Chapter - 5

Literature Survey On Quaternary Ammonium Compounds And Their Significance
5.1. Ammonium Tetrafluoroborate (NH$_4$BF$_4$):

General applications of ammonium tetrafluoroborate (AFB) include - finishing catalyst for resin in textile and printing industry; as catalyst for magnesium and magnesium based alloys, as fluxing agent to provide inert gas (welding flux for aluminum and copper), and making sand mould resin adhesive, and as fire retardant. Ammonium tetrafluoroborate has a melting point at 460.7°C, and decomposes at about 110°C and beyond. At higher temperatures it sublimes. It generates CO, CO$_2$, and oxides of nitrogen, NH$_3$, HF, as well as, oxides of boron through its decomposition.

5.2. Tetraalkylammonium Tetrafluoroborates (R$_n$N$^+$BF$_4$)

Quaternary salts have affinity for both polar and non-polar environments. This property has been exploited in the stoichiometric use of reagents containing a quaternary cation in place of the usual metal cation. However, the use of quaternary salts in sub-stoichiometric amounts in biphasic systems containing inorganic ionic species is of much interest both for researchers involved in the synthesis work, and for industrial applications. This technique, popularly known as "phase-transfer catalysis" came into prominence with the early work of Makosza, Brändström and Strarks et al [1-4].

To reach a sufficient degree of solubility in the organic phase, the quaternary cation should normally contain about eight or more carbon atoms, although smaller cations may be useful for specific purposes; for example, tetramethylammonium chloride is used as a thermally stable catalyst in halex fluorinations [5, 6]. Hardy et al [7] studied crystalline adduct formation between quaternary alkyl ammonium salts and simple aromatic compounds.
Quaternary salts containing a long chain of carbon atoms, such as (1-Hexadecyl) trimethylammonium chloride, have surfactant properties and have been used to catalyze heterogeneous reactions in micelles [8]. Enumerable examples of the use of quaternary salts as phase-transfer catalysts are covered in the literature [9–22].

A series of ionic liquids based on alkyl ammonium salts were synthesized and used as catalysts and medium for the esterification of acetic acid with 1-Octonol as a probe to understand their structure–activity relationship in the Fisher esterification [23]. Proton–conducting silica–gel films doped with HClO₄, H₃PW₁₂O₄₀·29H₂O, or (n-Bu)₄ NCIO₄ were prepared by the sol-gel method using tetraethoxysilane [24]. Tetraalkyl substituted ammonium salts (R₄N⁺X⁻) are widely used in electrochemistry as supporting electrolytes in both aqueous and non-aqueous solvents. [25]. Synthesis and characterization of tetraalkylammonium thiotungstates, employing characterization techniques such as thermolysis, Mass Spectrometry (MS), X-ray Diffraction, and scanning electron microscopy (SEM) has been reported [26].

Dariusz Wyrzykowski et al [27] studied the thermal degradation of [(C₄H₉)₄N] [FeCl₄] employing thermo analytical tools. Decomposition of tetraalkylammonium thiometallates has been used to prepare WS₂ catalyst for hydrodesulphurization [28]. Poisot et al [29] studied thermal decomposition pathways of tetraalkylammonium tetrathiomolybdates, employing thermoanalytical tools. Blazejowski et al [30] studied the degradation pattern of [(C₄H₉)₄N]⁺ ion generated from tetrabutylammonium chloride in nitrogen atmosphere.
Thermal degradation of ammonium chlorides of benzyl dimethyl-dodecyl, benzyl dimethyl tetradecyl, benzyl dimethyl hexadecyl, benzyl dimethyl stearyl, benzyl trimethyl, and benzyl triethyl, were studied through pyrolysis – gas chromatography – mass spectrometric techniques [31]. In capillary electrophoresis, alkylammonium salts have been used as electro-osmotic flow modifiers [32]. Maaike C. Kroon et al [33] made quantum chemical aided predictions of the thermal decomposition mechanisms and temperatures of ionic liquids. Coker et al [34] studied fusion properties of ionic quaternary ammonium – chlorides, bromides, iodides, nitrates, and thiocyanates. Many of the quaternary ammonium salts are low melting (<120°C), and such salts may be used for short periods at temperatures just above their melting points without decomposition [35], which was confirmed by the studies of Coker et al [34].

