwise with agitation after each addition until the liquid had a faint green colour, quite free from tinge of yellow. The solution was rapidly cooled under tap with protection from air and the slight excess of $SnCl_2$ was removed by adding 5 mL of a saturated solution of $HgCl_2$ rapidly in one portion and thorough mixing.

To the resultant solution containing the iron(II), was added 25 mL of Zimmermann and Reinhardt's solution (this was prepared by dissolving 5 g of crystallized $MnSO_4.4H_2O$ in 25 mL of water, adding a cooled mixture of 10 mL of conc. H_2SO_4 and 30 mL of water, followed by 10 mL of syrupy orthophosphoric acid). The mixture was well agitated before being titrated with standard 0.02 M $KMnO_4$ solution. The end point was appearance of a pale-pink color persistent for 30 seconds.

$$1 \text{ ml of } 1M\ KMnO_4 \equiv 0.0112 \text{ g of Fe}$$

Manganese(III) from $(NH_4)_3[MnF_6]$

Iodometry

To a solution of an excess of potassium iodide in water (100 mL) acidified with H_2SO_4 (5 mL of conc. H_2SO_4) was added a known amount of the Mn(III) compound with constant stirring. The stirring was continued until the compound was dissolved completely. The solution was then kept in dark for 5 min to ensure the complete liberation of iodine. The liberated iodine was titrated with standard sodium thiosulphate solution using starch as the indicator.

$$1 \text{ mL of } 1M\ Na_2S_2O_3 \equiv 0.0549 \text{ g of Mn}$$

Bromides form TBATB and CTMATB [7]

Volumetric

A known amount of (0.1g) the tribromide was dissolved in 20 mL of CH_3CN. The solution was treated with 20 mL of 20% NaOH solution and was shaken for a while, whereupon the orange-red color of the solution disappeared, indicating reduction of Br_3^- to Br^-. The solution was diluted to 100 mL and boiled on a steam bath for 1h. The whole was then cooled to room temperature and neutralized with 50% HNO_3 solution. The neutral solution was acidified with 5 mL of 6 M HNO_3 and to that an excess of 0.1 M $AgNO_3$ solution was added. The precipitate of AgBr thus formed was coagulated by warming the mixture on a steam bath for 15 min, filtered through a quantitative filter paper and washed several times with water. The combined filtrate and washings was titrated with 0.1 M NH_4SCN solution using iron(III) nitrate as an indicator. The volume of $AgNO_3$ found in the filtrate was subtracted from the original volume and the bromide content was calculated from the volume of $AgNO_3$ solution consumed.

Gravimetric

An accurately weighed amount of (0.1g) of the tribromide was dissolved in 20 mL of CH_3CN. The solution was treated with 20 mL of 20% NaOH solution and was shaken well. This resulted in the decolourisation of the solution indicating reduction of Br_3^- to Br^- by alkaline CH_3CN solution. The solution was diluted to 100 mL and boiled on a steam bath for 1h. The whole was cooled to room temperature and neutralized with 50% HNO_3 solution. The neutral solution was then acidified with 5 mL of 6 M HNO_3. To this solution was added a slight excess of 0.1 M $AgNO_3$ slowly with constant

stirring. The suspension was heated nearly to boiling for 5 min under constant stirring until the precipitate was coagulated and supernatant liquid became clear. In order to make certain that the precipitation was complete, a few drops of $AgNO_3$ solution was added to the supernatant liquid. The solution was allowed to stand for an hour and then the precipitate was filtered on a previously weighed sintered glass crucible. The precipitate was washed with 2 or 3 times with very dilute HNO_3. The precipitate was dried at 130-140 °C to a constant weight.

$$1 \text{ g of AgBr} \equiv 0.0426 \text{ g of } Br^-$$

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CHAPTER III

Some fluoro compounds of copper(I) and manganese(III): Synthesis of $CuF(PPh_3)_3.2ROH$ (R= Et or Me) and $(NH_4)_3[MnF_6]$

This chapter has been divided into two parts, A and B. While **Part A** deals with two mixed fluorocomplexes of copper(I), **Part B** addresses the synthesis of ammonium hexafluoromangante(III).

PART – A

Molecular Complexes of copper(I): Easy access to $CuF(PPh_3)_3.2ROH$ (R= Et or Me)

Introduction

Halo chemistry of copper(I) is important owing to the applicability of a large number of copper(I) halo compounds in a variety of organic transformations [1] including oxidation of organic molecules [2-4] and some photoredox reactions. [5-7] A vast majority of copper(I) halo compounds are used as precursors for organocopper reagents [8] as well. Significantly, unlike the other halo compounds, synthesis of fluorocompounds of copper(I) is fairly difficult due to a very weak interaction of the soft acid copper(I) and the hard base fluoride. [1] However, some fluorocuprates(I) have assumed renewed importance in recent times in view of their direct applications [9] in some useful transformations. Our attention was drawn specifically to compounds of the type,

$CuF(PPh_3)_3.2ROH$ (R= Me or Et) as these are expected to find application in some synthetically useful transmetallation reactions.[9]

Keeping the aforementioned considerations in mind we sought to synthesize $CuF(PPh_3)_3.2ROH$ (R= Me or Et) in order to gain an easy access to such compounds. It is pertinent to note that the compound $CuF(PPh_3)_3.2EtOH$ was reported in the literature. [10, 11] The literature synthesis is based on a reaction of copper(II) fluoride dihydrate, $CuF_2.2H_2O$, with triphenylphosphine in methanol under reflux. The crude product thus obtained was recrystallized twice from ethanol to give $CuF(PPh_3)_3.2EtOH$. The synthesis has a few limitations in scope. For example, (i) it is rather indirect as it first provides a crude product which on being recrystallised twice from ethanol affords the desired product, (ii) the reaction time is long, (iii) the oxidation product, $OPPh_3$, is soluble in the reaction solution, so the chances of contamination of the end product can not be ruled out, and finally (iv) the yield is rather low. Another concern in this investigation was to probe the thermal properties of the compounds, as it was believed that such investigation might give a clue to the feasibility of obtaining 'CuF' from such compounds.

This part (**Part A**) of **chapter III** presents the details of the investigation on $CuF(PPh_3)_3.2ROH$ (R = Et or Me) including thermogravimetric analysis of $CuF(PPh_3)_3.2MeOH$.

Experimental

All chemicals used were of reagent grade quality. Details of instruments /equipment used for characterization and physicochemical studies of these compounds have been

reported in **chapter II**. The procedures for chemical estimation for different constituents of these compounds have also been described in **chapter II**.

Preparation of $CuF(PPh_3)_3.2MeOH$

A solution of copper(II) sulfate pentahydrate, $CuSO_4.5H_2O$, (3.0 g, 12 mmol) in water (50 mL) was treated with hydroxylamine hydrochloride, $NH_2OH.HCl$, (0.83 g, 12 mmol) and to the resulting solution was added 10% NaOH solution slowly dropwise with constant stirring until the orange-red precipitate of copper(I) oxide, Cu_2O, ceased to appear. The complete precipitation was ensured by addition of a few drops of alkali to the supernatant liquid after allowing the solid to settle down. The precipitate was then separated by filtration, washed thoroughly to make it free of alkali and transferred to a 100 mL polyethylene beaker. To a methanol suspension of this product were added triphenylphosphine, Ph_3P, (9.43 g, 36 mmol) followed by 48% hydrofluoric acid, (1 mL, 24 mmol). The mixture was heated on a steam bath for *ca*. 15 min to provide a clear colorless solution thereby indicating completion of the reaction. The whole was further heated for 30 min to concentrate the solution to nearly one-third of its original volume. The concentrated solution on cooling to room temperature afforded the white compound. The compound was washed with methanol (3×3 mL) and petroleum ether (60-80) (3 ml $\times$ 2 mL) and finally dried *in vacuo*. Yield: 6.4 g, 57%. Anal. Calcd.0 for $C_{56}H_{53}CuFO_2P_3$: Cu, 6.8, F, 2.0, C, 72.0, H, 5.7%. Found: Cu, 6.2, F, 2.0, C, 72.5, H, 5.8%. M.P. = 199 or 200°C.

Preparation of $CuF(PPh_3)_3.2EtOH$

To an aqueous solution (50 mL) of copper(II) sulfate pentahydrate, $CuSO_4.5H_2O$, (3.0 g, 12 mmol) , hydroxylamine hydrochloride, $NH_2OH.HCl$, (0.83 g, 12 mmol) was

added. This was then treated with 10% NaOH solution slowly dropwise with constant stirring until the precipitation of orange-yellow copper(I) oxide, Cu_2O, was complete. The precipitate was washed free of alkali and the alkali free Cu_2O was transferred to a 100 mL polyethylene beaker. To an ethanol suspension of this product were added triphenylphosphine, Ph_3P, (9.43 g, 36 mmol) followed by 48% HF (1 mL, 24 mmol). The mixture was heated on a steam bath for *ca.* 10 min. A clear colorless solution thus obtained was heated for a further period of 30 min to reduce the solution to nearly one-third of the original volume. The concentrated solution was cooled to room temperature to afford a white solid product. The product was isolated by filtration, washed with methanol (3×3 mL) and petroleum ether (60-80) (3×3 mL) and finally dried *in-vacuo*. Yield: 6.7 g, 59%. Anal. Calcd for $C_{58}H_{57}CuFO_2P_3$: Cu, 6.6, F, 2.0, C, 72.5, H, 6.0%. Found: Cu, 6.1, F, 2.0, C, 72.0, H, 6.0%. M.P. = 193-195 °C.

Results and discussion

Synthesis

In view of the problems associated with the reported synthesis of the title compounds, a direct route was sought so as to avert the difficulties. It was preferred to use readily available and cost effective copper(II) compound as a starting material to reduce it to copper(I) followed by its reaction with triphenylphosphine, Ph_3P, and aqueous HF in an appropriate solvent to afford the desired products. Indeed, the strategy worked well. The reduction of copper(II) with hydroxylamine hydrochloride, $NH_2OH.HCl$, resulted in the precipitation of copper(I) oxide, Cu_2O. The freshly prepared orange-yellow Cu_2O, that was thoroughly washed free of other ions, readily reacted with hydrofluoric acid and

triphenylphosphine in methanol or ethanol to give the desired products. The products thus obtained were highly pure.

The white compounds were characterised by a combination of elemental analyses, magnetic susceptibility measurements, IR and electronic absorption spectroscopies, solution conductance measurements and thermogravimetric (TG) analysis. The IR spectral measurements in 400-4000 cm^{-1} did not provide much information, as there was a very little difference as regards the various peak positions of the compounds from those of free triphenylphosphine. A group of bands appearing between 550 and 480 cm^{-1} show a little shifting and splittings that are characteristic of the compounds. These bands owe their origin to vibrations involving P-C bonds. The low frequency IR spectra (**Fig.1**) of the compounds, however, provided useful information about the compounds. The medium intensity bands at 290 and 291 cm^{-1} for $CuF(PPh_3)_3.2MeOH$ and $CuF(PPh_3)_3.2EtOH$, respectively, could be assigned to Cu-F stretching frequency. [10, 11] These values are well in agreement with those of the other $CuX(PPh_3)_3$ (X= Cl 220, X= Br 166, X= I, 145cm^{-1}) [12] complexes. The IR results are indicative of a considerable covalent character in Cu-F bond. [13] A weak band at 127cm^{-1} could be assigned to Cu-P stretching frequency. Solution conductance measurements were carried out in CH_3CN as well as in CH_2Cl_2. The conductance for acetonitrile solutions of $CuF(PPh_3)_3.2MeOH$ and $CuF(PPh_3)_3.2EtOH$ measured at room temperature recorded Λ_m (10^{-3} M) = 65 $\Omega^{-1}cm^2mol^{-1}$ and Λ_m (10^{-3} M) = 67 Ω^{-1} cm^2 mol^{-1}, respectively. The Λ_m values in this solvent recorded gradual increase on standing for some time and approached a value in 90-100 $\Omega^{-1}cm^2mol^{-1}$. On the other hand the dichloromethane solutions of both the compounds recorded a low value of Λ_m (10^{-3} M)

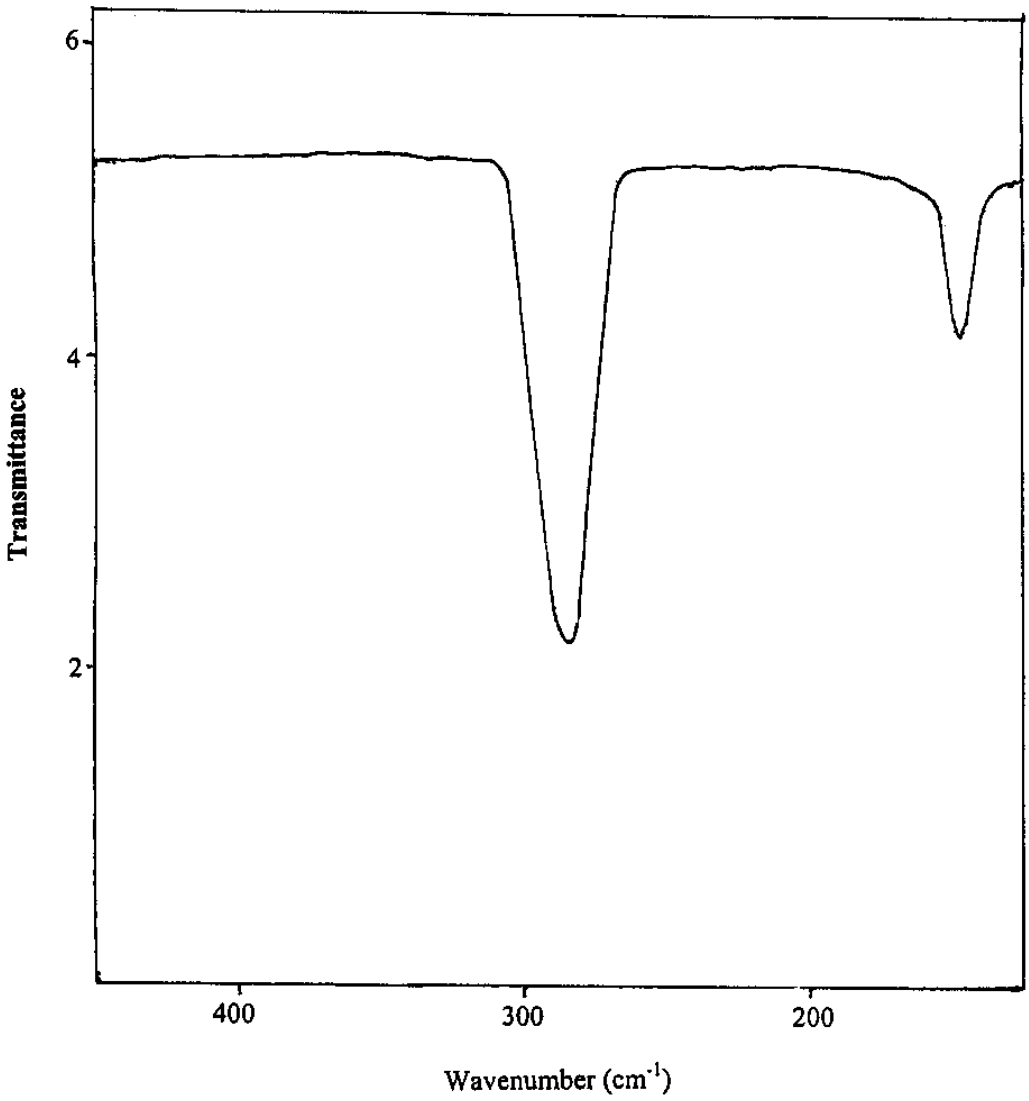

Figure 1. IR spectrum of $CuF(PPh_3)_3.2MeOH$ (100 – 450 cm^{-1})

= 10 $\Omega^{-1}cm^2mol^{-1}$. Such a low molar conductance in dichloromethane is suggestive of the fact that the compounds remain practically undissociated in a relatively less polar solvent. On the other hand much higher values in acetonitrile indicate a considerable dissociation of the products in a relatively more polar solvent. The UV-Visible spectra (**Fig.2**) of the compounds show a single peak at 38,461 cm^{-1} (ε = 1500 l mol^{-1} cm^{-1}) and 38,095 cm^{-1} (ε = 1671 l mol^{-1} cm^{-1}) for $CuF(PPh_3)_3.2MeOH$ and $CuF(PPh_3)_3.2EtOH$, respectively. This band originates from the phenyl groups of triphenylphosphine.[14] Magnetic susceptibility measurements showed the compounds to be diamagnetic as expected for a copper(I) system.

One of our major interests in this investigation, apart from the synthesis of these compounds, was to probe their thermal behaviour. Accordingly, thermogravimetric (TG) experiment was conducted on $CuF(PPh_3)_3.2MeOH$, as a typical example. The experiment was carried out under pure N_2 with a heating rate of 10 °C/ min. The thermogram (**Fig.3**) though is a straightforward one, yet appeared to be very informative. The TG events suggest that the compound is stable up to 118 °C with the first weight loss beginning immediately after this, which continues very steadily until 275 °C. The experimental weight loss for this event is 92.7%. This corresponds to the loss of two methanol and three triphenylphosphine molecules with the theoretical weight loss being 91.2% per formula weight. This clearly indicates the formation of 'CuF' at this stage (i.e. 275°C). Significantly, there was no plateau (not even for a small temperature range) at the stage of 'CuF' formation except for a break with a change of gradient of the thermogram. The 'CuF' species thus formed gradually volatilizes and the process is complete at 538 °C. An analysis of the thermogram

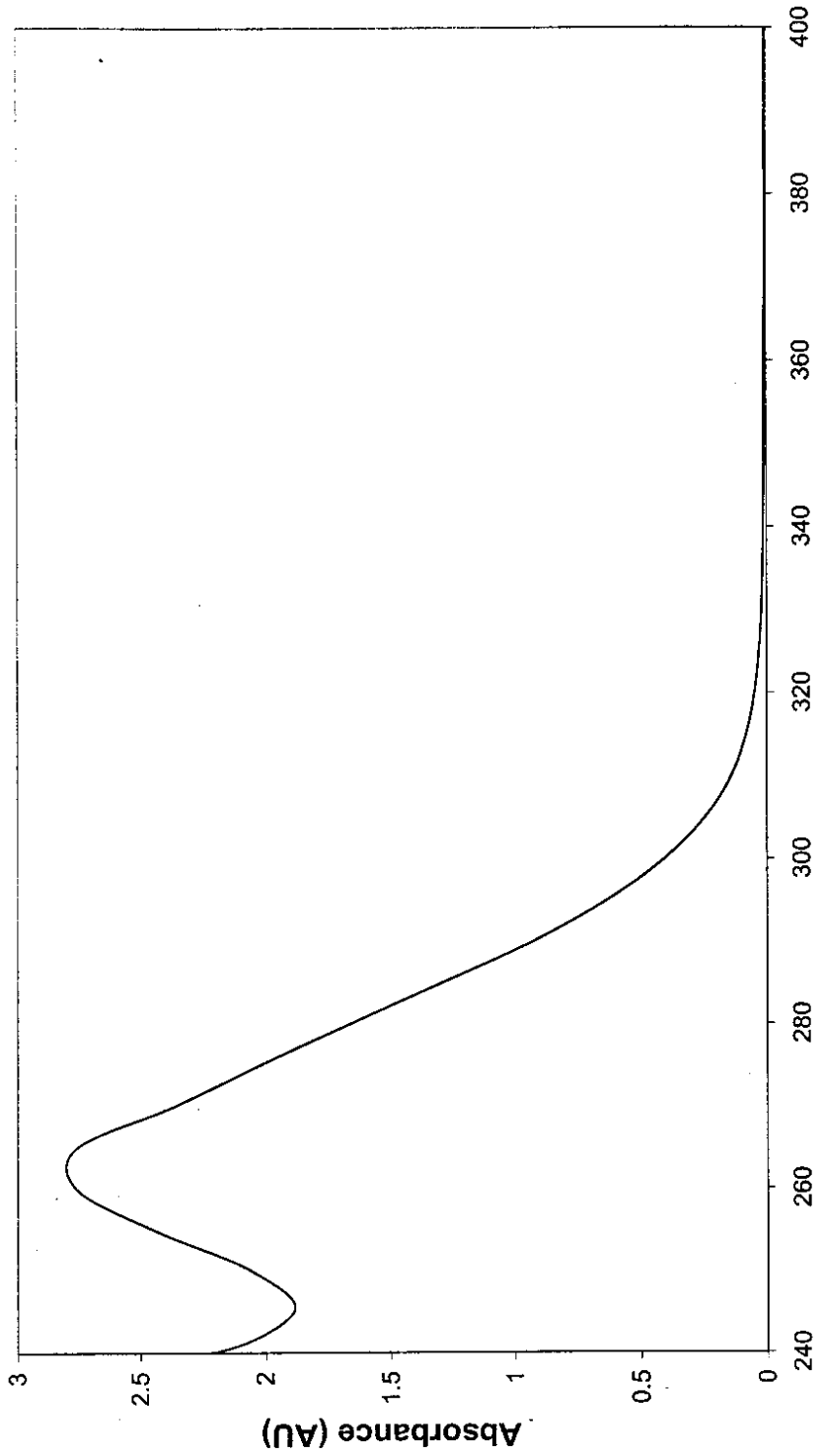

Figure 2. Electronic spectrum of $CuF(PPh_3)_3.2EtOH$

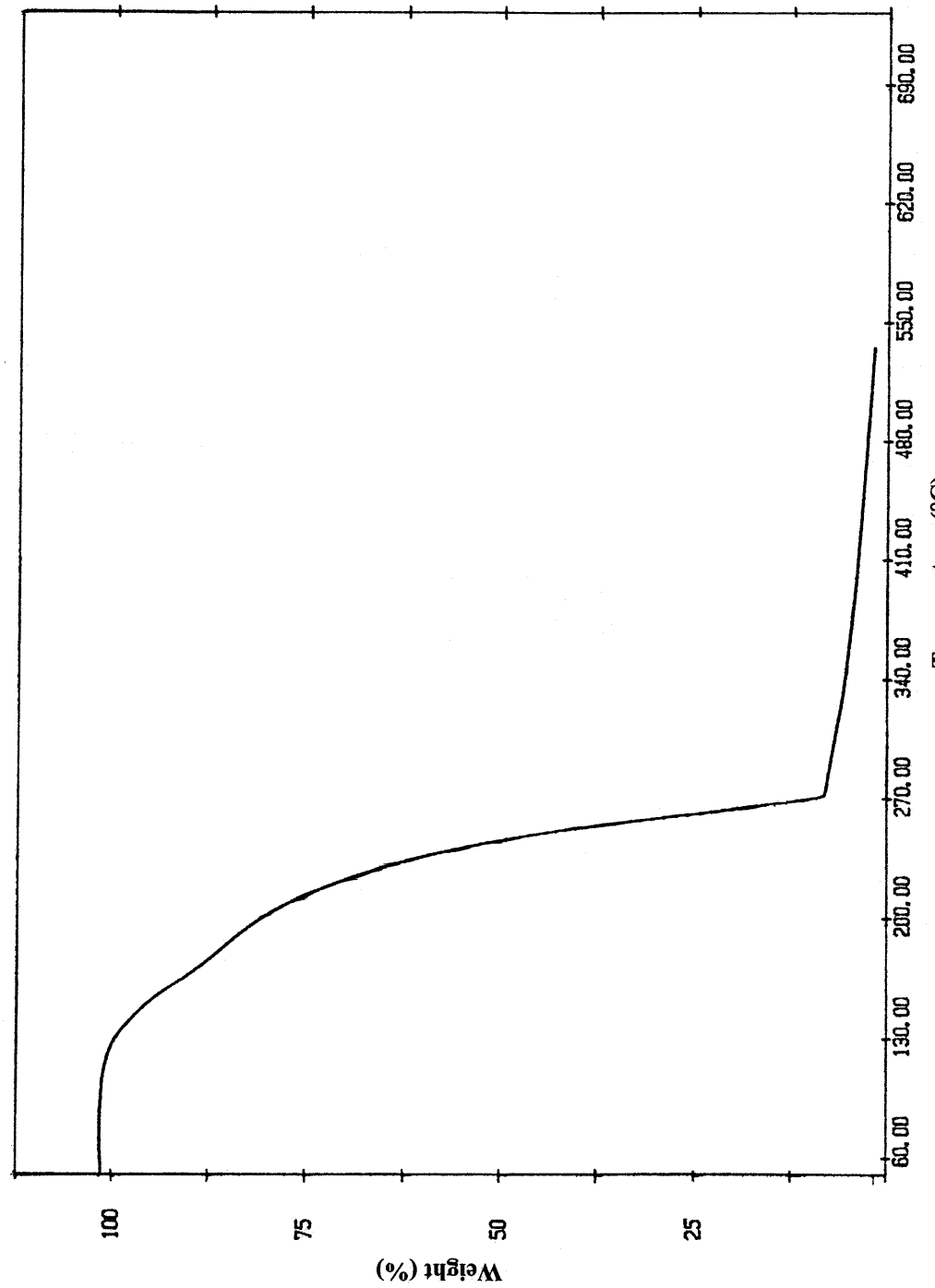

Figure 3. Thermogram of $CuF(PPh_3)_3.2MeOH$

(**Fig. 3**) suggests that under the TG experimental conditions, CuF exists as a gas with its volatility being lower than the parent compound, $CuF(PPh_3)_3.2MeOH$. The knowledge gathered from the TG experiments is expected to be quite relevant in the context of chemical vapor deposition (CVD) studies.

