

Review Article

Role of proton transfer reactions in the thermolysis of alkyl and arylammonium salts

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The thermolysis of nitrate, perchlorate, sulfate and chloride salts of various alkyl and arylamines have been reviewed in the present article. The mechanistic aspects of thermal decomposition have been described critically. It has been observed that proton transfer reactions do play a major role during the thermolysis of these salts.

Introduction

The decomposition of ammonium salts has been explained on the basis of the high temperature acid-base theory¹⁻³. The base strength of the anion increases with the rise in temperature until it reaches the base strength of the ammonia molecule. At this temperature, the anion base removes the proton from the ammonium cation. The weaker the anion base, the higher would be the decomposition temperature. Many ammonium salts have been investigated with the help of thermoanalytical techniques and results have been explained². Plateaux have been found to occur in TG curves which clearly indicates the formation of intermediates. Experimental weight losses agreed well in most cases with the theoretical losses expected for the formation of such compounds.

Thermolysis of inorganic ammonium salts of H_3PO_4 , H_2SO_4 , $HClO_4$, HCl , HI , HF , HBr , $AcOH$ has been studied extensively and reported in a good number of publications⁴⁻¹¹.

Thermolysis of alkyl and arylammonium salts of some of the acids have been undertaken in the last decade and most of the work is available in the literature in scattered manner, and hence, it was thought to review these studies. The mechanistic aspects of thermolysis of nitrate, perchlorate, sulfate, chloride of alkyl and arylamines have been described critically in the present review taking into account the role of proton transfer reactions.

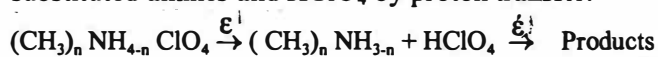
Alkyl and arylammonium perchlorates

Reaction of arylamine with $HClO_4$ to form arylammonium perchlorates is well-known^{11,12}. It has been reported that substitution of methyl groups into NH_4 cation stabilizes the perchlorate salts thermally

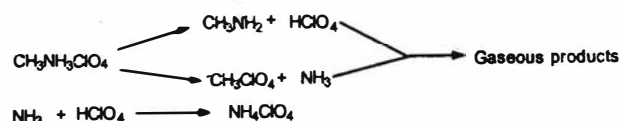
in the following order^{13,14} as compared to ammonium perchlorate.



Stammler *et al.*¹⁵ have also indicated monomethylammonium perchlorate to be most sensitive. These compounds decompose to methyl substituted amines and $HClO_4$ by proton transfer.



where n is the number of methyl groups (1-3), ϵ is the dissociation energy and ϵ' is the net dissociation energy. Thermal stability of these salts increases with the increase in the number of methyl groups. During thermolysis of methylammonium perchlorates, in addition to proton transfer, occurrence of methyl group transfer¹⁶ has also been reported.



Methyl perchlorate, being unstable in this temperature range, may decompose as soon as it is formed.

Tetraethylammonium perchlorate¹⁷ (TEAP) undergoes phase transition at 98 °C and explodes at 298 °C and fragmentation occurs through three routes namely, perchlorate anion and its disintegration products, tetraethylammonium cation and its products involving dealkylation process¹⁸ and the oxidation of organic group by the perchlorate. The decomposition of ethylenediammonium perchlorate¹⁹ (EDP) involves four stages. Proton transfer takes place in the temperature range of 275-310 °C and 320-360 °C and



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the whole material is oxidised to gaseous products. Udupa^{20,21} has reported that thermal decomposition of triethylammonium perchlorate and diphenylammonium perchlorate undergoes by proton transfer mechanism. Pentaerythrityl tetrammonium perchlorate²² undergoes decomposition in a complicated fashion. The decomposition products such as HCl, CO₂, ClO₃ and H₂O were detected but the nitrogen containing products were not traceable which suggests that N₂ may be the product and /or it is retained as a part of condensed phase reactions. Propyl -1, 3-diammonium perchlorate²³ (PDP) undergoes a solid-solid phase transition at 150 °C and significantly changes the lattice structure and the ion dynamics. The decomposition of PDP starts immediately after melting at 280 °C forming HCl, CO, CO₂ and H₂O as thermodynamically stable products.

Jain *et al.*²⁴ have studied the thermal decomposition and explosion characteristics of ring (mono) substituted anilinium perchlorate (RSAP) by DTA, explosion delay and impact sensitivity measurement and involvement of proton transfer from anilinium ion to perchlorate ion. Very recently, Singh *et al.*^{25,26} have prepared and characterised a large number of RSAP. The thermolysis of these salts was undertaken by thermoanalytical techniques, explosion characteristics (by explosion delay), impact and friction sensitivity measurements. The explosion temperatures, energies of activation for decomposition and impact sensitivity data (*h*_{50%}) were found to be linearly related to *pK_a* values of the corresponding arylamines and substituent constants, σ^+ and σ^- . Proton transfer process has been proposed as rate determining step. It seems that oxidation reaction between arylamines and HClO₄ and/or its decomposition products cause explosion. A reaction Scheme I has been proposed based on the formation of reaction intermediates during decomposition and explosion.