Coker et al [34] reported the enthalpy, entropy, and molar volume changes during the fusion process of a wide range of quaternary ammonium – tetrafluoroborates and tetraphenylborates. The temperatures of phase transition and fusion; enthalpies of transition and fusion; and the entropy of transition and fusion, for \((\text{C}_4\text{H}_9)_4\text{N}^+\text{BF}_4^-\) are: \(T_t = 68\degree\text{C}, T_f = 166\degree\text{C}, \Delta H_t = 1.6\) kcal.mol\(^{-1}\), \(\Delta H_f = 2.5\) kcal.mol\(^{-1}\), \(\Delta S_t = 4.7\) eu and \(\Delta S_f = 5.8\) eu [34].

Based on powder diffraction data and nuclear magnetic resonance (NMR) measurements on \(^{11}\text{B}\), Giuseppetti et al [36] determined the crystal structure of \((\text{C}_2\text{H}_5)_4\text{NBF}_4\) at 25°C. The ‘N’ atoms of the tetraethylammonium cation were fixed at \(\frac{1}{2}, \frac{y}{2}, \frac{1}{2}\) in the space group Cc. The crystal structure is non-centrosymmetric and the configuration of the BF\(_4\) tetrahedron is ordered [36], and is shown in Fig.1.
Fig. 1: Non-centrosymmetric crystal structure of (C₂H₅)₄NBF₄
The B—F bond distances range between 1.22 Å and 1.37 Å (mean value 1.28 Å) and corresponding bond angles between 105° and 113° (mean angle 109°). The deviation from the regular tetrahedral coordination is ascribed to the large amplitude of the fluorine thermal vibration. The ordered BF₄ configuration in this structure is very different from the remarkably disordered configuration of the fluoroborate tetrahedron in the tetramethylammonium salt [25, 36]. The packing of the crystal structure of tetraethylammonium tetrafluoroborate is illustrated in Fig.2, and the non-centrosymmetric configuration of the crystal is apparent [36].

The ¹¹B NMR spectrum consists of a central line and two satellite lines broadened by first order quadrupole effects in a frequency range

\[ v_L - v_Q + v_L + v_Q, \]

Where \( v_L \) is the Larmor frequency and \( v_Q \) is the quadrupole coupling constant. The ¹¹B signal was maximized by a pulse length \( \tau_{n/2} \), where \( \tau_{n/2} \) is the pulse duration maximizing the signal in \( H_2BO_3 \) water solution, and the structural description of the BF₄ group is consistent with the NMR results with a discrepancy of about eight percent [36].

In the series of \((C_nH_{2n+1})_4N^+BF_4^-\), with \( n=1, 2, 3, 4 \ldots \) of which the first four are known to have phase transition upon varying temperature. Zabinska et al [37] have mapped out these transitions using differential scanning calorimetric methods. Fig.3 summarizes the known thermal features of this group of compounds.

Table 1 summarizes the crystallographic (CRY) and Nuclear Magnetic Resonance (NMR) data on the different known phases of tetraalkylammonium tetrafluoroborate salts. Stammler et al [39], Kobler et al
Fig. 2: Packing of the crystal structure of (C$_2$H$_5$)$_4$NBF$_4$
Fig. 3: Known thermal features of \( n, (\text{C}_{n+1}\text{H}_{2n+1})_4\text{N}^+\text{BF}_4^- \).
[40], Lind Jr., et al [41], Barton et al [42], and Del Rosario et al [43], and their reported temperatures and enthalpies of phase-transition and fusion are summarized in Table -2.