PART-B

Hexafluoromanganate(III): A new synthetic route to $(NH_4)_3[MnF_6]$

Introduction

Manganese exhibits a very large spectrum of oxidation states, possibly the largest known so far, ranging from +VII to –III.[15] Among these the +VII and +II states are known to be more usual than the others. From biological point of view, the metal plays very significant roles in +II to +IV oxidation states.[16, 17] Without going into details of all or many of these oxidation states, we wish to focus our attention to the +III state of the metal for there has been a continued interest of our group to understand several aspects of Mn(III) chemistry. Especially important has been to bring about stability of manganese(III) in aqueous medium. To this end, it was demonstrated by some of my predecessors of the group that fluoride (F^-) served as a very important probe for this purpose. [18] Following this, a large number of fluoro and mixed-fluoro compounds of manganese(III) were studied.[19-24] Taking a lead from the previous studies and also taking note of the importance of fluoro-compounds of metals in general and those of Mn(III) in particular, we became interested in the title compound especially because several attempts made earlier in our laboratories to synthesise $(NH_4)_3[MnF_6]$ ended up with failure, whereas the interest on this compound still existed. One of the principal reasons as to why the compound has been so sought after is that it might serve as a precursor for MnF_3, a very useful fluorinating agent. [25] The choice of ammonium as the counter ion for MnF_6^{3-} has also been considered to be important in this context as NH_4F is expected to be quite volatile.

It may be noted that ammonium salt of hexafluoromanganate(III) is already known in literature [26] but its accessibility is, however, not very easy. It would be an important achievement, therefore, if the compound could be synthesized rather easily by a simple method, particularly without involving any chemicals that might be difficult to handle.

Part B of **chapter III** presents an easy and straight forward synthesis of $(NH_4)_3[MnF_6]$ and its characterization by physico-chemical techniques. The other prime concern in this investigation was to explore the feasibility of obtaining MnF_3 from $(NH_4)_3[MnF_6]$. To this end, the compound was subjected to thermogravimetric experiment for it was believed that such experiment would provide clue to the contention.

Experimental

The chemicals used were of reagent grade quality. Details of the instruments/equipment used for the characterization including chemical procedures for estimation of manganese(III) and fluoride have been given in **chapter II**.

Preparation of $(NH_4)_3[MnF_6]$

To an aqueous solution (250 mL) of $MnCl_2.4H_2O$ (3.0 g, 15.1 mmol) was added 30% H_2O_2 (3 mL, 26.5 mmol) under constant stirring. The solution was then treated with dilute ammonia solution (2 M) dropwise under constant agitation that resulted in the formation of a brown flocculent precipitate. The addition of ammonia solution was continued till the precipitation was complete. The whole was then heated over steam bath for 15 min whereupon the flocculent brown precipitate was transformed into a flesh colored mass. The mass was isolated and washed free of chloride. This was then

transferred to a 100 mL polyethylene beaker. To an aqueous (15 mL) suspension of this product was added ammonium hydrogen fluoride, NH_4HF_2, (1.7 g, 30 mmol) followed by 48% aqueous HF (1 mL, 24 mmol). The resulting clear solution was then heated over steam bath for 30 min in order to facilitate completion of the reaction as well as concentrate to nearly half of its original volume. This was then cooled to room temperature and left undisturbed for 2 h whereupon pink-brown crystals of the compound were formed. The compound was separated by filtration, dried by first pressing it between the folds of a filter paper and finally in a vacuum desiccator over conc. H_2SO_4. Yield: 1.74 g, 52%. Anal. Calcd for $H_{12}N_3MnF_6$: Mn, 24.6, F, 51.1, N, 18.8, H, 5.4%. Found: Mn, 24.8, F, 50.8, N, 19.0, H, 5.4%.

Results and discussion

Synthesis

In view of the anticipated usefulness of the ammonium salt of hexafluoromanganate(III) as a precursor for MnF_3, our group has a sustained interest in this compound. [18-24] Unfortunately, however, the earlier attempts in our laboratories to synthesise $(NH_4)_3[MnF_6]$ by an easy-to-handle method were not successful. During the present research it was decided to draw a renewed attention to $(NH_4)_3[MnF_6]$. The main concerns were the development of an easy and straightforward synthesis of the compound and probing its thermal behaviour. The literature method of preparation for this compound has a few limitations in scope.[26] The most prominent among these is the involvement of multiple synthetic steps. For example, the first step involved the preparation of ammonium salt of MnF_5, which was then reacted with NH_4F and HF to give the compound. In order to overcome these difficulties, it was planned to start with

a readily available Mn(II) source and then oxidise to Mn(III) by alkaline H_2O_2. This would be followed by the treatment of Mn(III) intermediate with NH_4HF_2 and aqueous HF to afford $(NH_4)_3[MnF_6]$. The strategy worked well this time to afford the compound in a high yield as detailed in experimental section.

The compound has been found to be stable for a prolonged period in the absence of moisture. The composition of the compound was ascertained by a variety of physical techniques in addition to chemical estimation of manganese and fluoride. The atom ratio of manganese to fluoride (Mn:F) was found to be 1:6. The chemical determination of oxidation state of the metal by iodometry suggested the occurrence of manganese(III) in the product. The physical methods used for characterization of this compound include IR and reflectance spectroscopies, magnetic susceptibility measurement and TG analysis. The IR spectrum (**Fig. 4 and Fig. 5**) in the range of 400-4000 cm^{-1} shows features due to both NH_4^+ and MnF_6^{3-}. The observed bands at 3160 (m), 3025 (s) and 1418 cm^{-1} (s) are attributed to the IR features of ammonium ion [27, 28] as these correlate very well with those observed for NH_4^+ ion of fluorometallate systems.[27, 29] These bands were assigned to ν_3, ν_1 and ν_2 modes of vibrations, respectively, of the ammonium ion.[30] The other prominent bands observed at 620 and 567 cm^{-1} owe their origin to ν_3 and ν_4 modes of Mn-F stretching frequencies. These values are in well agreement with stretching frequencies of Mn-F of other salts MnF_6^{3-}.[24, 26] The reflectance spectrum of the compound exhibited three bands at 9,000, 17,800 and 19,400 cm^{-1}. These bands could be assigned to $^5B_{1g} \rightarrow {}^5A_{1g}$, $^5B_{1g} \rightarrow {}^5B_{2g}$ and $^5B_{1g} \rightarrow {}^5E_g$, respectively. The reflectance spectrum suggests the splitting of ^5E_g ground state for Mn^{3+} as a consequence of Jahn-Teller distortion.[30] In order to gain information on the magnetic

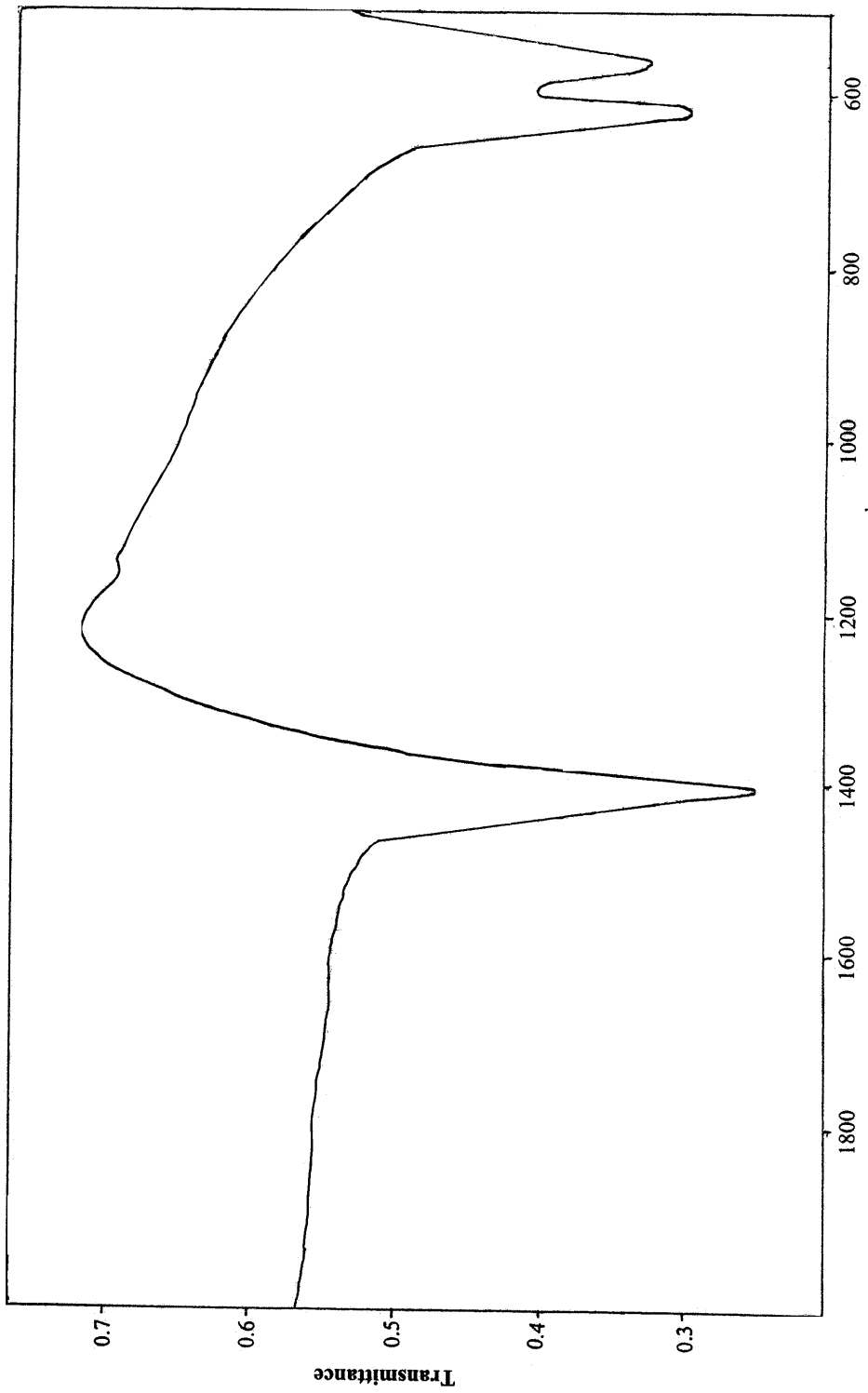

Figure 4. IR spectrum of $(NH_4)_3[MnF_6]$ (500-2000 cm^{-1})

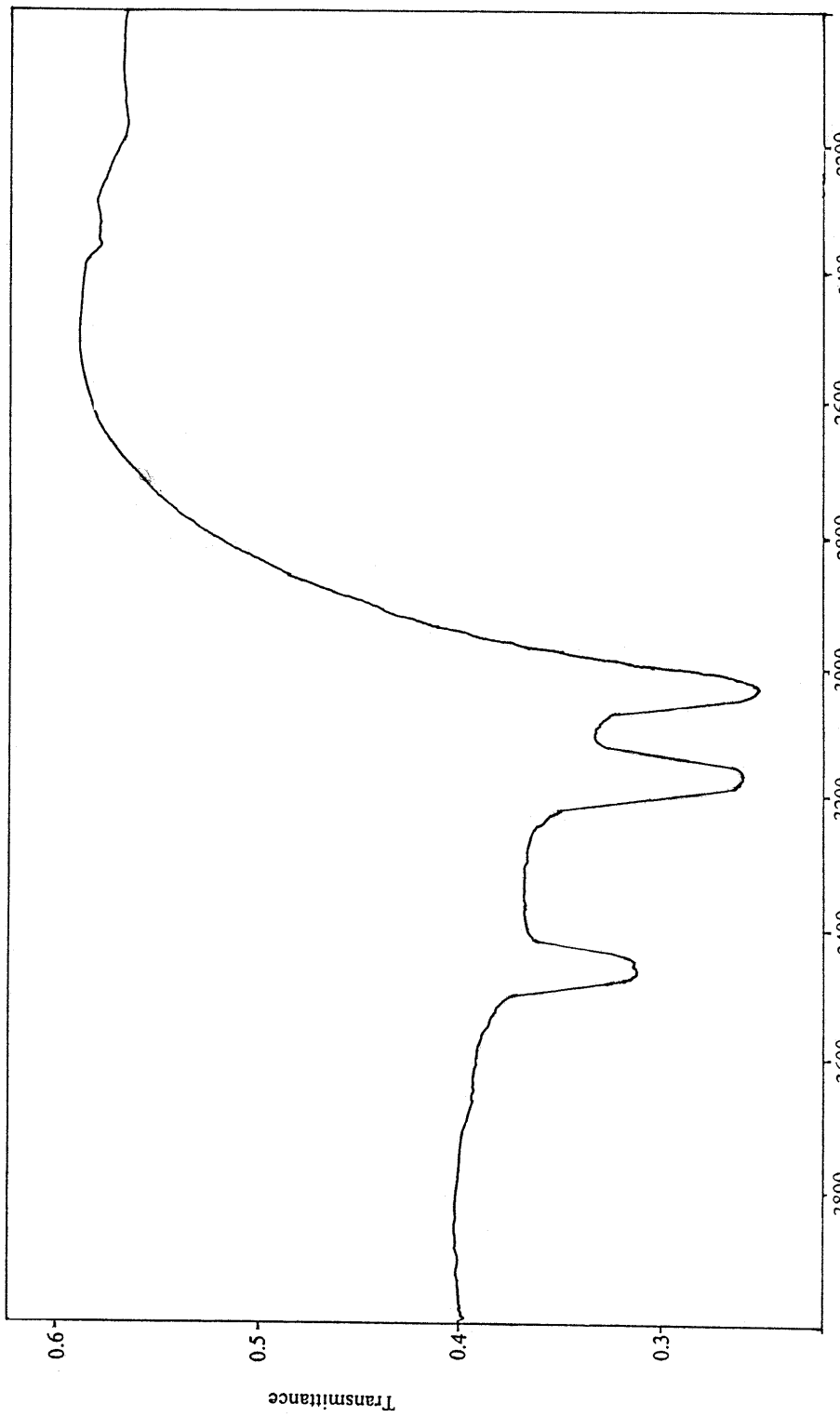

Figure 5. IR spectrum of $(NH_4)_3[MnF_6]$

properties of the compound magnetic susceptibility measurement was carried out at room temperature. The results of replicate determinations gave the magnetic moment value to be 4.7 BM indicating that the compound has a very low antiferromagnetic interaction. The observed value is, however, in line with those of other the salts of hexafluoromanganate(III). [31]

One of our prime concerns in this investigation was to probe the thermal properties of $(NH_4)_3[MnF_6]$. Accordingly, TG experiments were conducted on the compound under pure N_2 with a heating of rate of 10°C/min for a temperature range of 25 to 600 °C. The TG profile (**Fig. 6**) revealed that the compound is stable up to 220°C and then loses three molecules of NH_4F between 220 and 310 °C. The experimental weight loss for this event is 48.4% with the corresponding theoretical value being 49.7% per formula weight. This amply suggests the formation of MnF_3 at this stage. The MnF_3 thus formed does not seem to undergo any further weight loss till the 600°C, which is the upper limit of the temperature range employed in the present experiment.

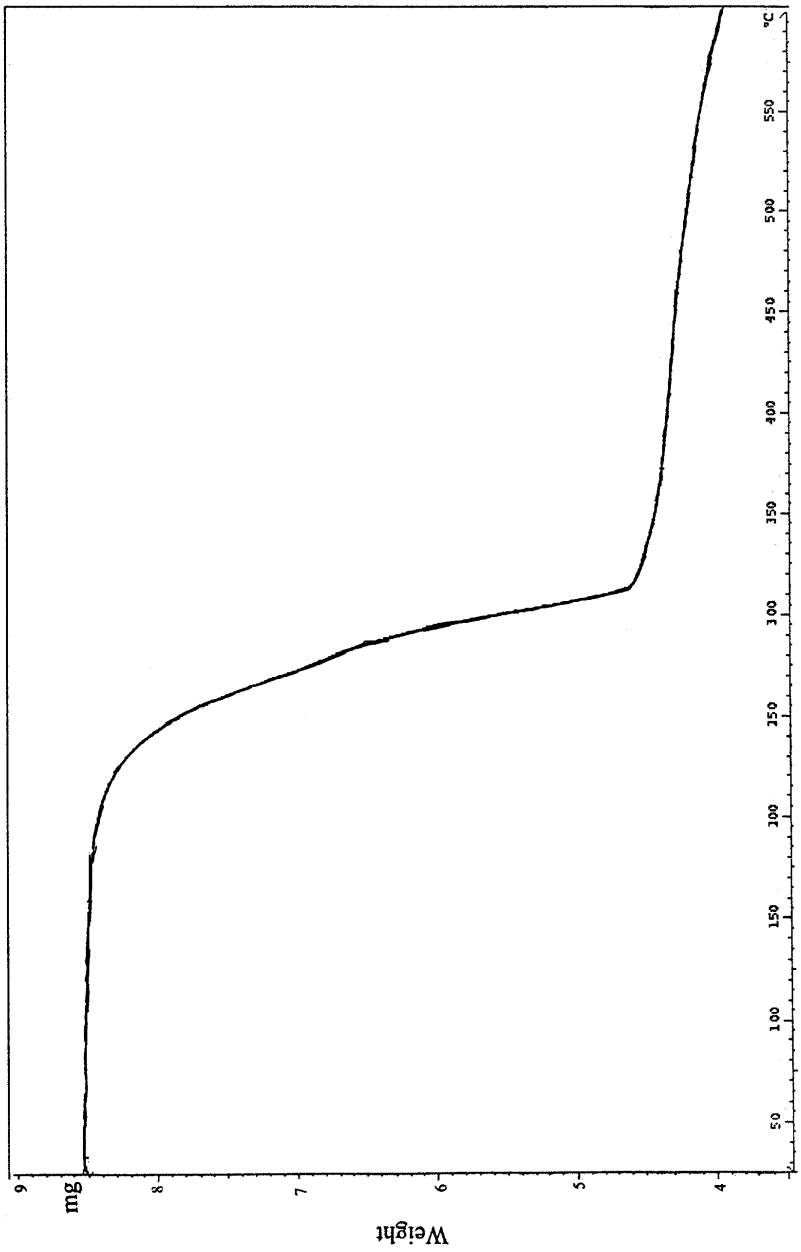

Figure 6. Thermogram of $(NH_4)_3[MnF_6]$

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CHAPTER IV

An environmentally friendly biomimetic synthetic methodology for the bromination of organic substrates by Tetrabutylammonium bromide (TBAB) promoted by V_2O_5-H_2O_2

Introduction

There has been a great demand of bromoaromatics in recent years in view of their increasing pharmaceutical and industrial applications.[1-4] For example, bromoaromatics are used as potent antitumor, antibacterial, antifungal, antineoplastic, antiviral and antioxidizing agents and also as industrial intermediates for the manufacture of speciality chemicals, pharmaceuticals, and agrochemicals.[5] However, routes to such compounds by most of the conventional methods and reagents have some important limitations.[4] The most prominent among these are their hazardous impact on the environment and lack of operational safety.[6] Consequently, an environmentally safe and operationally simple yet efficient, selective, and cost effective methodology for bromination has become a much sought after venture.

Taking cue from the knowledge of V-BrPOs, [7, 8] particularly their role in biobromination in marine animals and also from our earlier experiences with reactivity of peroxovanadium systems in general, [9, 10] and TBATB in particular, [11] we have been able to develop an environmentally favourable biomimetic synthetic protocol for bromination of organic substrates. The protocol involves V_2O_5 as the promoter, H_2O_2 as

the oxidant and tetrabutylamonium bromide (TBAB) as the source of bromine. The solvent of choice was CH_3CN/H_2O. The details of the methodology and its major advantages are presented in this chapter.

Experimental

The chemicals used were all of reagent grade quality. Details of the instruments used for characterization of the products have been reported in **chapter II.**

Bromination of organic substrates by TBAB promoted by V_2O_5-H_2O_2

Bromination of aniline (1)

To a 1:1 mixture of CH_3CN/H_2O (36 mL) taken in a 100 mL round-bottomed flask, vanadium pentoxide, V_2O_5, (0.24 g, 1.33 mmol) was added and the suspension was stirred for 5 min at room temperature. The flask was then immersed in an ice-bath and 30% H_2O_2 (3.6mL, 31.7mmol) was added to the V_2O_5 suspension maintained at 4°C under constant stirring. The mixture was stirred at 4°C for 10 min and to this was added tetrabutylammonium bromide, $(n\text{-}Bu)_4NBr$, (1.93g, 6.0 mmol) followed by the addition of the substrate, (aniline, 0.186g, 2.0 mmol). The reaction mixture was stirred for 0.5h while maintaining the temperature of the bath at 4°C. The mixture was then poured into 50 mL of ethylacetate. After the separation of phases, the aqueous layer was extracted with ethyl acetate (2×10 mL), the combined organic layer was washed with sodium metabisulfite ($Na_2S_2O_5$) solution and dried over anhydrous Na_2SO_4. The solvent was then removed *in vacuo* and the residue was purified by column chromatography (silica gel, hexane: ethyl acetate = 20:80) to give 4-bromoaniline. Yield: 0.282 g (82%).

Bromination of β- naphthol (2)

To a suspension of V_2O_5 (0.24 g, 1.33 mmol) in 1:1 CH_3CN/H_2O (36 mL) taken in a 100 mL round-bottomed flask, was added 30% H_2O_2 (4.8 mL, 42.2 mmol) and the mixture was stirred for 5 min at 4°C. To this was then added tetrabutylammonium bromide (TBAB) (2.57 g, 7.98 mmol) followed by the substrate (β- naphthol, 0.383g, 2.66 mmol). The reaction mixture was left stirred for 1h while maintaining the temperature at 4°C. The whole was then poured into 50 mL of ethylacetate. After the separation of phases, the aqueous layer was extracted with ethyl acetate (2×10 mL), the combined organic layer was washed with sodium metabisulfite ($Na_2S_2O_5$) solution and dried over anhydrous Na_2SO_4. The solvent was then removed *in vacuo* and the residue was purified by column chromatography (silica gel, hexane: ethyl acetate = 75:25) to give 1-bromo-β- napthol. Yield: 0.45 g (76%). ^{1}H NMR: δ 5.90 (s, 1H, *-OH*), 7.22 (d, 1H, *-ArH*), 7.35 (t, 1H, *-ArH*), 7.55 (t, 1H, *-ArH*), 7.70 (m, 2H, *-ArH*), 7.95 (d, 1H, *-ArH*).

Bromination of cinnamic acid (3)

To a suspension of V_2O_5 (0.24 g, 1.33 mmol) in 1:1 CH_3CN/H_2O (36 mL) taken in a 100 mL round-bottomed flask was added 30% H_2O_2 (4.8 mL, 42.3 mmol) at 4°C. After being stirred for 10 min at 4°C, tetrabutylammonium bromide, $(n\text{-}Bu)_4NBr$, (2.57 g, 7.98 mmol) was added to the mixture followed by the substrate (cinnamic acid, 0.394g, 2.66 mmol) and stirring was continued for 1.5h at the same temperature. The mixture was then poured into 50 mL of ethylacetate. After the separation of phases, the aqueous layer was extracted with ethyl acetate (2×10 mL), the combined organic layer

was washed with sodium metabisulfite ($Na_2S_2O_5$) solution and dried over anhydrous Na_2SO_4. The solvent was then removed *in vacuo* and the residue was purified by column chromatography (silica gel, ethyl acetate) to give α,β-dibromocinnamic acid. Yield: 0.614g (75%). ^{1}H NMR: δ 5.05 (d, 1H, -*OH*), 5.35 (d, 1H, -*CH*), 7.37 (m, 3H, -*ArH*), 7.42 (m, 2H, -*ArH*), 8.04 (s, 1H, -*COOH*).

Bromination of anthracene (4)

A suspension of V_2O_5 (0.24 g, 1.33 mmol) in 1:1 mixture of CH_3CN/H_2O (36 mL) taken in a 100 mL round-bottomed flask was stirred magnetically at room temperature for 5 min. The flask was then immersed in an ice-bath and 30% H_2O_2 (4.8mL, 42.3 mmol) was added to the mixture while maintaining the temperature at 4°C under constant stirring. The mixture was stirred at 4°C for further 10 min and to this was added tetrabutylammonium bromide, $(n\text{-}Bu)_4NBr$, (2.57 g, 7.98 mmol) followed by the addition of the substrate (anthracene, 0.473g, 2.66 mmol). The reaction mixture was stirred for 1h while maintaining the temperature of the reaction at 4°C. The mixture was then poured into 50 mL of ethylacetate. After the separation of phases, the aqueous layer was extracted with ethyl acetate (2 × 10 mL), the combined organic layer was washed with sodium metabisulfite ($Na_2S_2O_5$) solution and dried over anhydrous Na_2SO_4. The solvent was then removed *in vacuo* and the residue was purified by column chromatography (silica gel, hexane: ethyl acetate = 9:1) to give 9,10-dibromoanthracene. Yield: 0.833 g (93%).

Bromination of crotyl alcohol (5)

To a suspension of V_2O_5 (0.24 g, 1.33 mmol) in 1:1 CH_3CN/H_2O (36 mL) taken in a 100 mL round-bottomed flask 30% H_2O_2 (4.8 mL, 42.3 mmol) was added at 4°C. After being stirred for 10 min at 4°C, tetrabutylammonium bromide, $(n\text{-}Bu)_4NBr$, (2.57 g, 7.98 mmol) was added to the mixture followed by the substrate, (crotyl alcohol, 0.192g, 2.66 mmol) and stirring was continued for 2h at the same temperature. The mixture was then poured into 50 mL of ethylacetate. After the separation of phases, the aqueous layer was extracted with ethylacetate (2 × 10 mL), the combined organic layer was washed with sodium metabisulfite ($Na_2S_2O_5$) solution and dried over anhydrous Na_2SO_4. The solvent was then removed *in vacuo* and residue was purified by column chromatography (silica gel, ethylacetate: methanol = 95:05) to give 2,3-dibromo-1-butanol. Yield: 0.370 g (60%).

Bromination of cyclohexanone (6)

To a 1:1 mixture of CH_3CN/H_2O (36 mL) taken in a 100 mL round-bottomed flask, vanadium pentoxide, V_2O_5, (0.24 g, 1.33 mmol) was added and the suspension was stirred at room temperature for 5 min. The flask was then immersed in an ice-bath and 30% H_2O_2 (4.8mL, 42.3mmol) was added to the V_2O_5 suspension maintained at 4°C under constant magnetic stirring. The mixture was stirred at 4°C for 10 min and to this was added tetrabutylammonium bromide (TBAB) (2.57 g, 7.98 mmol) followed by the addition of cyclohexanone (0.261g, 2.66 mmol). The reaction mixture was stirred for 2h while maintaining the temperature of the bath at 4°C. The mixture was then poured into 50 mL of ethylacetate. After the separation of phases, the

aqueous layer was extracted with ethylacetate (2 × 10 mL), the combined organic layer was washed with sodium metabisulfite ($Na_2S_2O_5$) solution and dried over anhydrous Na_2SO_4. The solvent was then removed *in vacuo* and the residue was purified by column chromatography (silica gel, hexane) to give 2-bromocyclohexanone. Yield: 0.24 g (52%).

Bromination of cyclohexene (7)

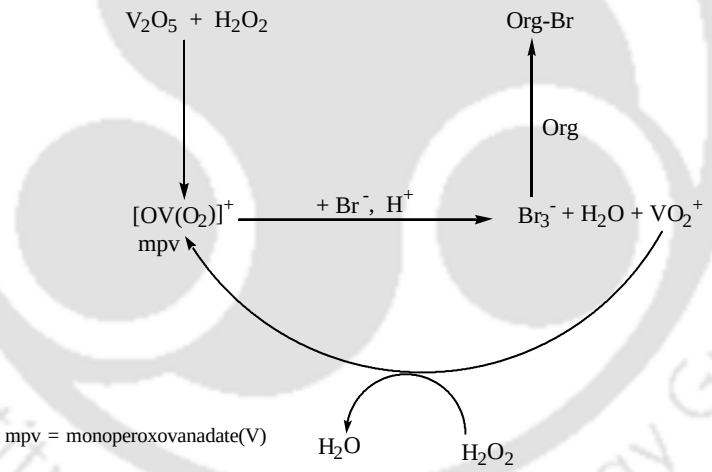
To a suspension of V_2O_5 (0.24 g, 1.33 mmol) in 1:1 CH_3CN/H_2O (36 mL) taken in a 100 mL round-bottomed flask 30% H_2O_2 (4.8 mL, 42.3 mmol) was added at 4°C. After being stirred for 10 min at 4°C, tetrabutylammonium bromide, $(n\text{-}Bu)_4NBr$, (2.57 g, 7.98 mmol) was added to the mixture followed by the substrate (cyclohexene, 0.218 g, 2.66 mmol) and stirring was continued for 2h at the same temperature. The mixture was then poured into 50 mL of ethylacetate. After the separation of phases, the aqueous layer was extracted with ethyl acetate (2 × 10 mL), the combined organic layer was washed with sodium metabisulfite ($Na_2S_2O_5$) solution and dried over anhydrous Na_2SO_4. The solvent was then removed *in vacuo* and the residue was purified by column chromatography (silica gel, hexane) to give 1,2-dibromocyclohexane. Yield: 0.45 g (70%). ^{1}H NMR: δ 1.52 (m, 2H, -*CH*$_2$), 1.82 (m, 4H, -*CH*$_2$), 2.45 (m, 2H, -*CH*$_2$), 4.45 (m, 2H, -*CH*).

Results and discussion

The methodology is based on (i) the activation of hydrogen peroxide through its coordination to vanadium with the formation of monoperoxovanadium(V) intermediate

[(λ = 430 nm)], followed by (ii) oxidation of bromide by the peroxovanadium(V) (λ = 266 nm) species ultimately generating the tribromide (Br_3^-) *in situ* in the solution and finally, (iii) bromination of organic substrates by Br_3^-.

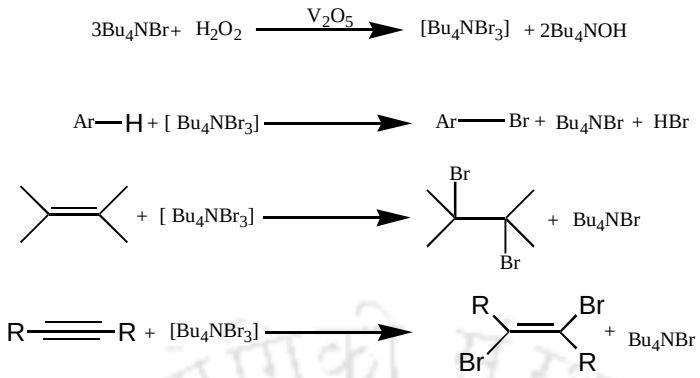
In this methodology the amount of H_2O_2 was used in large excess compared to V_2O_5 in order to impart sufficient acidity to the reaction solution thereby facilitating the bromination of organic substrates. It is believed that under this condition H_2O_2 not only maintains the pH required for the formation of monoperoxovanadate(V) (as evident from the red colouration of the reaction solution and UV-Visible studies) species but also partly regenerates the species after being used up for the oxidation of bromide (**scheme 1**).



Scheme 1

(The H^+ shown in the **scheme 1** indicates the inherent acidity generated in the reaction solution).

The tribromide, Br_3^-, thus generated *in situ* then brominates the organic substrates. The following **scheme 2** shows a few representative examples of the bromination of organics by the tribromide.



Scheme 2

Generation of TBATB and bromination of organic substrates

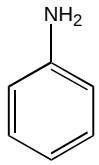
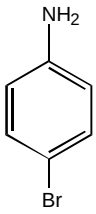
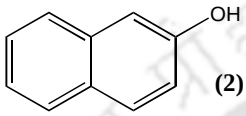
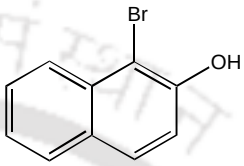
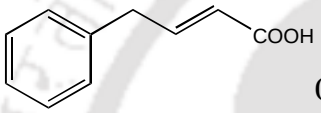
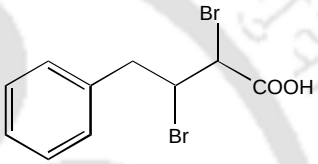
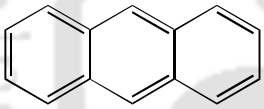
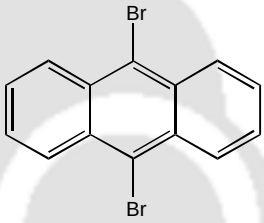
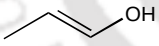
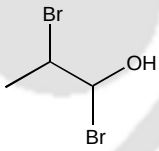
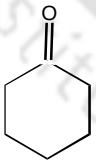
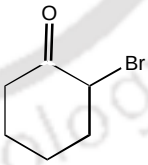
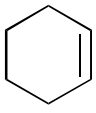
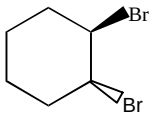
With a view to optimize the methodology several conditions were sampled but the one with a ratio of 1:3:0.5:16 of substrate to TBAB to V_2O_5 to H_2O_2 was found to work best. The solvent system CH_3CN/H_2O worked very well in this methodology and was used in an amount of 8 mL/ mmol of TBAB. The promoter V_2O_5, the oxidant H_2O_2 and the solvent are considered to be environmentally compatible chemicals. The bromination reactions were carried out at *ca.* 5°C with stirring for time period given in the **Table 1**. The reported products were obtained in high to very high yields (**Table 1**).

It was observed that the bromination also takes place with a much lesser amount of V_2O_5 (0.1 mmol) than what is used in this methodology. However, conversion to products was found to be significantly low after a reasonably long reaction time. This could be explained on the basis of acidity of the reaction medium. With other conditions maintained the same the observed pH of the reaction solution was 2.1 in presence of 0.5 mmol of V_2O_5, while the pH of the solution containing 0.1 mmol of V_2O_5 was found to be ~ 5. This signifies that the methodology works efficiently only under reasonably

acidic condition obtained by dissolution of a certain amount of V_2O_5 in H_2O_2. Thus, in order to achieve the desired acidity the amount of V_2O_5 was used much in excess of a catalytic one. However, no addition of acid was required in this methodology.

The assessment of the versatility and efficiency of the methodology was made, by conducting brominations on a number of a variety of substrates (the substrates reported herein form only a part of the total list). The chosen substrates with the reaction times and yields of the products have been presented in **Table 1**. In addition to the advantages like high yields and mild reaction conditions, the other salient feature of this methodology is the product selectivity. For majority of the substrates the methodology was found to be highly regioselective. As for example, aniline gave 4-bromoaniline in very high yield without forming other likely products viz., 2, 4-dibromoanilne and 2,4,6-tribromoaniline (GC and TLC profiles showed exclusively the monobromo-derivative). In order to assess the efficiency on the polycyclic aromatic compounds, the methodology was tested on anthracene. The reaction afforded 9,10-dibromoanthracene as the exclusive product in a very good yield. Similarly, cyclohexanone yielded 2-bromocyclohexanone as the major product.

Table 1 Bromination [a] of aromatics and some other substrates by TBAB and V_2O_5-H_2O_2

substrate	t/h	product	yield(%)[b]
 **(1)**	0.5		82
 **(2)**	1		76
 **(3)**	1.5		75
 **(4)**	1		93
 **(5)**	2		60
 **(5)**	2		52
 **(7)**	2		70

[a] Brominations reactions were monitored by TLC and GC, [b] Isolated yields.

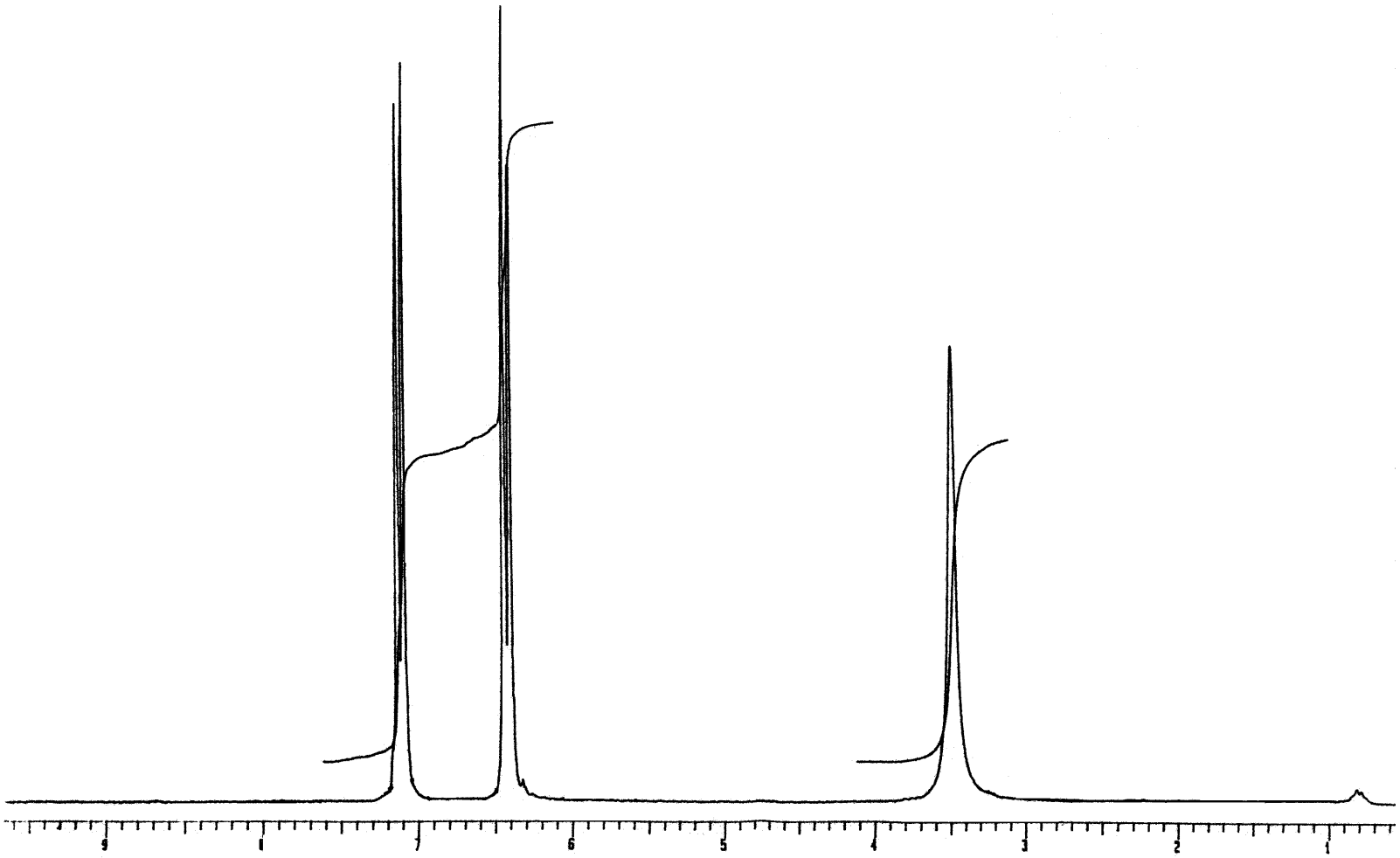


Figure 1. ^{1}H NMR spectrum of 4-Bromoaniline

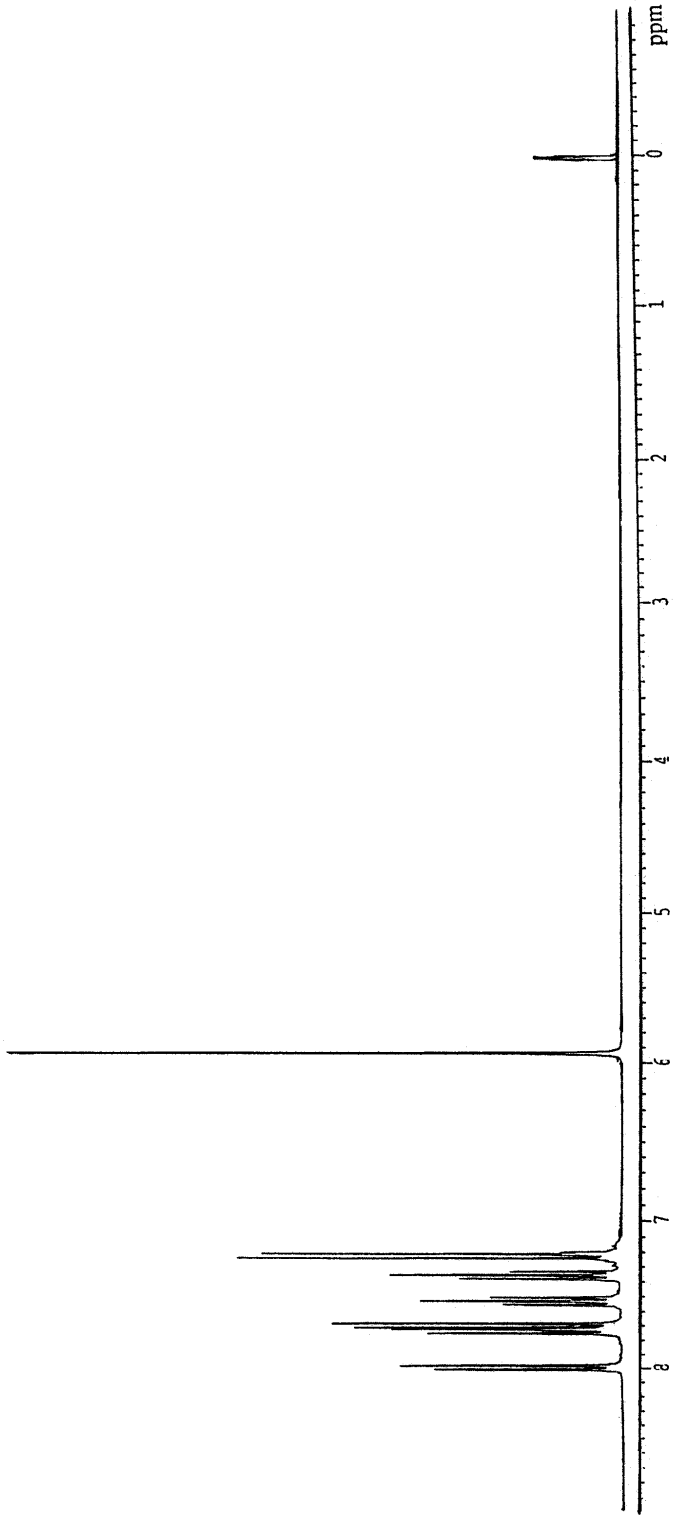


Figure 2. ^{1}H NMR spectrum of 1-Bromo-β-naphthol

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CHAPTER V

An acid assisted peroxo-molybdate(VI) catalysed methodology for *in situ* bromination of organic substrates by tetrabutylammonium bromide (TBAB)

Introduction

The methodology described in the previous chapter employed V_2O_5 much in excess of a catalytic amount. The reason for using a higher amount of V_2O_5 was to generate sufficient acidity to facilitate the bromination with high yields of the products. Consequently, the development of a metal catalyzed methodology of comparable efficiency and versatility was considered a worthwhile excercise. Having comprehended the role of an acidic medium in the peroxo-metal promoted *in situ* bromination of organic substrates, [1, 2] it was thought to use an acid to render the protocol catalytic with respect to the metal catalyst.