Prasad et al [45] studied the thermal stability of $R_4N^+BF_4^-$, where $R = \text{Me, Et, Pr, and n-butyl}$. Thermal decomposition studies of primary alkylammonium haloborates leading to the syntheses of polyborazynes [46–49], and those of tetraalkylammonium haloborates [50] have been reported. Studies oriented towards thermal decomposition and stability of tetrafluoroborate copper (I) complexes have been carried out by de Lucca Neto et al [51]. The thermal or photochemical decomposition of arene-diazonium-tetrafluoroborate salts in trifluoromethanesulfonic acid, with or without organic bases such as pyridine, provides aryl triflates in high yields [52]. The fluoro-dediazoniation of $ArN_2BF_4$ using HF-pyridine solution has been successfully carried out either thermally or photochemically to afford the corresponding $ArF$ in good yields. Particularly, the photochemically induced reaction in HF-pyridine was a useful tool for the preparation of $ArF$ having polar substituents such as halogens, OH, OMe, CF$_3$, etc [53].
Table – 1: Crystallographic, nuclear magnetic resonance data on $R_4NBF_4$s ($R=$ Et and n-Butyl)

<table>
<thead>
<tr>
<th>Salt</th>
<th>Phase-Transition Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1st Transition</td>
</tr>
<tr>
<td>$(C_2H_5)_4NBF_4$</td>
<td>63 [36] - CRY</td>
</tr>
<tr>
<td>$(C_4H_9)_4NBF_4$</td>
<td>$-3$ [45] - NMR</td>
</tr>
</tbody>
</table>

Table – 2: Temperatures of Phase-transitions and Fusion and Associated Enthalpies in respect of $R_4NBF_4$s
($R =$ Et and n – Butyl)

<table>
<thead>
<tr>
<th>$R$</th>
<th>Transition (s)</th>
<th>Fusion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature (°C)</td>
<td>$\Delta H_1$ (kJ.mole$^{-1}$)</td>
</tr>
<tr>
<td>$C_2H_5$</td>
<td>$63 \pm 1$ [38]</td>
<td>$11.7 \pm 0.4$[38]</td>
</tr>
<tr>
<td>$n-C_4H_9$</td>
<td>$62 \pm 1$ [38]</td>
<td>$7.9 \pm 0.1$[38]</td>
</tr>
</tbody>
</table>
5.3. Tetraalkylammonium Perchlorates (R₄NClO₄) 

There has been increasing interest in the thermal studies of methyl-substituted ammonium perchlorates [39, 54-57]. These compounds are highly sensitive to external stimuli and explode violently. Monomethylammonium perchlorate was found to be more impact sensitive; whereas the decomposition temperatures of this methyl substituted ammonium perchlorates (revealed by DTA studies) decrease as the methyl substitution increases, indicating that their stabilities probably decrease with increasing substitution [39]. From a thermal decomposition study employing mass spectrometer, Guillory et al [55] have concluded that the substitution of methyl groups into the ammonium cation stabilizes these perchlorates. This is based on their observation that the dissociation temperatures increase with increasing methyl substitution into the cation.

The methyl substituted ammonium perchlorates, being structurally similar to AP, have been considered as auxiliary oxidizers or additives to solid propellant compositions [58]. The increase of burning rate of AP - based composite solid rocket propellants by trimethylammonium perchlorate is attributed to its melting and low-temperature exotherm, while the increase of burning rate due to the addition of tetramethylammonium perchlorate (TEAP) is attributed to its non-melting and high-temperature exotherm. The contrasting effects of tetramethylammonium perchlorate on decomposition and burning rate of AP – based propellant suggest that the enhancement of the burning rate is due to the catalysis of the gas-phase reactions [58]. Jain et al [58, 59] showed that the burning and decomposition rates of solid composite propellants and the thermochemical behavior of AP are...
considerably altered in the presence of small amounts (<10%) of methylammonium perchlorates. Jain et al [59] dealt with the thermochemistry and lower combustion limit of AP in the presence of methylammonium perchlorate.