It may be pertinent to mention in passing that the chemistries of vanadium(V), molybdenum(VI) have a great similarity.[3] There is also a striking resemblance between different aspects of peroxo-molybdate(VI) and peroxo-vanadate(V) chemistries. Molybdenum forms binary compounds with peroxide in all the four metal to peroxide ratios, viz., 1:4, 1:3, 1:2 and 1:1 (*cf.* vanadium(V)) in pH sensitive reactions.[4] The metal is known also to form a host of oxo mono-and di-peroxo binary and hetero-ligand complexes, some of which have been shown to be important stoichiometric reagents [5] e.g., $[MoO(O_2)_2(pic)]^-$, $[MoO(O_2)(H_2O)(dipic)]$, $[MoO(O_2)_2(ox)]^{2-}$ and $[MoO(O_2)_2(phen)]$ for epoxidation of alkenes. In view of the close resemblance of

peroxochemistry of molybdenum(VI) to that of vanadium(V), it is quite logical to assume that an acid assisted MoO_4^{2-}-H_2O_2 catalyzed bromination protocol could as well be possible.

Keeping these in mind and also taking into account of the general importance of bromoaromatics, [6-13] we have developed yet another methodology for bromination of organic substrates catalyzed by MoO_4^{2-} in presence of $HClO_4$ (catalytic amount). Hydrogen peroxide was used as the oxidant and tetrabutylammonium bromide (TBAB) as the source of bromine in this methodology.

Details of the methodology including its main advantages and environmental implications are presented in this **chapter.**

Experimental

Chemicals used were of all reagent grade quality. Details of instruments used for characterization of the products have been presented in **chapter II.**

Bromination of organic substrates by TBAB and H_2O_2 catalyzed by MoO_4^{2-} in presence of $HClO_4$ (cat.)

Bromination of 2-naphthol (1)

To a stirred suspension containing $H_2MoO_4.H_2O$ (0.035 g, 0.2 mmol) in 9:1 CH_3CN/H_2O (20 mL) at 4°C was added 30% H_2O_2 (1.8 mL, 16 mmol). After about 10 min, tetrabutylammonium bromide (TBAB) (0.966 g, 3.0 mmol) was added to the mixture followed by the addition of 70% $HClO_4$ (0.02 mL, 0.2 mmol). After being stirred for 5 min at 4°C, the substrate (2-naphthol, 0.144 g, 1 mmol) was added to the mixture and stirring was continued for nearly 3h. The whole was then poured into 30 mL of ethyl acetate. The aqueous layer, after being separated from organic layer, was

extracted with ethyl acetate (2×20 mL). The combined organic layer was washed with 5% sodium metabisulfite solution, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. Purification of the residue by column chromatography (hexane: EtOAc = 8:2) gave 1-bromo-2-naphthol. Yield: 0.18 g (76%) ^{1}H NMR: δ 5.90 (s, 1H, -*OH*), 7.22 (d, 1H, -*ArH*), 7.35 (t, 1H, -*ArH*), 7.55 (t, 1H, -*ArH*), 7.70 (m, 2H, -*ArH*), 7.95 (d, 1H, -*ArH*)

Bromination of o-Cresol (2)

To a suspension of $H_2MoO_4.H_2O$ (0.035 g, 0.2 mmol) in 9:1 CH_3CN/H_2O (20 mL) was added 30% H_2O_2 (1.8 mL, 16 mmol) and the mixture was stirred at 4°C for *ca*. 10 min. To this was then added tetrabutylammonium bromide (TBAB) (0.966 g, 3.0 mmol) followed by the addition of 70% $HClO_4$ (0.02 mL, 0.2 mmol). The reaction mixture after being stirred for 5 min at 4°C was added to the substrate (*o*-cresol, 0.108 g, 1 mmol). The mixture was stirred for *ca*. 1h. The whole was then poured into 30 mL of ethylacetate and the aqueous layer was separated from the organic layer. The aqueous layer was then extracted with ethylacetate (2×20 mL). The organic phase collected together was washed with 5% sodium metabisulfite solution, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. Purification of the residue by column chromatography (hexane: EtOAc = 9:1) gave 4-bromo-2-cresol. Yield: 0.14 g (75%). ^{1}H NMR: δ 2.25 (s, 3H, -CH_3), 4.7 (s, 1H, -*OH*), 6.68 (d, 1H, -*ArH*), 7.71 (dd, 1H, -*ArH*), 7.20 (s, 1H, -*ArH*).

Bromination of m-Cresol (3)

A suspension of $H_2MoO_4.H_2O$ (0.035 g, 0.2 mmol) in 9:1 CH_3CN/H_2O (20 mL) was treated with 30% H_2O_2 (1.8 mL, 16 mmol) at 4°C and the mixture was stirred

magnetically for *ca*. 10 min. To the resulting mixture was added tetrabutylammonium bromide (TBAB) (0.966 g, 3.0 mmol) followed by 70% $HClO_4$ (0.02 mL, 0.2 mmol). After being stirred for 5 min at 4°C, the substrate (*m*-cresol, 0.108 g, 1 mmol) was added to the mixture and left stirred for 2h. The mixture was then poured into 30 mL of ethylacetate. The aqueous phase, after being separated from organic layer, was extracted with ethylacetate (2 × 20 mL). The combined organic layer was washed with 5% sodium metabisulfite solution, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. Purification of the residue by column chromatography (hexane: EtOAc = 9:1) gave 4-bromo-3-cresol. Yield: 0.13 g (70%).

Bromination of cyclohexene (4)

A suspension of $H_2MoO_4.H_2O$ (0.03 g, 0.2 mmol) in 9:1 CH_3CN/H_2O (20 mL) was treated with 30% H_2O_2 (1.8 mL, 16 mmol) at 4°C under continuous stirring. After about 10 min, tetrabutylammonium bromide (TBAB) (0.966 g, 3.0 mmol) was added to the mixture followed by the addition of 70% $HClO_4$ (0.02 mL, 0.2 mmol). After being stirred the mixture for about 5 min at 4°C, the substrate (cyclohexene, 0.25 g, 3 mmol) was added to this and stirring was continued for 3h. The mixture was then poured into 30 mL of ethyl acetate and the aqueous layer was separated from the organic phase. After being separated from the organic layer, the aqueous layer was extracted with ethyl acetate (2 × 20 mL). The organic phase combined together was washed with 5% sodium metabisulfite solution, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue thus obtained was purified by column chromatography (hexane) to afford 1,2-dibromocyclohexane. Yield: 0.51 g (70%). ^{1}H NMR: δ 1.52 (m, 2H, -*CH*$_2$), 1.82 (m, 4H, -*CH*$_2$), 2.45 (m, 2H, -*CH*$_2$), 4.45 (m, 2H, -*CH*).

Bromination of Crotyl alcohol (5)

A mixture of $H_2MoO_4.H_2O$ (0.035 g, 0.2 mmol) and 30% H_2O_2 (1.8 mL, 16 mmol) in 9:1 CH_3CN/H_2O (20 mL) was stirred at 4°C for *ca.* 5 min. To this was then added tetrabutylammonium bromide (TBAB) (0.966 g, 3.0 mmol) followed by the addition of 70% $HClO_4$ (0.02 mL, 0.2 mmol). After being stirred for 5 min at 4°C, the substrate (crotyl alcohol, 0.216 g, 3 mmol) was added to the mixture and was left stirred for nearly 5h. The reaction mixture was then poured into 30 mL of ethyl acetate. The aqueous layer, after being separated from organic layer, was extracted with ethyl acetate (2 × 20 mL). The combined organic layer was washed with 5% sodium metabisulfite solution, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. Purification of the residue by column chromatography (ethyl acetate) gave 2,3-dibromo-1-butanol. Yield: 0.50 g (72%).

Bromination of o-nitroaniline (6)

To a stirred suspension containing $H_2MoO_4.H_2O$ (0.035 g, 0.2 mmol) in 9:1 CH_3CN/H_2O (20 mL) at 4°C was added 30% H_2O_2 (1.8 mL, 16 mmol). After being stirred for about 10 min, tetrabutylammonium bromide (TBAB) (0.966 g, 3.0 mmol) was added to the mixture followed by the addition of 70% $HClO_4$ (0.02 mL, 0.2 mmol). After about 5 min, the substrate (*o*-nitroaniline, 0.138 g, 1 mmol) was added to the mixture and stirring was continued for *ca*. 2.5h. The mixture was then poured into 30 mL of ethylacetate. The aqueous layer, after being separated from organic layer, was extracted with ethylacetate (2 × 20 mL). The combined organic layer was washed with 5% sodium metabisulfite solution, dried over anhydrous Na_2SO_4 and evaporated under

reduced pressure. The residue was purified by column chromatography (hexane: EtOAc = 8:2) to give 4-bromo-2-nitroaniline. Yield: 0.19 g (88%).

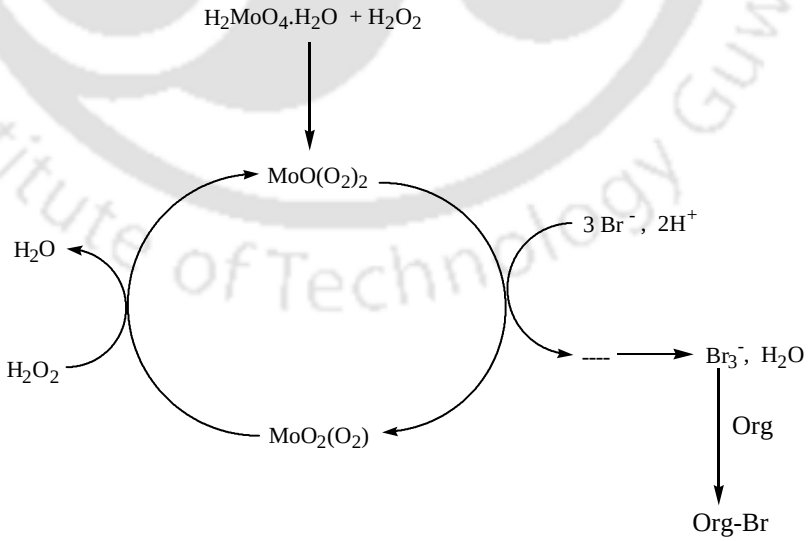
Results and discussion

The methodology is based on the (i) activation of H_2O_2 by the catalyst, $H_2MoO_4.H_2O$, followed by (ii) an acid assisted *in situ* oxidation of bromide to Br_3^- (λ= 266 nm) by the activated peroxide and finally (iii) bromination of organic substrates by Br_3^-. Under the present experimental condition molybdenum(VI) would coordinate with O_2^{2-} thereby activating peroxide in the process. However, the activated peroxide as such may not oxidize Br^- to Br_3^- very efficiently. What would be needed is an acid to facilitate the formation of tribromide. This (*cf*. Br_3^-) in turn would do bromination rapidly, as happened in the present case.

Typically, the catalyst $H_2MoO_4.H_2O$ (20 mol%) was reacted with an excess of H_2O_2 and TBAB in CH_3CN/H_2O. The reaction solution was rendered acidic by the addition of a catalytic amount of $HClO_4$ (20 mol%) and to that was then added the substrate. The sequence of addition was found to be important in the optimisation process. The reaction was carried out at *ca*. 5 °C under stirring for the time period set out in **Table 1**. Different conditions were tried out but the ratio of 1:3:0.2:16 of substrate: reagent: catalyst: H_2O_2 was found to be optimal. Importantly, the methodology required an amount of 20 mol% of acid in so far as optimisation of product yield is concerned. The pH of the reaction solution at this stage was observed to be ~ 1 that rose to 2.1 on completion of the reaction, indicating thereby that added acid in part was consumed in the process of bromination. This suggests *inter alia* that the addition of an acid was imperative for the methodology to work efficiently. It has also

been observed that a much higher amount of $H_2MoO_4.H_2O$ in the absence of an acid was not able to bring about the bromination with equal efficiency. This implies that the unlike vanadium(V) (*vide* ***chapter IV***), the molybdenum(VI) is not capable of promoting bromination of organic substrates without being assisted by an acid.

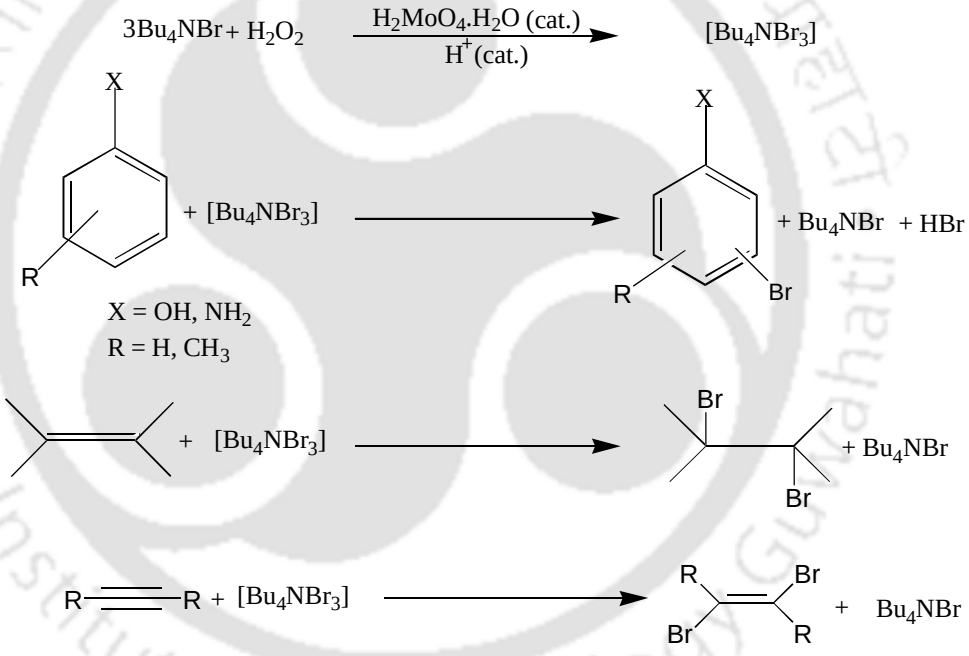
Mechanistically, the reaction of the catalyst $H_2MoO_4.H_2O$ and H_2O_2 leads to the formation of oxodiperoxo species $MoO(O_2)_2$ (λ = 328 nm) [14] under the pH of the reaction solution attained upon the addition of a catalytic amount of $HClO_4$. The species $MoO(O_2)_2$ is believed to be responsible for the oxidation of Br^- to Br_3^- while in the process it gets converted into oxomonoperoxo molybdate(VI), $MoO_2(O_2)$. There could be a possibility that monoperoxo species is involved in the oxidation of a second equivalent of bromide, however, a consistent decrease in λ = 328 nm band in electronic absorption spectra indicates that the diperoxo species is the oxidant. This observance was also consistent with fact that monoperoxo molybdate(VI) is less reactive than the diperoxo species. [14]



Scheme 1

Therefore, it is believed that monoperoxo species disproportionates into $MoO(O_2)_2$ and MoO_3; MoO_3 could then recoordinate two equivalent of H_2O_2 re-forming $MoO(O_2)_2$ (**scheme 1)**.

The efficacy of the methodology was ascertained by conducting bromination on a wide variety of substrates including alkenes, alkynes and α, β-unsaturated ketones in addition to some aromatic compounds (**Scheme 2** shows a few representative examples). The new procedure involving the catalyst ($H_2MoO_4.H_2O$), TBAB and H_2O_2, appears to be economically viable and environmentally acceptable.

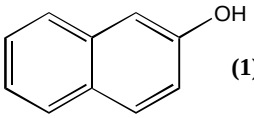
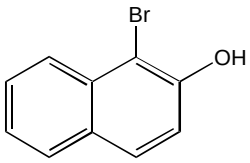
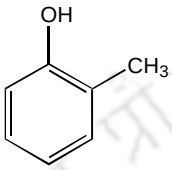
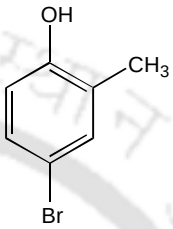
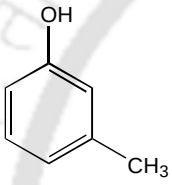
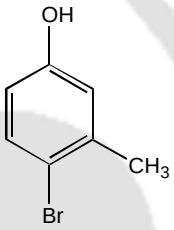
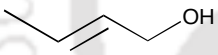
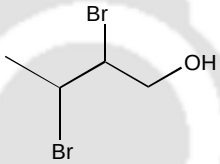
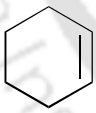
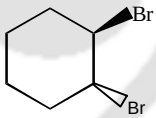
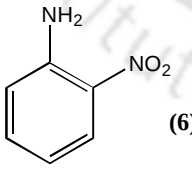
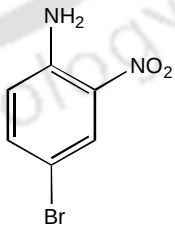


Scheme 2

One of the major advantages of this methodology is that it affords regioselective products for a majority of the substrates. For example, *o*-cresol and *m*-cresol gave selectively the corresponding 4-bromo derivatives, while 1-bromo-β-naphthol was the exclusive product obtained from the bromination of β-naphthol. In case of cresols the

nature of the products indicate that the –OH group has a stronger directing influence than the $–CH_3$ group. For the other substrates of different variety, for example, phenol, acetanilide, anthracene and *m*-nitroaniline, which do not form a part of the thesis, the regioselectivity has been found to be very high as well. Interestingly, a comparison of the products profile of this methodology to that of V_2O_5 promoted one (vide **chapter IV**) reveals that for some substrates the product selectivity is different in two cases. For example, anthracene gave 9,10-dibromoanthracene and phenol gave 2,4,6-tribromophenol in presence of V_2O_5 as a promoter, but in the acid assisted catalytic bromination by Mo (VI), the major products are 9-bromoanthracene and 4-bromophenol, respectively. This points to the fact that by selecting a suitable catalyst or a promoter one can tune the selectivity of a bromination protocol. The yields for majority of the products reported herein have been high to very high (**Table 1**).

Table1. Bromination [a] of organic substrates by TBAB and MoO_4^{2-}-H_2O_2 assisted by H^+(cat.)

substrate	t/h	product	yield (%) [b]
 **(1)**	3.0		76
 **(2)**	1.0		75
 **(3)**	2.0		70
 **(4)**	5.0		72
 **(5)**	3.0		70
 **(6)**	2.5		88

[a] Reactions were monitored by TLC and GC, [b] isolated yields

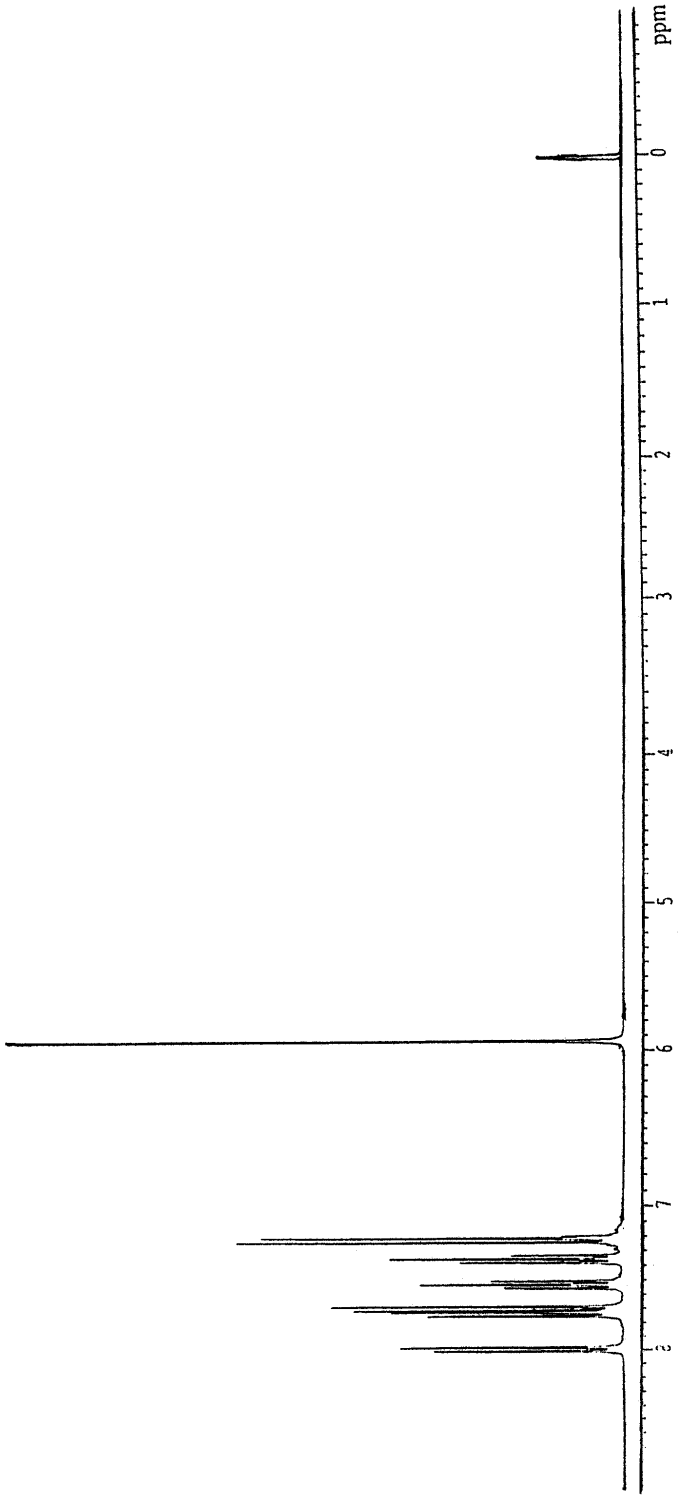


Figure 1. ^{1}H NMR spectrum of 1-Bromo-β-naphthol

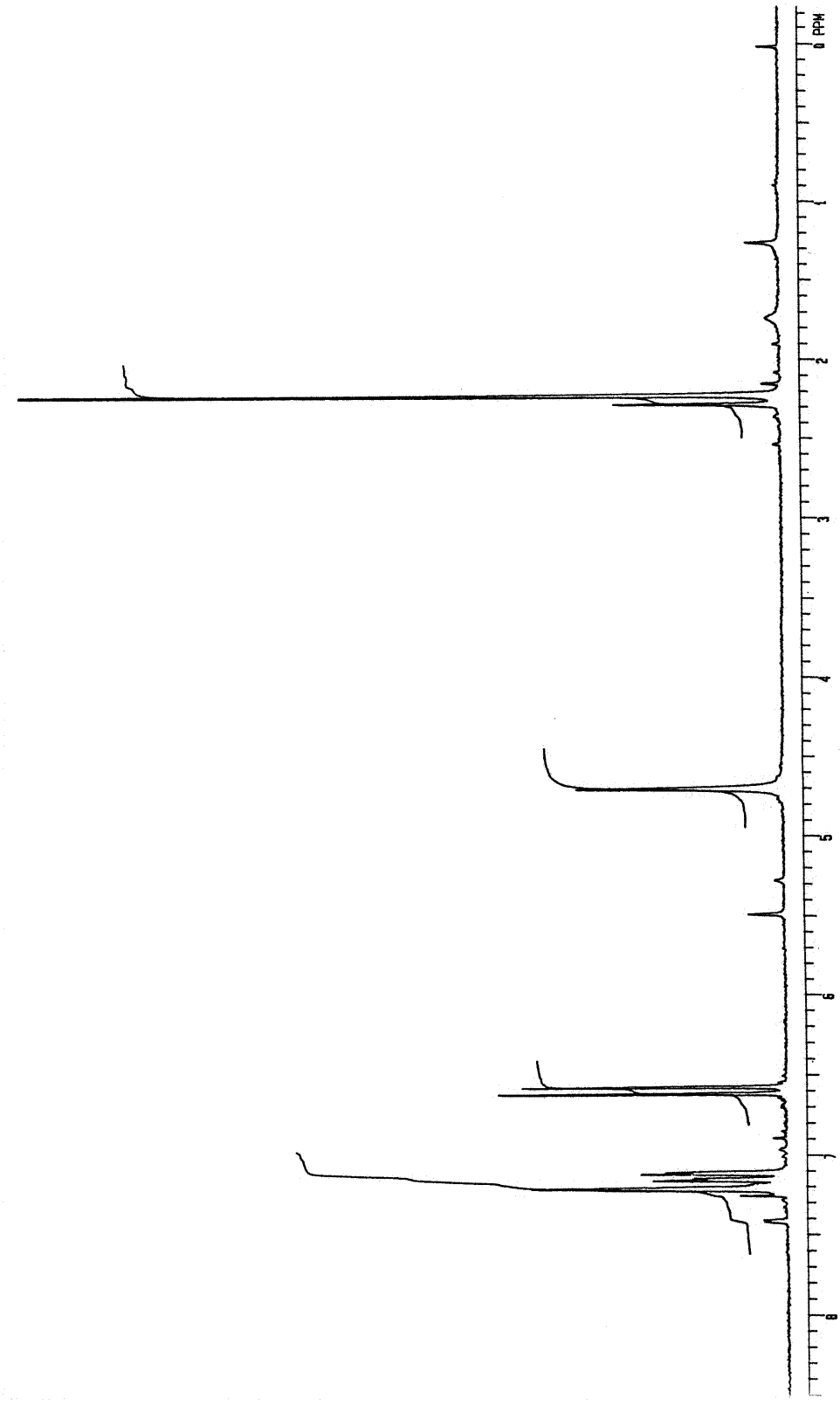


Figure 2. ^{1}H NMR spectrum of 4-Bromo-*o*-cresol

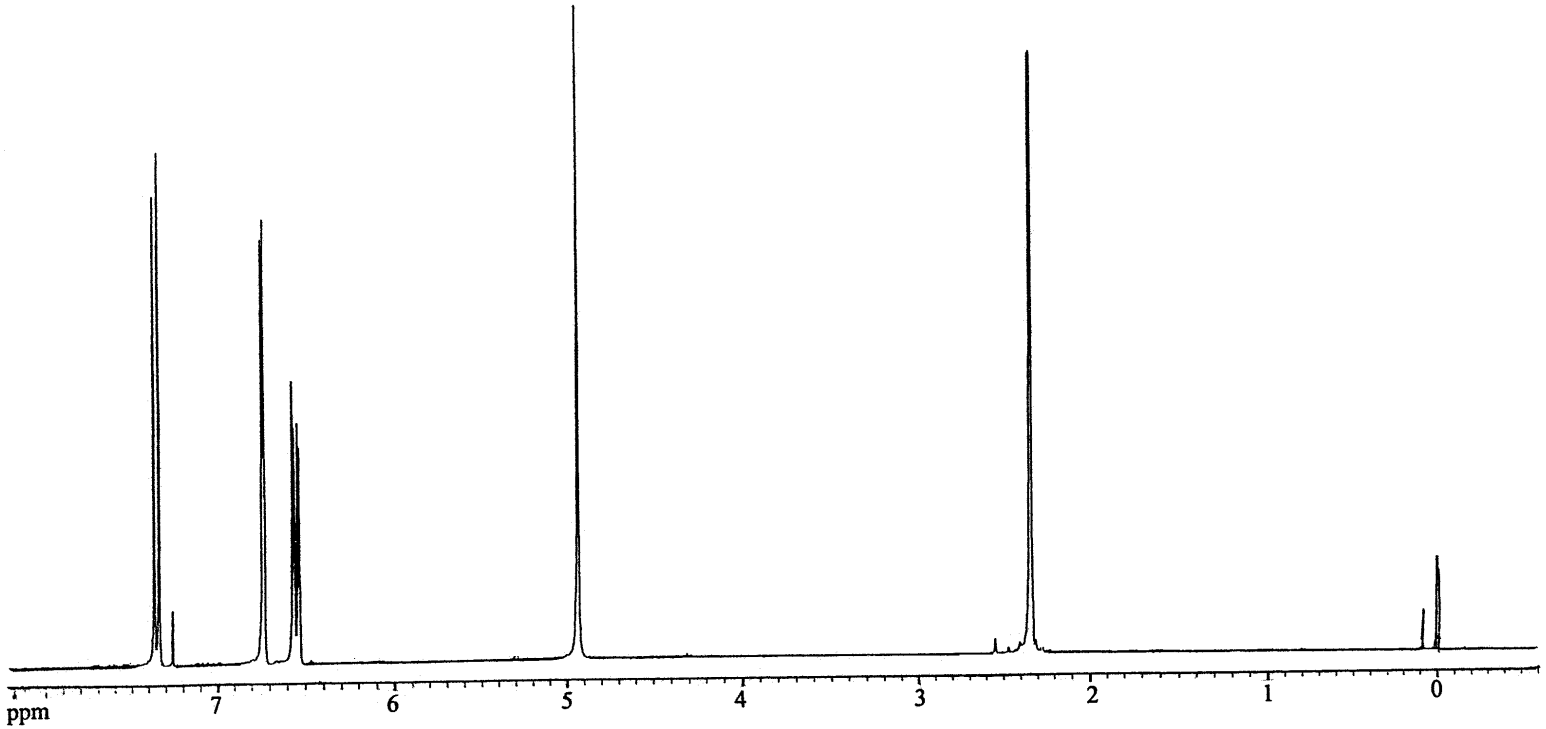


Figure 3. ^{1}H NMR spectrum of 4-Bromo-*m*-cresol

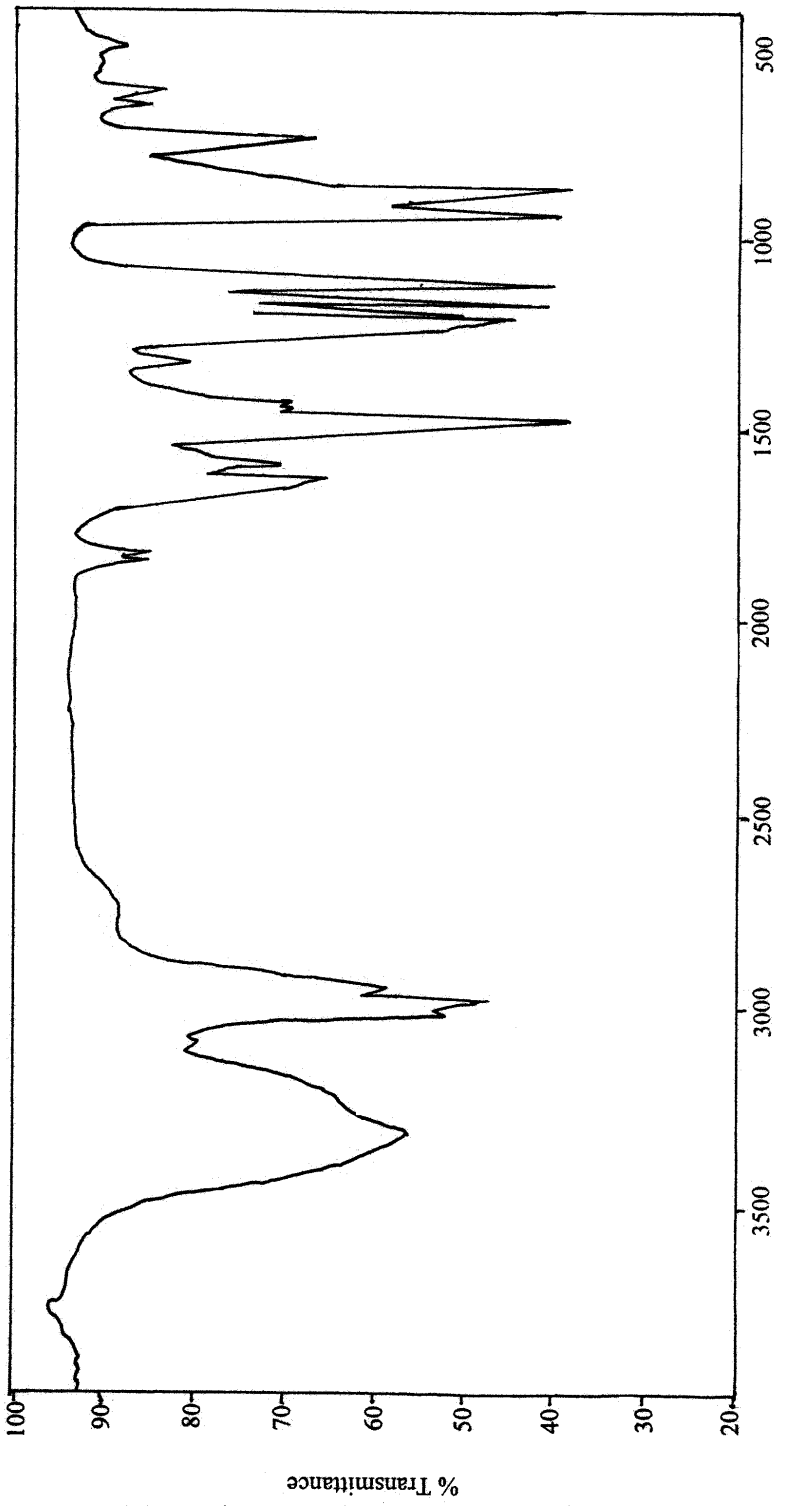


Figure 4. IR spectrum of 4-Bromo-*o*-cresol

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CHAPTER VI

Cetyltrimethylammonium tribromide (CTMATB), $C_{19}H_{42}NBr_3$: A new environmentally favourable synthesis and studies of its reaction profile involving a few selected substrates

Introduction

In the preceding two chapters, we have reported the development of two versatile and efficient methodologies for *in situ* bromination of organic substrates by tetrabutylammonium bromide (TBAB) and H_2O_2, promoted or catalyzed by the metals. In continuation to this endeavour [1,2] it was considered imperative to explore the possibilities of working out a clean and facile synthesis of cetyltrimethylammonium tribromide, $C_{19}H_{42}NBr_3$ (CTMATB), and study its efficacy as a brominating agent. Incidentally, there is a description of the preparation of CTMATB and some of its pharmacological properties as reported [3] in a patent. The patented method involves the use of Br_2 and HBr that are not only considered to be environmentally hazardous but also highly toxic. In view of the drawbacks of the reported preparation of CTMATB, it was considered to be a worthwhile exercise to develop an efficient and cleaner synthesis of this reagent and investigate its reaction profile. Based on our earlier experience and information, CTMATB was anticipated to be yet another important and cost effective reagent for organic bromination. It is pertinent to mention in passing that bromoaromatics have attracted enormous attention [1,2,4,5] in recent times due to their wide range of applicability. [6-9] And this point has been emphasised earlier. The reagent CTMATB is expected to be a stable, long-lived, easy to handle and non-toxic. In

addition to this, a salt of cetyltrimethylammonium ion has some special features that make it to be a useful compound for organic reactions. For example, (i) CTMAB is a very efficient phase transfer agent, which renders it to be very effectively used in biphasic organic transformations [10,11] and (ii) the presence of cetyltrimethylammonium cation has been known to facilitate the oxidation of bromide to tribromide due to its ability to form ion pair with the anion. [12] Thus, the synthesis of CTMATB from CTMAB appeared to be all the more attractive proposition.

In view of the aforesaid rationales as well as consideration of the fact that CTMAB is cheaper relative to other common organic ammonium bromides, we undertook the synthesis of cetyltrimethylammonium tribromide (CTMATB) and studies of its reactivity as a brominating reagent.

This **chapter** reports the details of the preparation and characterization of the reagent and bromination of a few selected organic substrates by it.

Experimental

The chemicals used were of reagent grade quality. Details of instruments/ equipment used and chemical procedures employed for characterisation of the reagents and the products have been reported in **chapter II**.

Preparation of cetyltrimethylammonium tribromide, $C_{19}H_{42}NBr_3$ (CTMATB)

To a suspension of $H_2MoO_4.H_2O$ (0.02 g, 0.11 mmol) in water (5 mL) taken in a 100 mL beaker was added 30% H_2O_2 (5 mL, 44.1 mmol) at 4°C and the mixture was stirred for 10 min to provide a clear yellow solution (**solution A**). Separately, in a 200 mL beaker, cetyltrimethylammonium bromide (CTMAB), (3.95 g, 10.8 mmol) and KBr (2.6 g, 21.8 mmol) were taken in water (50 mL) and the mixture was acidified with H_2SO_4

(10 mL of 2N). The whole was then stirred magnetically for *ca*. 5 min to provide a clear colorless solution (**solution B**). The **solution A** was then added to the **solution B** slowly under constant stirring at ambient temperature. The mixture thus obtained was stirred for 30 min whereupon a yellow product was formed. The product was filtered under reduced pressure, washed first with water (2 × 10 mL) and then with diethyl ether (2 × 10 mL) (diethyl ether also helped to reduce froth formation during the filtration) and finally dried *in vacuo*. The product on crystallization from acetonitrile afforded shiny orange-yellow tribromide. Yield: 5.3 g, (93.3%). Anal. Calcd for $C_{19}H_{42}NBr_3$: C, 43.53, H, 8.07, N, 2.67, Br, 45.7%. Found: C, 43.15, H, 8.1, N, 2.65, Br, 45.8%. The melting point of the compound determined by DSC (**Fig. 1**) recorded to be 94 °C.

Bromination of organic substrates by cetyltrimethylammonium tribromide (CTMATB)

Bromination of phenol (1)

To a solution of CTMATB (0.577 g, 1.1 mmol) in CH_3CN (15 mL) was added the substrate (phenol, 0.094 g, 1 mmol) at ambient temperature under stirring. The mixture was then allowed to stir for 0.5 h at room temperature. The reaction mixture was then concentrated under reduced pressure and the solvent was completely removed. The residue was extracted with ethyl acetate (30 mL). The ethyl acetate extract was washed with 5% sodium metabisulfite solution, dried over anhydrous Na_2SO_4 and finally evaporated *in vacuo*. Purification of the residue by column chromatography (hexane: ethylacetate = 9:1) afforded 4-bromophenol. Yield: 0.12 g (70%)

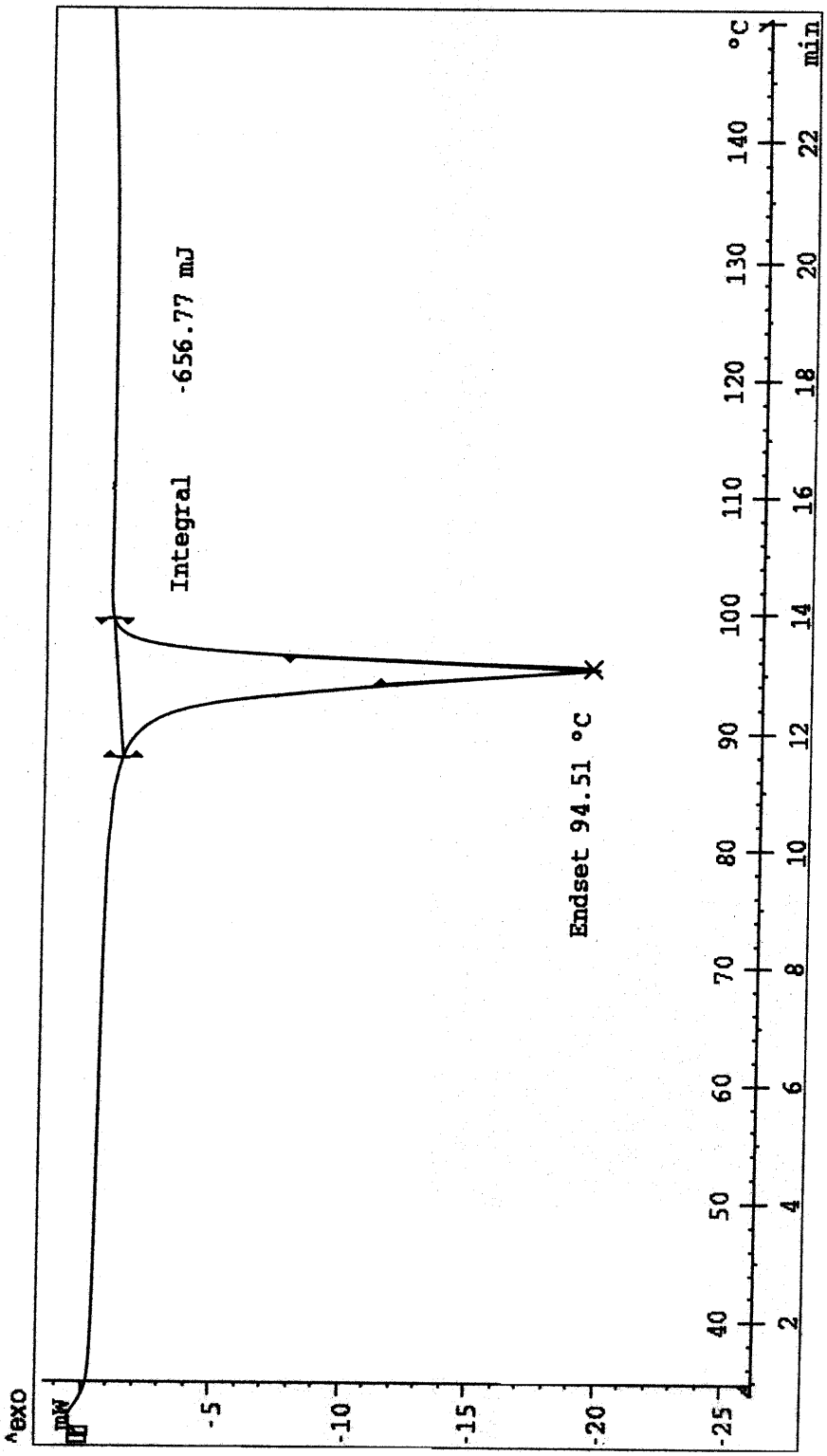


Figure 1. DSC Curve of CTMATB

Bromination of aniline (2)

An amount of CTMATB (0.546 g, 1 mmol) was dissolved in CH_3CN (15 mL). To this solution was added the substrate, (aniline, 0.093 g, 1 mmol) at ambient temperature. The mixture was stirred for 0.5 h at room temperature. The reaction mixture was then concentrated under reduced pressure and the residue extracted with ethyl acetate (30 mL). The ethyl acetate extract was washed with 5% sodium metabisulfite solution, dried over anhydrous Na_2SO_4 and finally evaporated under reduced pressure. The residue obtained thereof was purified by column chromatography (hexane: ethylacetate = 9:1) afforded 2,4-dibromoaniline. Yield: 0.16 g (65%)

Bromination of o-cresol (3)

To a solution of CTMATB (0.629 g, 1.2 mmol) in CH_3CN (15 mL), was added the substrate, (*o*-cresol, 0.130 g, 1.2 mmol) at ambient temperature. The mixture was stirred for 2h at room temperature. This was then concentrated under reduced pressure and the residue extracted with ethyl acetate (30 mL). The extract was washed with 5% sodium metabisulfite solution, dried over anhydrous Na_2SO_4 and finally evaporated *in vacuo*. Purification of the residue by column chromatography (hexane: ethylacetate = 8:2) afforded 4-bromo-*o*-cresol. Yield: 0.15 g (67%).

Bromination of p-cresol (4)

An amount of CTMATB (0.692 g, 1.2 mmol) was dissolved in CH_3CN (15 mL) and to the resulting solution was added the substrate, (*p*-cresol, 0.108 g, 1 mmol) at ambient temperature. The mixture was stirred magnetically for 2h at room temperature.

The reaction mixture was then concentrated under reduced pressure and the solvent was removed completely. The residue thus obtained was extracted with ethyl acetate (30 mL). The ethyl acetate solution was washed with 5% sodium metabisulfite solution, dried over anhydrous Na_2SO_4 and finally evaporated *in vacuo*. Purification of the residue by column chromatography (hexane: ethylacetate = 8:2) afforded 2-bromo-*p*-cresol. Yield: 0.13 g (71%).

Bromination of phluoroglucinol (5)

To a stirred solution of CTMATB (0.524 g, 1.0 mmol) in CH_3CN (15 mL), was added the substrate (phluroglucinol, 0.126 g, 1 mmol) at ambient temperature. The mixture was allowed to stir for 40 min at room temperature. The reaction mixture was then concentrated under reduced pressure and the residue was extracted with ethyl acetate (30 mL). The ethyl acetate extract was washed with 5% sodium metabisulfite solution, dried over anhydrous Na_2SO_4 and finally evaporated *in vacuo*. Purification of the residue by column chromatography (hexane: ethylacetate = 6:4) afforded 2,4-dibromophluroglucinol. Yield: 0.18 g (62%).

Bromination of o-nitroaniline (6)

To a solution of CTMATB (0.524 g, 1 mmol) in CH_3CN (15 mL), was added the substrate (*o*-nitroaniline, 0.138 g, 1 mmol) at ambient temperature. The mixture was stirred for 0.5h at room temperature. The reaction mixture on being concentrated under reduced pressure, yielded a solid residue. The residue was extracted with ethyl acetate (30 mL). The organic layer was washed with 5% sodium metabisulfite solution, dried over anhydrous Na_2SO_4 and finally evaporated *in vacuo*. Purification of the residue by

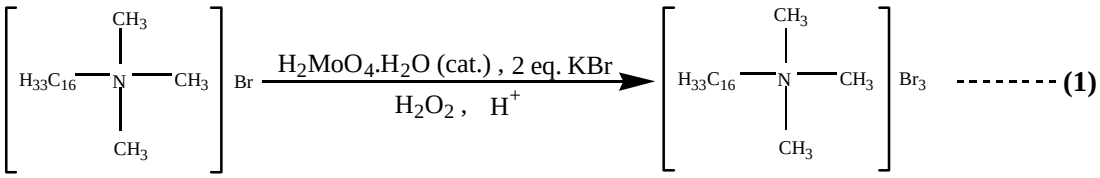
column chromatography (hexane: ethylacetate = 9:1) afforded 4-bromo-2-nitroaniline. Yield: 0.19 g (85%).