A preliminary study of organic perchlorates [60, 61] has shown that they burn 7–10 times faster than secondary explosives. Fogel'zang et al [62] investigated the combustion behavior of perchlorates of aliphatic amines, aromatic amines, heterocyclic amines, and amidines. Thermal characterization of tetramethylphosphonium perchlorate, nitrate, and picrate carried out by Nambiar et al [63]. Chemical analysis and IR spectrum of the residue obtained during the thermal decomposition of monomethylammonium perchlorate studied under isothermal and non-isothermal conditions revealed that, it contains ammonium perchlorate, and the results are explained on the basis of a methyl group transfer in addition to proton transfer [64]. The effect of tetramethylammonium perchlorate on AP and AP-based propellant decomposition was also reported [65]. Sundararajan et al [66] studied the thermal ignition behavior of AP in presence of fuel–rich compounds such as tetramethylammonium perchlorate. Tetraethylammonium perchlorate undergoes crystallographic transformation at 98°C and explodes at 298°C. The mass spectral data suggest that the salt undergoes thermal decomposition into neutral particles, which are then vaporized and ionized as well as oxidized [67]. Fadhil Jasim et al [68], have studied the thermal decomposition of tetra-n-butyl-ammonium perchlorate (TBAP), except for the kinetic and mechanistic aspects.
Ionic association and conductance of some symmetrical tetraalkylammonium perchlorates in 2-Methoxyethanol + Water at 298.15 K; and viscosities of some symmetrical tetraalkylammonium perchlorates in 2-methoxyethanol + Water at 298.15, 308.15, and 318.15 K were reported by Bijan Das et al [69, 70]. Ultra performance liquid chromatography analysis of adenine nucleotides and creatine derivatives for kinetic studies applying the reversed phase technique, where the eluting buffer solution is supplemented by a large hydrophobic cationic, typically a tetrabutylammonium (TBA) compound is reported [71].

John J. Banewicz et al [72] determined the electrical conductance of TEAP in valeronitrile. Gerhard Fuchas et al [73] studied the influence of TEAP on the electrode kinetics of Eu³⁺ in DMSO. Jussi Kivikoski et al [74] studied the crystal structure of TEAP at 150K. The conductivities of tetraethylammonium and ammonium salt in methyl alcohol [75]; conductance of tetraalkylammonium salts in 1-Butanol and 1-Pentaňol at 25°C [76] were studied. Taylor dispersion measurements at low electrolytes concentrations of tetraalkylammonium perchlorate aqueous solutions [77]; Solute ¹³C Nuclear magnetic resonance spectrometric investigation of acetonitrile-tetraalkylammonium salt interactions [78] was reported. Thermochemical study of the influence of tetraalkylammonium cationic size and interaction of their salts with formamide and carbamide in aqueous solutions [79] was reported. Solvent effect on rotational correlational times of symmetric tetraalkylammonium ions [80]; were reported. Property data for tetraalkylammonium cations are reviewed [81]. Conductance measurements are reported for tetraethylammonium halide and perchlorate salts in water-
methanol mixtures over the complete composition range [82]. Tetraethylammonium cations were shown to inhibit the potentiostatic iron dissolution because [83]. Apparent Molar Volumes of multicharged cations in DMSO solutions at 25°C were determined [84]. The conductance of tetrabytylammonium nitrate, perchlorate, and picrate and of tetr methyl-, tetr propyl-, and tetr butylammonium tetraphenylborides has been measured [85].