Results and Discussion

Synthesis cetyltrimethylammonium tribromide, $C_{19}H_{42}NBr_3$ (CTMATB)

Taking a cue from our recent experience of MoO_4^{2-} catalyzed *in situ* bromination of organic substrates by H_2O_2 (*vide* chapter V), it was thought to be possible to synthesize a solid, stable tribromide reagent applying a similar strategy. In view of this, it was planned to develop an environmentally favourable synthesis of cetyltrimethylammonium tribromide, $C_{19}H_{42}NBr_3$ (CTMATB), as it is anticipated to be a stable and highly efficient brominating reagent. Additionally, the cation, cetyltrimethylammonium ion, is expected to lend some distinct advantages to the reagent (CTMATB).

Typically, the catalyst $H_2MoO_4.H_2O$ reacts with an excess of H_2O_2 to form a peroxomolybdate(VI) intermediate and in this process it activates the peroxide. The activated peroxide then oxidizes the bromide to tribromide in presence of catalytic amount of an acid. The reaction time for optimum conversion to the product was found to be *ca.* 30 min.



(1)

Formation of CTMATB from CTMAB

An amount of two equivalents of potassium bromide was added in the reaction in order to increase the yield of the product. This is because one equivalent of cetyltrimethylammonium bromide (CTMAB) would afford the same equivalent (see **equation 1**) of tribromide (CTMATB) only if two more equivalents of bromide are supplied from another source. The synthetic procedure thus developed does not have any adverse effect on the environment.

The reagent CTMATB is orange-yellow in color and was found to be stable in air. It is insoluble in water. Its solubility is high in polar organic solvents like acetonitrile, acetone, dicholoromethane and chloroform but low in less polar solvents like hexane, benzene. The identity of the compound was ascertained from the results obtained from various physical studies in addition to chemical estimation of bromide. The physical techniques used for the characterization of the compound were IR, laser Raman and electronic absorption spectroscopies and solution electrical conductance measurements. The thermogravimetric analysis of the compound was also carried out in order to ascertain if there was any correlation of thermal behaviour with the efficiency of the reagent. The solution electrical conductance (10^{-3} M) of the compound at room temperature was measured to be 154 $\Omega^{-1}cm^2mol^{-1}$. This is in well agreement with the values documented for a 1:1 electrolyte.[13]

The IR spectrum (**Fig. 2**) of CTMATB shows two bands at 172 cm^{-1} and 190 cm^{-1}, which can be assigned to ν_1 and ν_2 stretching modes, respectively, of linear triatomic molecules. [14] The other band due to ν_3 bending mode [15] that was expected to occur at 50 cm^{-1}, could not be observed as it fell below the frequency range of the

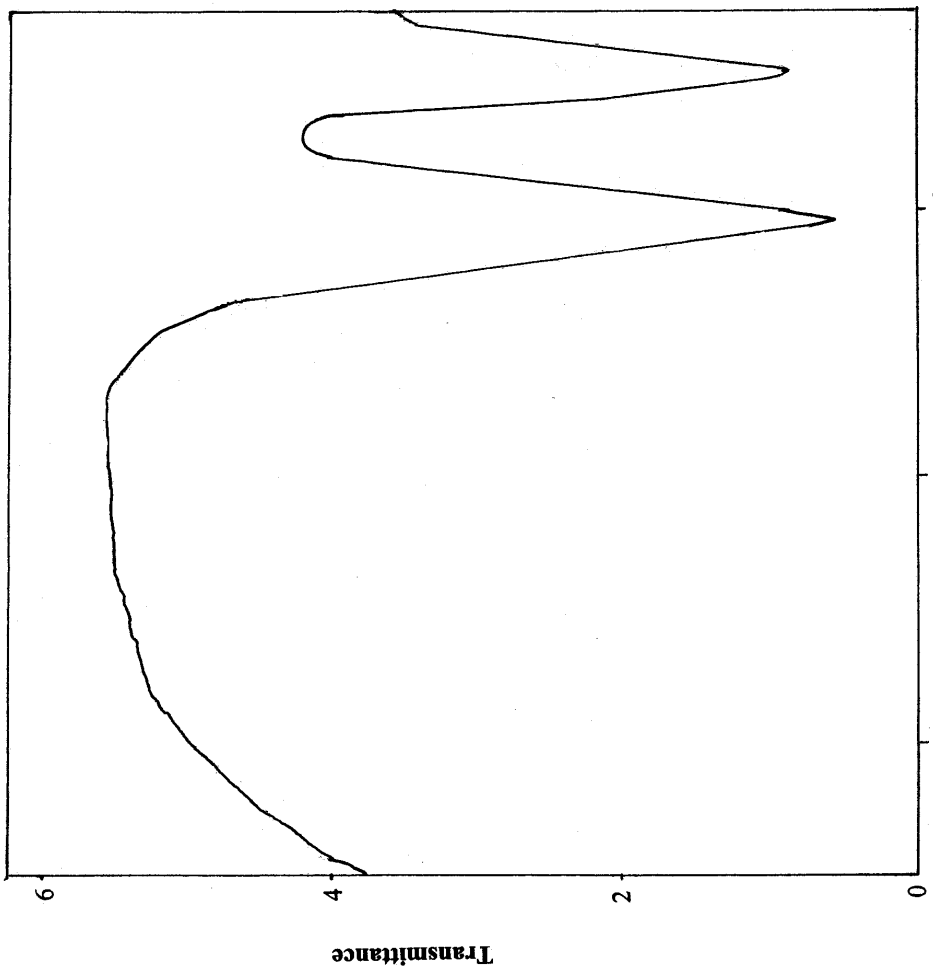
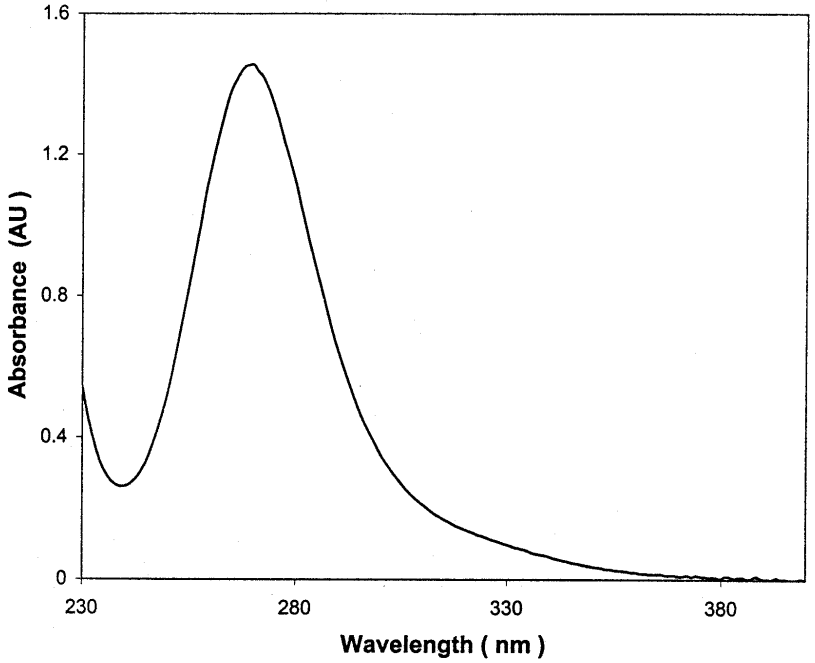


Figure 2. IR spectrum of CTMATB

instrument used in the present studies. The electronic absorption spectrum (**Fig. 3**) of CTMATB in acetonitrile showed two absorption bands that are characteristics of the Br_3^- absorption.[16, 17] These bands were observed at 267 nm (ε = 14, 721 $dm^3mol^{-1}cm^{-1}$) and at 373 nm (sh) (ε = 610 $dm^3mol^{-1}cm^{-1}$).

In order to ascertain if there was any correlation between efficiency of the reagent and its thermal bahaviour, TG analysis was carried out on CTMATB. For comparison TG of the corresponding bromide was studied under similar experimental conditions. The thermogram (**Fig. 4**) of CTMATB revealed that the tribromide loses Br_2 as the tail fragment between 265 and 267 °C. The experimental weight loss for this event was 46.8% with the corresponding theoretical value being 45.7% per formula weight. The thermogram (**Fig. 5**) of CTMAB showed that there is a complete loss of the compound in a single step in the temperature range of 230 – 270 ° C. It might be quite tempting to comment from the TG results that the compound could be safely considered to be a carrier of bromine and might serve as a very potential source of Br_2.



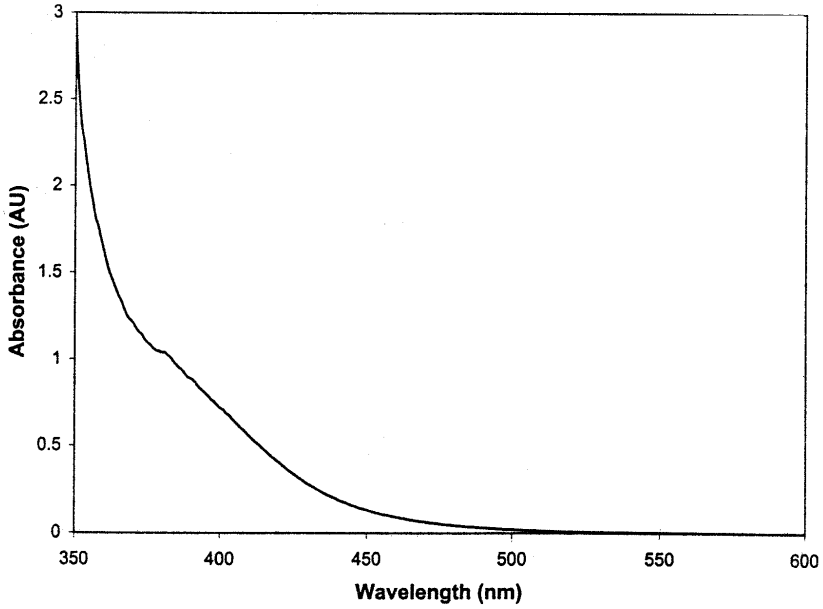


Figure 3. Electronic spectra of CTMATB

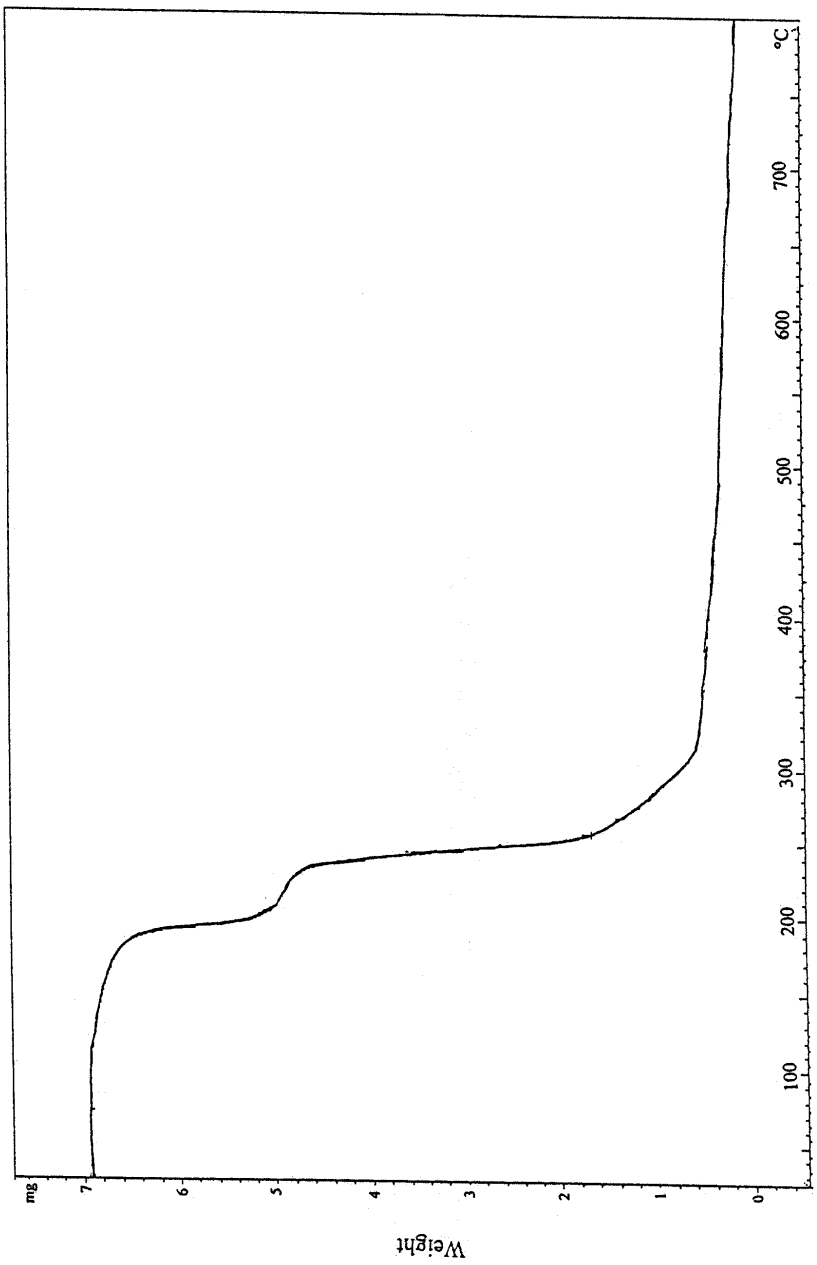


Figure 4. Thermogram of CTMATB

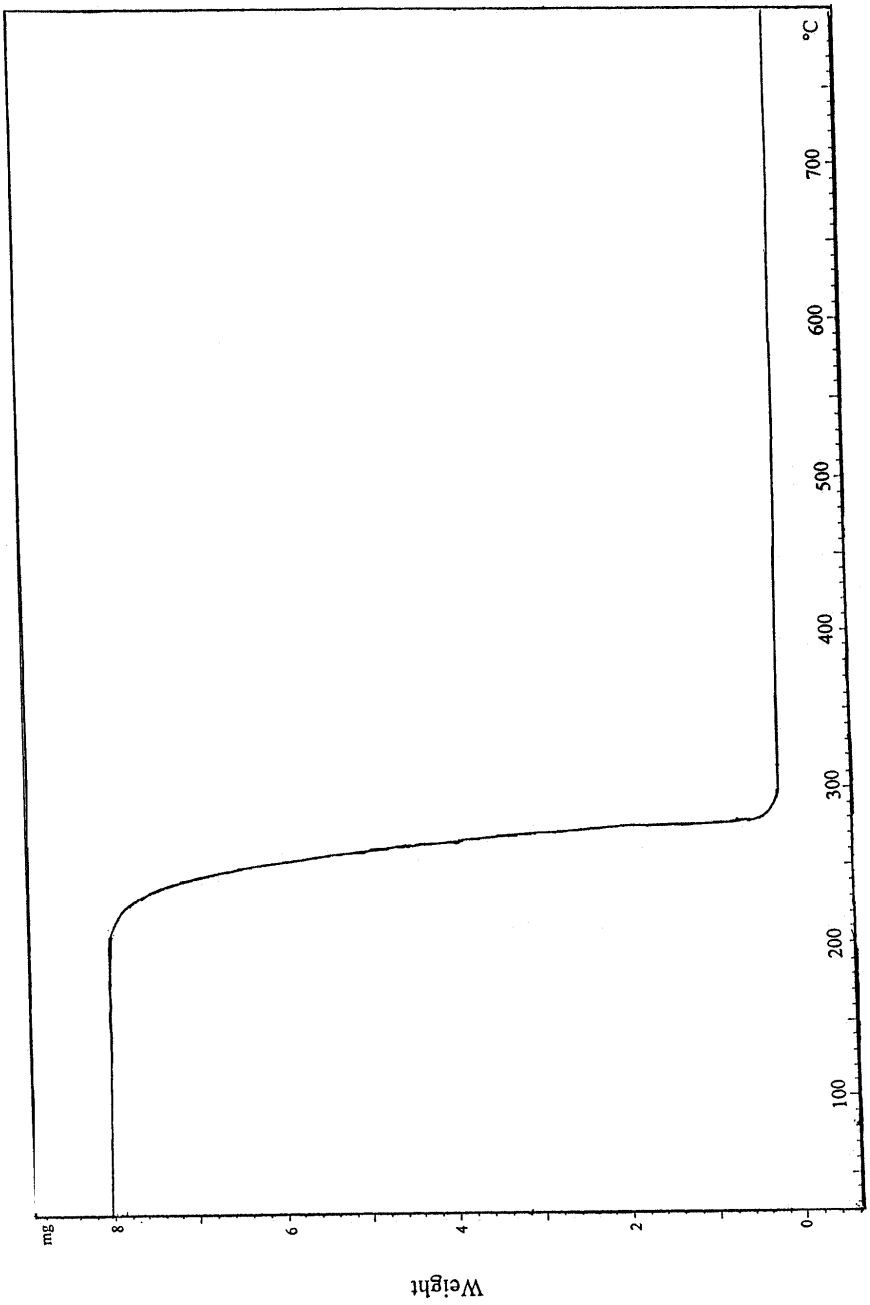
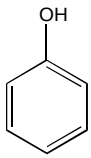
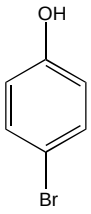
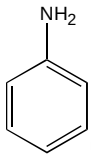
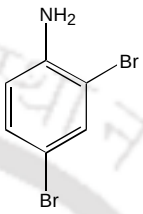
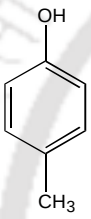
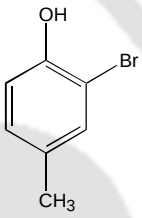
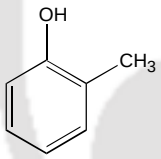
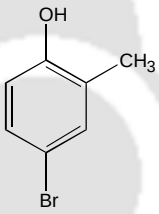
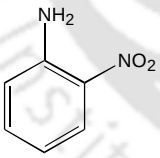
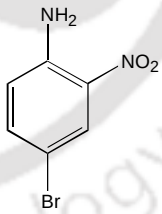
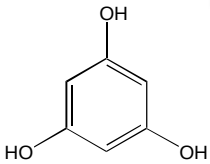
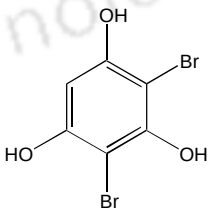


Figure 5. Thermogram of CTMAB

Bromination of organic substrates by CTMATB

The efficacy of CTMATB as a brominating reagent was ascertained by carrying out bromination on a few selected aromatic substrates. The list of substrates, the corresponding bromoproducts with their yields and the reaction times have been presented in **Table 1**. Majority of the products were obtained in high to very yields in a reasonably short time. The substrates like phenol, *o*-cresol and *m*-cresol gave 4-bromophenol, 4-bromo- *o*-cresol and 4-bromo-*m*-cresol, respectively, showing high regioselectivity and stronger directing influence of –OH compared to $–CH_3$ group. For aniline the product obtained was 2, 4-dibromoaniline in nearly 65% yield although formation of a very small amount of monobromoproduct was also observed. This suggests that the reagent is more selective towards the formation of dibromo- rather than usual mono-bromo derivatives. It was also our interest to see as to how the reagent reacted with an activated phenol, viz., phluoroglucinol (1, 3, 5- trihydroxybenzene). Interestingly, the compound gave 2, 4– dibromophluoroglucinol as the exclusive product again showing a very good selectivity. The efficacy of the reagent was also tested by conducting bromination on a variety of other substrates, the results of which will be described elsewhere. These include a few enone systems in addition to some biologically relevant compounds like 16-DPA (16-dehydropregnonalone acetate) and imidazole. All the reactions were carried out at room temperature in an environmentally favourable solvent acetonitrile. It was interesting to note that this reagent has thus been found to be comparable to TBATB in so far as the yields of the products, reaction times and versatility are concerned.

Table 1. Bromination of some aromatic substrates by CTMATB

substrate	time/ h	product	yield
	0.5		70%
	0.5		65%
	2.0		71%
	2.0		67%
	0.5		85%
	0.5		62%

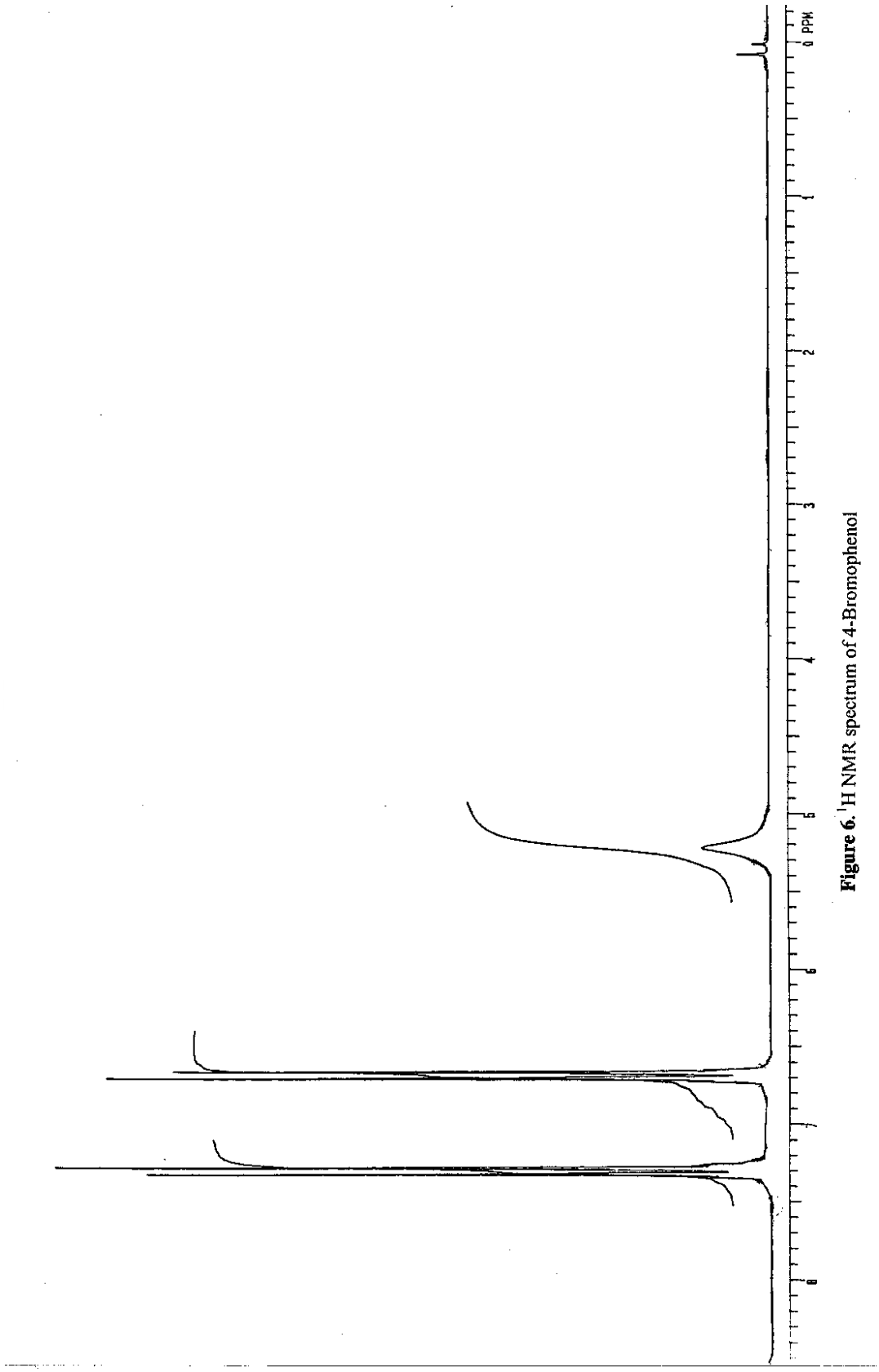


Figure 6. ^{1}H NMR spectrum of 4-Bromophenol

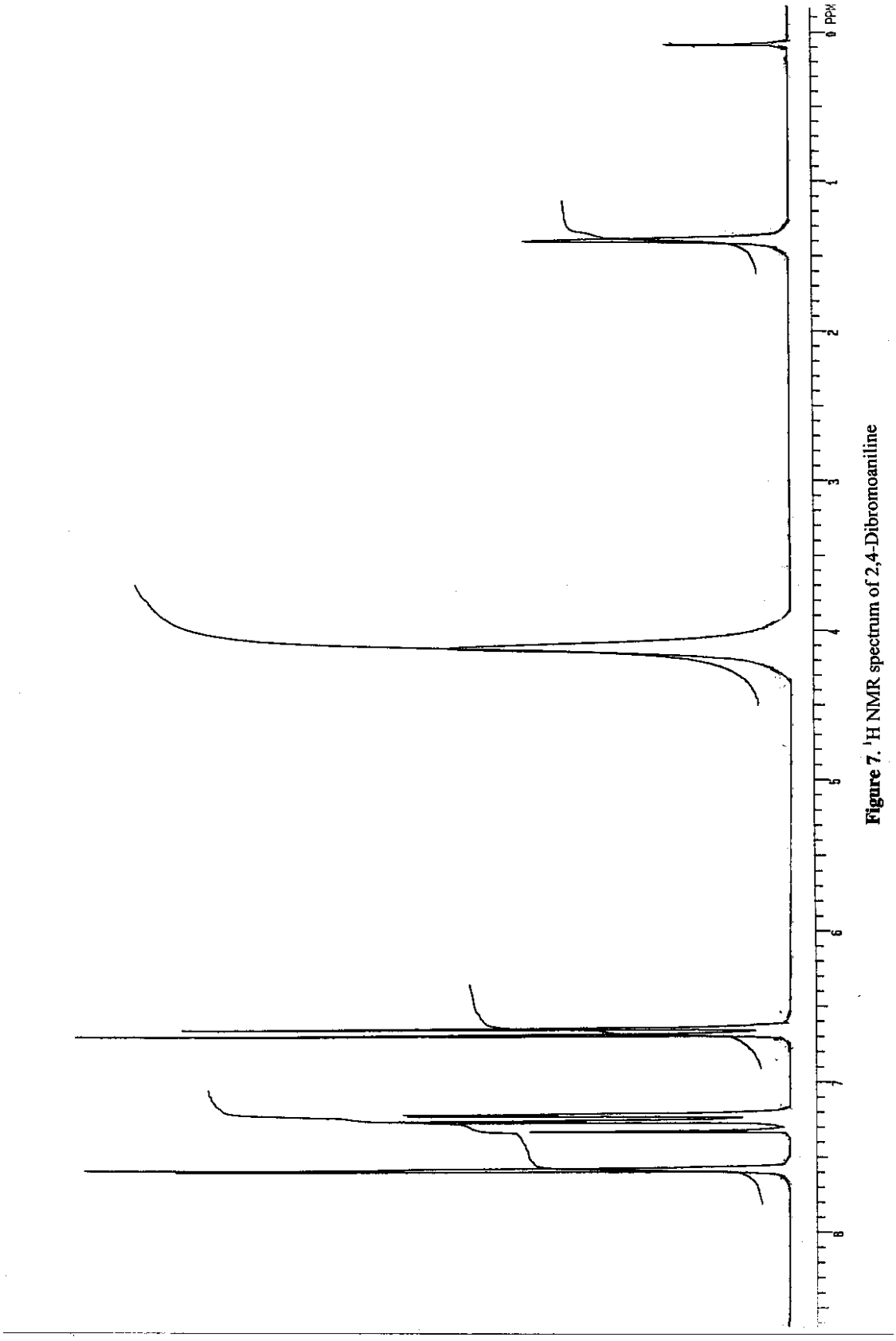


Figure 7. ^{1}H NMR spectrum of 2,4-Dibromoaniline

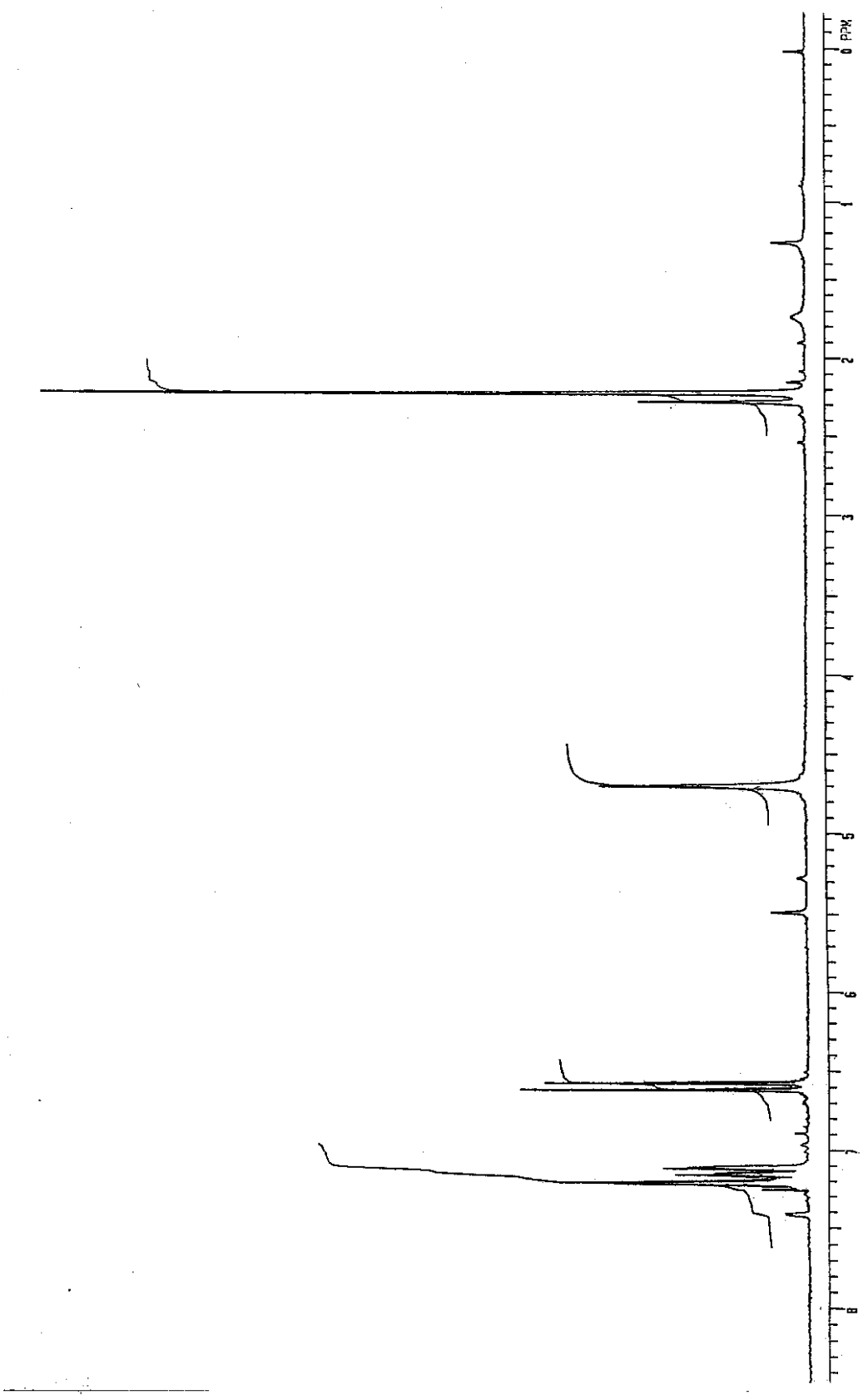


Figure 8: ^{1}H NMR spectrum of 4-Bromo-*o*-cresol

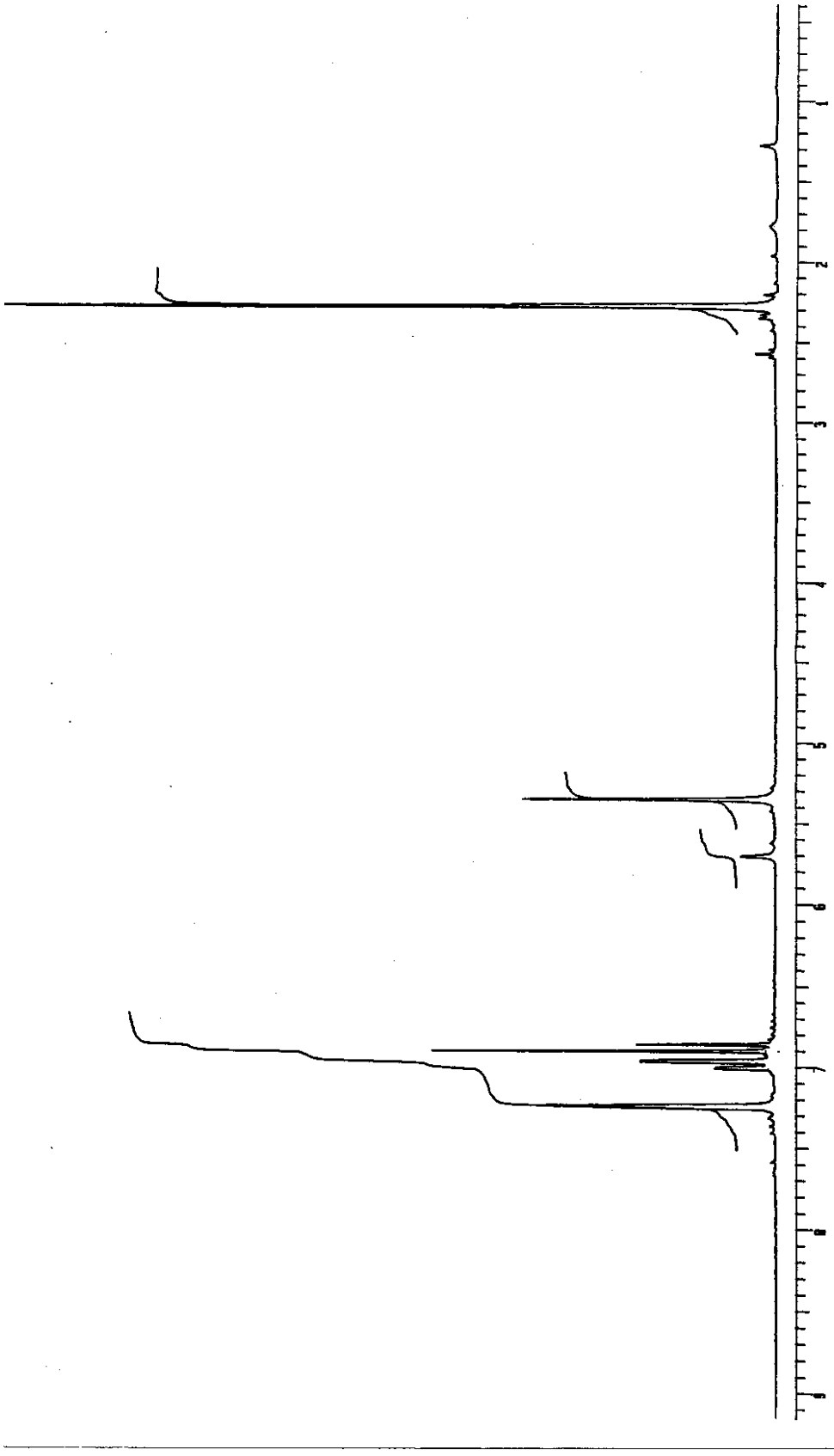


Figure 9. ^{1}H NMR spectrum of 2-Bromo-*p*-cresol

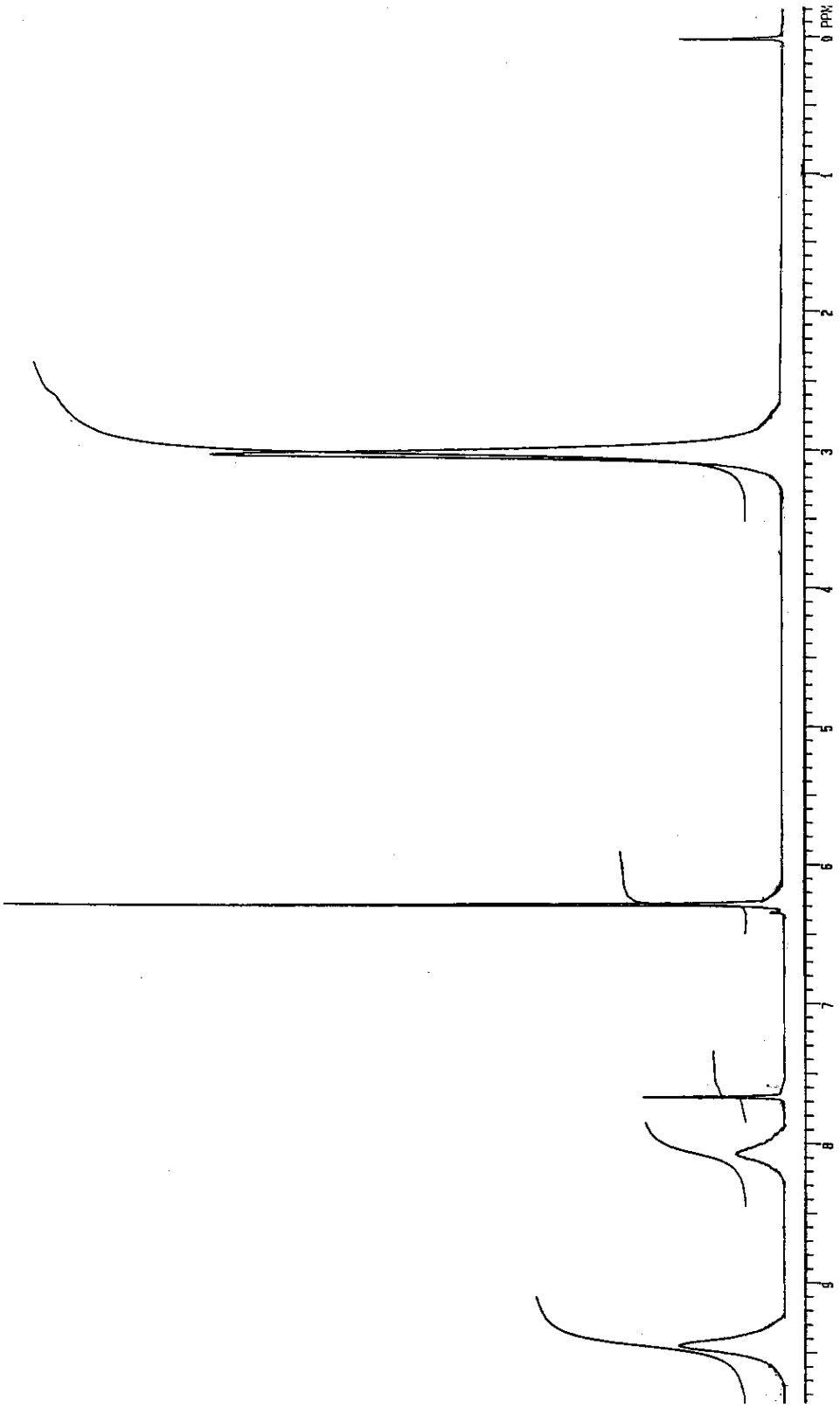


Figure 10. ^{1}H NMR spectrum of 2, 4-Dibromophluoroglucinol

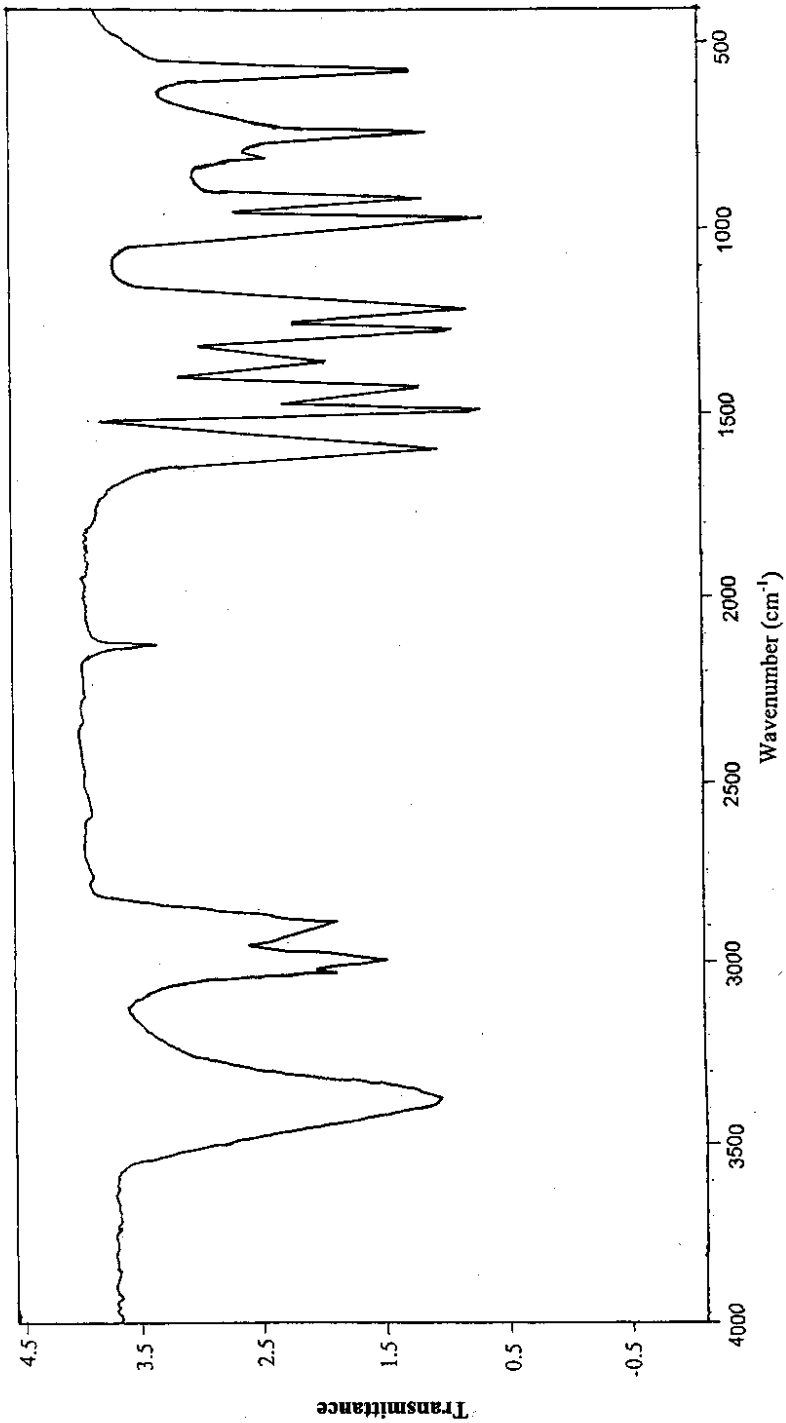


Figure 11. IR spectrum of 4-Bromophenol

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Scanned Picture of Cetyltrimethylammonium Tribromide (CTMATB)
(~ 3 times magnified)

CHAPTER VII

Isolation of $[(C_4H_9)_4N][FeCl_3Br]$ from the reaction of $FeCl_3$ with $(C_4H_9)_4NBr_3$ (TBATB) and evidence for $FeCl_3$ as a catalyst in environmentally clean bromination by TBATB

Introduction

Considering the similarities of the products profile [1-5] of bromination reactions of organic substrates by tetrabutylammonium tribromide (TBATB) as well as by molecular bromine, it was conjectured that the attacking species in both the types of reactions might as well be similar. It may be recollected that in the bromination of aromatics by molecular bromine, iron(III) chloride ($FeCl_3$) has been shown to act as a catalyst, and in the process 'Br^+' is generated as the attacking species with the formation of $[FeCl_3Br]^-$ [2, 3] (**Fig.1**).

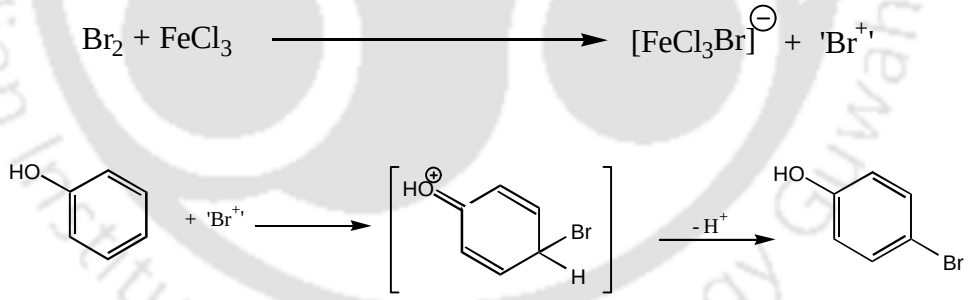

Fig. 1

In order to gain support to this contention, it was considered necessary to carry out the reaction of $FeCl_3$ with TBATB and to probe the product obtained thereof. If the product would characterize as a salt of $[FeCl_3Br]^-$, it would be quite certain that 'Br^+' was also formed in the reaction. Assuming the results to be in affirmative, it was thought to be possible to demonstrate that $FeCl_3$ acted as a catalyst in the TBATB bromination of aromatic substrates.

The results of the reactions of TBATB with $FeCl_3$ are presented in this **chapter**. Also presented are the results of the $FeCl_3$ catalysed bromination of a few aromatic compounds including chalcone by TBATB.

Experimental

The chemicals used were all reagent grade products. The details of instruments used for physicochemical studies have been reported in **chapter II.** The chemical procedures for the estimation of different constituents of $[((n\text{-}C_4H_9)_4N)]$ $[FeCl_3Br]$ have also been presented in **chapter II.**

Reaction of $FeCl_3$ with Tetrabutylammonium Tribromide (TBATB), $(n\text{-}C_4H_9)_4NBr_3$

To a solution of 0.65 g (4.0 mmol) of anhydrous $FeCl_3$ in 15 mL of acetonitrile was added a solution of 1.93 g (4.0 mmol) of tetrabytylammonium tribromide, $(n\text{-}C_4H_9)_4NBr_3$ (TBATB), in 20 mL of acetonitrile with continuous stirring. A reaction took place instantaneously with the colour of the reaction solution turning deep red. The whole was warmed on an oil-bath at *ca.* 60^o C for 30 min during which process the solution was concentrated to nearly two-third of its original volume. This was first cooled to room temperature and then left standing for *ca.* 2 h whereupon orange-red crystals were formed. The product was isolated by filtration, washed 3 or 4 times with a very small amount of ethanol-acetonitrile mixture (9:1) and finally dried *in vacuo* over conc. H_2SO_4. The quantity of the product thus isolated weighed 1.6 g (80.5%, calculated on the basis of $FeCl_3$). Anal. Found: Fe, 12.0, Cl, 22.0, Br, 16.6, C, 39.1, H, 7.5, N, 2.8 %. $C_{16}H_{36}BrCl_3NFe$ Calcd: Fe, 11.5, Cl, 21.9, Br, 16.5, C, 39.6, H, 7.5,N, 2.9 %.