Investigation of the complex formation of tetrabutylammonium perchlorate with boron halides by the NMR-11B method [86] was carried out. The reaction of free chlorine with tertiary ammonium or amine compounds in aqueous solution was studied by the amperometry at a rotating Pt-disk electrode [87]. TBAP was used as supporting electrolyte in DCM deaerated solution was for the synthesis and characterization of electropolymerized nano-structured aminophenylporphyrin films [88]. Titova et al [89] discussed the decomposition characteristics of tetraethylammonium fluoro perchlorato-borides. In the kinetics and product studies related to Quinone-sensitized steady state photolysis of acetophenone oximes under aerobic conditions TEAP served as an electrolyte [90].

The electrochemical reduction of CO₂ in tetraethylammonium perchlorate - methanol electrolyte was investigated with a copper wire electrode at an extremely low temperature (-30 degrees C) [91]. To study redox-induced changes in the ion and solvent content of polybithiophene/polyxylyliviologen (PBT/PXV) bilayers, experimental measurements were taken under slow scan voltammetric conditions in 1 mol dm⁻³ tetraethylammonium perchlorate + CH₃OH [92].
A Vibrational spectroscopic study of ion solvant in LiClO₄ and
tetraethylammonium perchlorate acetonitrile solutions has been performed
using attenuated total reflection FTIR spectroscopy [93]. The differential
capacity of the Mercury/solution interfaces has been measured for various
tetraalkylammonium and alkali metal perchlorates in dimethylformamide
(DMF) at 25°C, and for tetraethylammonium perchlorate (TEAP) in DMF at –
15°C, 0°C, and 40°C [94].
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5.4 Scope of the Study

Despite a long investigative history of AP and AP-fuel mixtures, it is still construed as the most confounding materials in the research setting. The search for new materials that incorporate desired performance characteristics to propellant formulations continues. Various production quality controls related aspects are increasingly becoming relevant. Keeping these aspects in view, the author focused research attention in the direction of (i) studying the effect of varying the source of supply of ammonium perchlorate (AP); (ii) Effect of sample heating rate on the kinetics of AP decomposition; (iii) Effect of particle-size on AP decomposition; (iv) Applicability of thermogravimetry (TG) and differential scanning calorimetry (DSC) as effective tools for AP production quality control.

Further, quaternary ammonium compounds also find extensive applications in electro-chemistry and as phase-transfer catalysts in organic synthesis, and polymer chemistry. However, their use as additives in solid rocket propellant technology is still in its nascent stage. Accordingly, in the present investigation, researcher focused attention to the study of thermal decomposition of pure compounds of quaternary ammonium tetrafluoroborates (R₄BF₄s) and perchlorates (R₄ClO₄s) which include – NH₄BF₄, (C₂H₅)₄NBF₄, [(C₆H₅CH₂)(C₂H₅)₃]NBF₄, (C₂H₅)₄NCIO₄, and (C₄H₉)₄NCIO₄.

Subsequent to understanding the thermal behaviour of pure quaternary ammonium compounds, the author also extended research work to study thermal behaviour of mixtures of AP with NH₄BF₄, (CH₃)₄NBF₄, (C₂H₅)₄NBF₄, [(C₆H₅CH₂)(C₂H₅)₃]NBF₄, (C₂H₅)₄NCIO₄, and (C₄H₉)₄NCIO₄ towards identifying suitable compounds for propellant formulation.
In the present research work, the researcher employed versatile thermoanalytical tools which include – hyphenated techniques of TG, DTG, DTA, DSC, MS (Mass Spectrometry) and Quadrupole Mass Spectrometry (QMS).

The present research investigation will enrich practical subject knowledge significantly on thermal decomposition behaviour of solids. It also enlarges the scope of materials (catalytic additives) to which these thermoanalytical tools can be effectively employed towards screening of materials (quaternary ammonium compounds) for end use applications, and provide good tools for production related quality control applications. This research investigation will add new dimensions to the existing literature of hyphenated thermoanalytical studies on kinetic and mechanistic aspects of ammonium perchlorate decomposition.