Bromination of organic substrates by TBATB in presence of catalytic amount of $FeCl_3$

Bromination of Chalcone

To a solution of chalcone (0.51 g, 2.5 mmol) in CH_3CN (25 mL) were added anhydrous $FeCl_3$ (0.02 g, 0.125 mmol) and TBATB (1.61 g, 5 mmol) and the mixture was then stirred for 30 min. The reaction mixture was concentrated by evaporation under reduced pressure. The residue was then extracted with ethyl acetate and the organic extract was washed with sodium metabisulfite solution, dried over anhydrous Na_2SO_4 and finally evaporated *in vacuo*. The crude product thus obtained was purified by column chromatography (1:1 mixture of ethylacetate and hexane) to obtain threo-dibromochalcone as the product. Isolated yield of the product was 0.64 g (70%).

Bromination of aniline

To a solution of aniline (0.28 g, 3 mmol) in CH_3CN (25 mL) was added the catalyst, $FeCl_3$ (0.024 g, 0.15 mmol), and the mixture was stirred for some time. To this was then added the reagent, TBATB (2.90 g, 9.0 mmol), and the whole was stirred vigorously for 2 or 3 min (the progress of the reaction as monitored by TLC did not reveal any starting material in the mixture after 3 min). The reaction mixture was then concentrated under reduced pressure to remove CH_3CN completely. The solid residue thus obtained was extracted with ethylacetate and the organic extract was washed with 5% sodium metabisulfite solution, dried over anhydrous Na_2SO_4 and finally evaporated under reduced pressure to provide a crude product. The crude product upon purification by column chromatography (ethyl acetate: hexane, 1:9) provided 2,4,6-tribromoaniline. Yield = 0.64 g (65%).

Bromination of phenol

To a solution of phenol (0.28 g, 3 mmol) in CH_3CN (25 mL) was added the catalyst, $FeCl_3$ (0.024 g, 0.15 mmol) and the mixture was stirred for some time. To this was added the reagent (TBATB, 2.9 g, 9.0 mmol) and the whole was stirred vigorously for 15 min. The reaction mixture was then concentrated under reduced pressure and CH_3CN was removed completely in the process. The solid residue thus obtained was extracted with ethyl acetate and the organic layer was washed with 5% sodium metabisulfite solution, dried over anhydrous Na_2SO_4 and finally evaporated under reduced pressure to provide a crude product. The crude product upon purification by column chromatography (ethyl acetate: hexane, 1:9) provided 2,4,6-tribromophenol. Yield = 0.74 g (73%).

Control experiment: Bromination of chalcone, aniline and phenol by tetrabutylammonium tribromide, $(n\text{-}C_4H_9)_4NBr_3$ (TBATB), in the absence of the catalyst

Reactions similar to those described above were conducted **in the absence of $FeCl_3$ catalyst** for the three substrates viz., chalcone, aniline and phenol. The yields of the products were found to be much lower than those of the catalytic reactions although the reaction times were maintained the same. The results have been summarised in **Table 1**.

Table 1

Substrate	Amount of catalyst	Reaction time (min)	Product [a]	Yield (%) [b]
Chalcone	5 mol%	30	Threo-dibromochalcone	70
Chalcone	0	30	Threo-dibromochalcone	10
Aniline	5 mol%	2 or 3	2,4,6-tribromoaniline	65
Aniline	0	5	2,4,6-tribromoaniline	20
Phenol	5 mol%	10	2,4,6-tribromophenol	73
Phenol	0	10	2,4,6-tribromophenol	15

[a] products were characterized by comparison with the authentic samples, [b] isolated yields

Results and discussion

Reactions of $FeCl_3$ with TBATB

In order to gain support to the assertion that both Br_2 and TBATB work in a similar fashion as well as to ascertain the catalytic role of iron(III) chloride in the bromination by TBATB, a reaction of $FeCl_3$ with $(n\text{-}C_4H_9)_4NBr_3$ was first carried out in acetonitrile. The reaction solution assumed a deep red color readily. In order to ensure completion of the reaction, the solution was warmed at *ca.* 60^oC for 30 min. In this process this was concentrated as well, which on cooling to room temperature afforded the orange-red crystalline product. The product on being chemically analyzed tested positive for the presence of chloride and bromide with the stoichiometry of Fe(III):Cl^-:Br^- as 1:3:1 rendering the compound to be formulated as $[Bu_4N][FeCl_3Br]$. The compound has been found to be stable for a prolong period. It is soluble in acetonitrile, acetone and dichloromethane but only sparingly soluble in methanol, ethanol and water. The melting point of the compound was observed to be 133-135^oC.

The identity of the compound was ascertained on the basis of the results of elemental analyses, IR and electronic absorption spectroscopies, solution electrical

conductance and magnetic susceptibility measurements and TG analysis. The IR spectrum (**Fig. 2**) was recorded as a Nujol mull between 500 and 70 cm^{-1} showed two intense bands at 395cm^{-1} and 345cm^{-1} which have been assigned to two expected [6] modes of ν(Fe — Cl) while another strong band at 291cm^{-1} has been attributed to ν(Fe — Br). A weak vibrational band at 135 cm^{-1} and a shoulder at 121 cm^{-1} owe their origin to Fe — Cl bending modes. The pattern and the assignments are consistent with those reported in the literature [6] for similar species. The electronic absorption spectrum of the compound in acetonitrile indicated that the intense color of the compound originates from charge-transfer transition. In consonance with this the compound shows three absorption bands with the intensities typical of charge-transfer transitions (**Fig. 3**). The positions of the bands along with the molar extinction coefficients as given in the parentheses are 40,984 cm^{-1} (10,300 dm^3mol^{-1} cm^{-1}), 32,154 cm^{-1} (6,900 $dm^3mol^{-1}cm^{-1}$), and 27,984 cm^{-1} (6,100 $dm^3mol^{-1}cm^{-1}$), respectively. The values are in excellent agreement with the data reported [5, 7] for tetrahaloiron(III) compounds. A lesser number of bands observed for this compound as compared to $FeCl_4^-$ and $FeBr_4^-$ could be due to low resolution of the broad band appeared between 32,000 cm^{-1} and 35,000 cm^{-1}.

In order to probe the thermal behaviour, the compound was subjected to TG analysis. What was evident from the thermogram (**Fig. 4**) was that the compound was stable up to 300°C with the first weight loss beginning at 300 °C had continued up to 390 °C. The percentage weight loss experimentally found for this event is 65.2% which corresponds to the expulsion of $(n\text{-}C_4H_9)_4NBr$ with the calculated weight loss being 66.5% per formula weight suggesting thereby the formation of

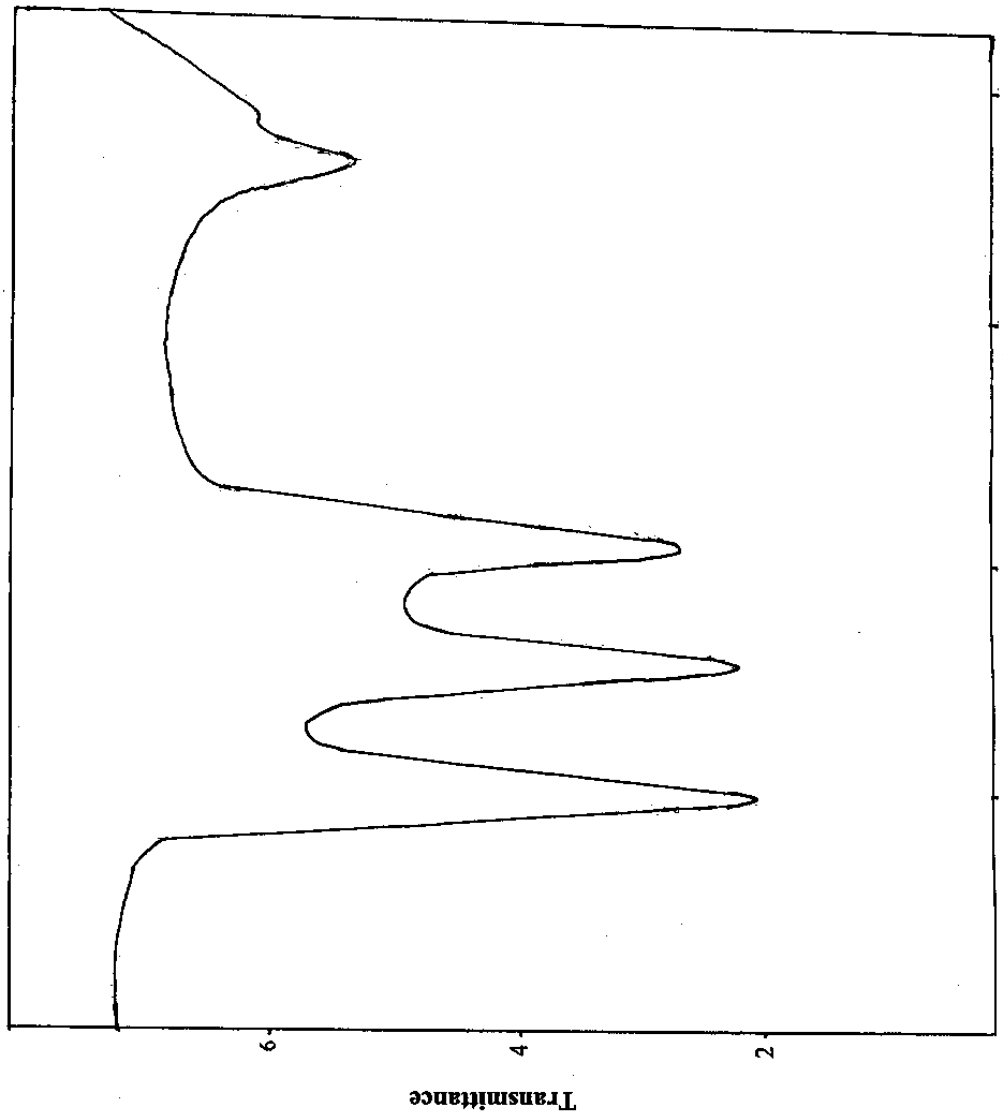

Figure 2. IR Spectrum of $[(C_4H_9)_4N][FeCl_3Br]$ (500-70 cm $^{-1}$)

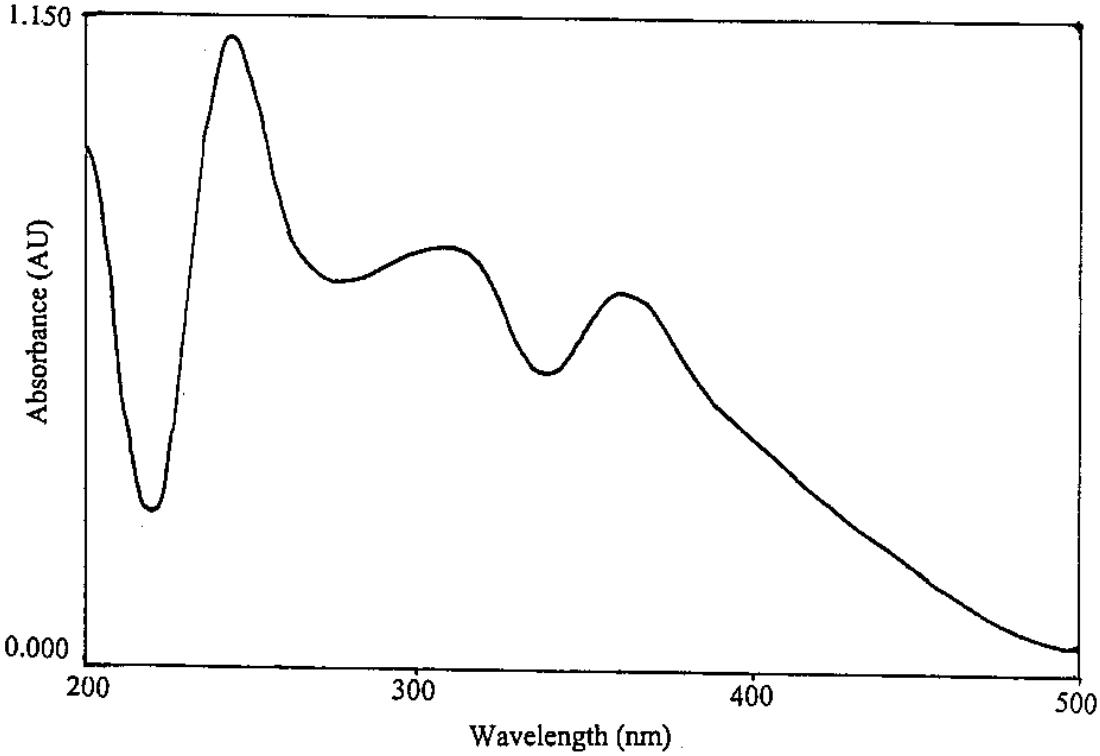

Figure 3. Electronic spectrum of $[(n\text{-}C_4H_9)_4N][FeCl_3Br]$

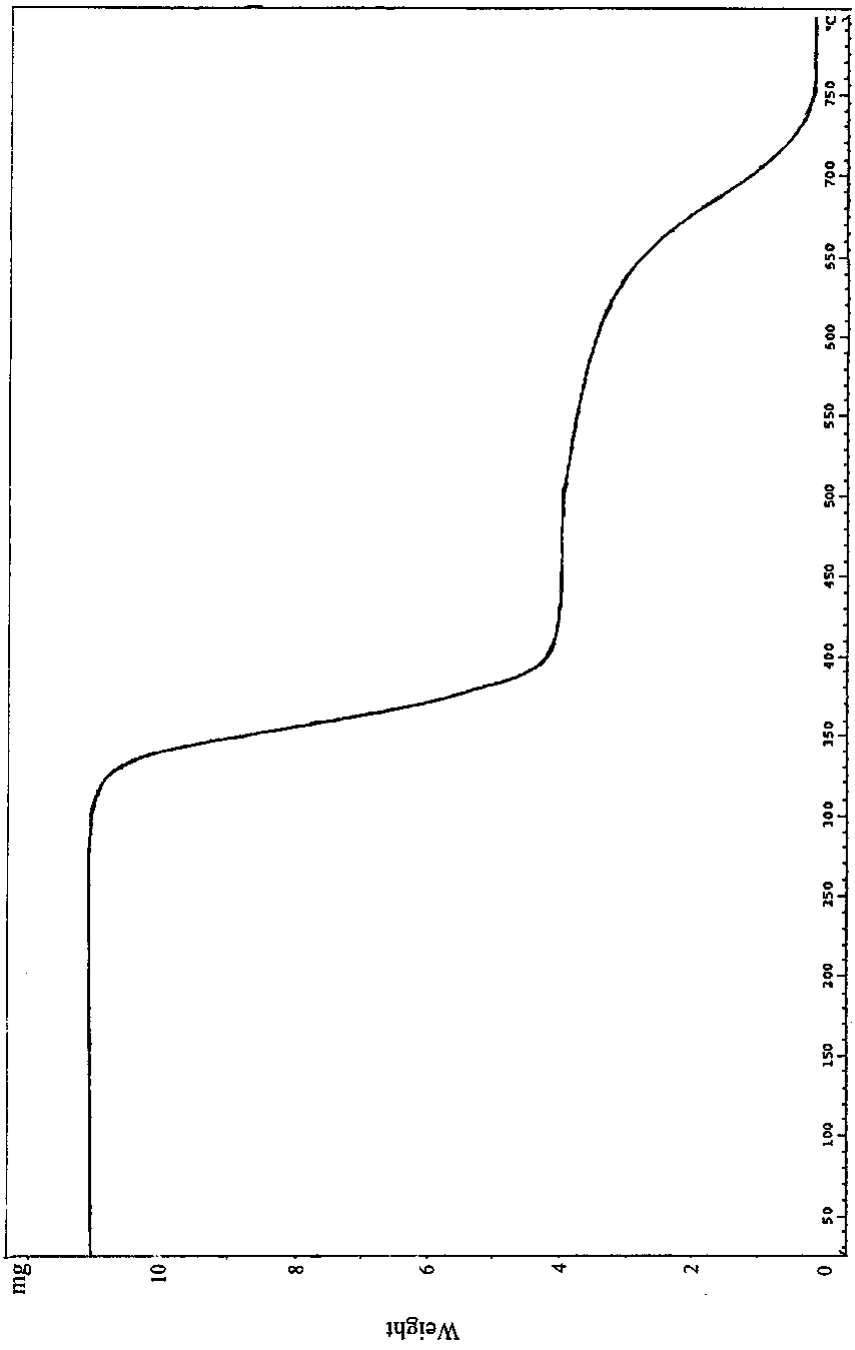

Figure 4. Thermogram of $[(C_4H_9)_4N][FeCl_3Br]$

$FeCl_3$ at this stage. The next event is the gradual volatilization of $FeCl_3$ in the temperature range of 500 ^oC to *ca*. 730 ^oC. The results obtained from TG analysis appear to be consistent with the fact that Fe — Br bond is comparatively less stable than Fe — Cl. The volatilization of $FeCl_3$ that started at 500 ^oC, as observed in the present study, is consistent with its thermal properties reported in the literature. [8]

The solution electrical conductance (Λ) in acetonitrile was recorded to be 156 $\Omega^{-1}mol^{-1}cm^2$ (10^{-3} M), which is in line with the values reported in the literature for 1:1 electrolytes of similar species. [9] The magnetic susceptibility measured at room temperature for the compound gave the magnetic moment of 5.94 BM, a value that corresponds to the spin-only magnetic moment of high-spin Fe(III) compounds. All these results clearly suggest that the product is $[(n\text{-}C_4H_9)_4N][FeCl_3Br]$.

Catalytic brominations by TBATB

Having ascertained the identity of the complex to be $[FeCl_3Br]^-$, same as that obtained in the bromination reaction involving Br_2 and $FeCl_3$ (catalyst), [1, 2] it was reasonable to state that the active brominating species in the bromination by Br_2 as well as Bu_4NBr_3 (TBATB) is apparently the same. The other important implication of this investigation is that $FeCl_3$ might act as a good catalyst for bromination by TBATB. To this end, bromination reactions of phenol, aniline and chalcone were carried out in acetonitrile by TBATB separately in the presence of the catalyst (*vide experimental*) as well as in the absence of the catalyst ($FeCl_3$). The results show that in the presence of 5mol% of $FeCl_3$, the reactions of the aforesaid substrates (**Fig. 5**) afforded 2,4,6-tribromophenol, 2,4,6-tribromoaniline and threo-dibromochalcone, respectively, in very good yields within a relatively shorter reaction time. Control reactions carried out for the same period of time in the absence of the catalyst gave the products in much lower yields (**Table 1**).

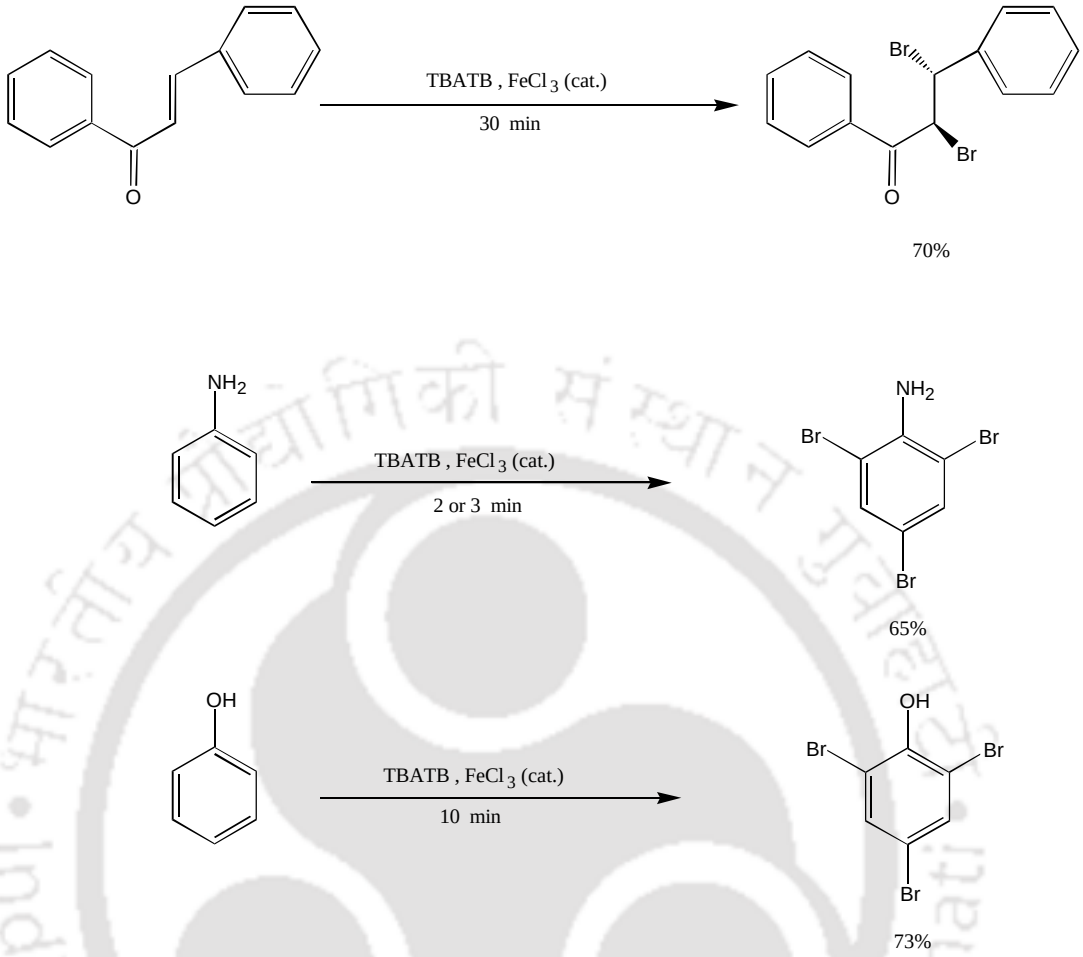

Fig. 5

Thus, it becomes evident that $FeCl_3$ catalyses the bromination by TBATB. The isolation of $[FeCl_3Br]^-$ from the reaction of TBATB with $FeCl_3$ provides additional (though an indirect) evidence for the involvement of "Br^+" as the attacking entity in the bromination by TBATB. It is relevant to add that the reagent (TBATB), the catalyst and the solvent are environmentally safe chemicals. The knowledge gained from the present investigation is expected to be useful for practicing chemists.

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