Dimethylanilinium perchlorates (DMAP) have also been prepared and characterised²⁷. Thermolysis of these salts have been investigated using TG, DTA, explosion delay, explosion temperatures, impact and friction techniques. It seems that thermolysis of DMAP involves competitive decomposition reaction paths. The proton transfer seems to control the decomposition induced by impact and free radical mechanism predominantly involved in thermal reactions induced by heat as shown in Scheme II.

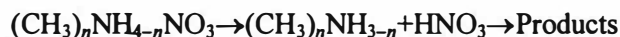
Alkyl and arylammonium nitrates

These amine salts can be prepared by neutralising,

the aqueous solution of the corresponding amine with HNO₃. Thermolysis of the partially substituted methylammonium nitrates has been investigated by TG and MS techniques^{28,29}. The decomposition temperature of these compounds increases in the order:

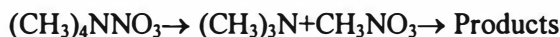


The dissociation involving proton transfer and the overall decomposition can be represented as:



The chief decomposition products are N₂, NO, NO₂ and H₂O. However, methylammonium nitrate (MAN) also yields CH₃NH₂ and NH₃ by methyl group transfer.²⁸⁻³⁰

Tetramethylammonium nitrate (TMAN) has no explosive properties and undergoes decomposition as follows:³¹⁻³³

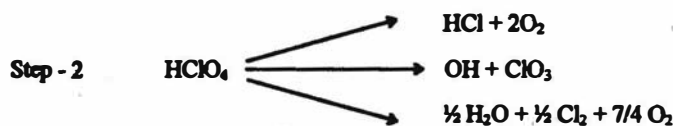
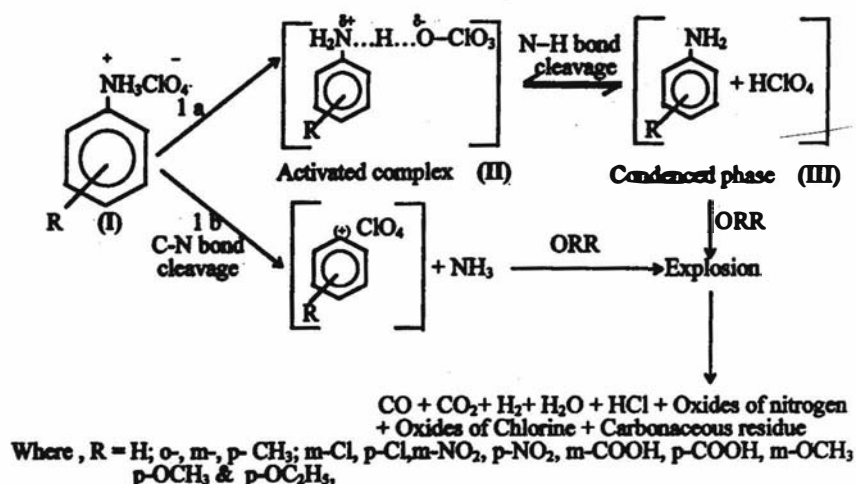


Methyl nitrate was found to decompose above 200 °C forming HCHO, CH₃OH, H₂O, CO, NO, NO₂.

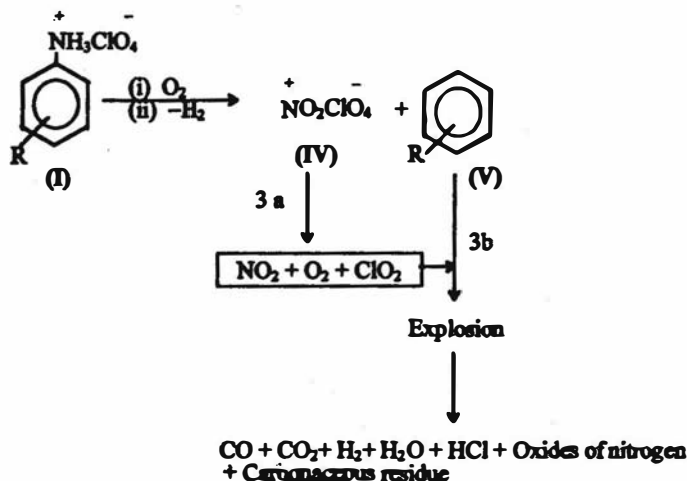
Recently Mckenney *et al.*³⁴ have synthesised a series of selected organodi- and polyammonium nitrate salts, and characterised by ¹H NMR, DTA, DSC, FTIR and MS. Thermolysis of these salts has been reported to be quite complex. Fast thermolysis pattern and pre-ignition reaction of ethylenediammonium dinitrate (EDD), 1,3-propanediammonium dinitrate (PDD), 1,4-butanediammonium dinitrate (BDD), 1,6-hexanediammonium dinitrate (HDD) and methanediammonium dinitrate (MDD) have been described by Russell and Brill³⁵. EDD decomposes to HNO₃ and NO₂ at about 275 °C and NH₃ appears at about 300 °C as a result of C-N bond fission and proton transfer³⁶. The reaction of HNO₃ with NH₃ in the gas phase produces NH₄NO₃ aerosol at about 310 °C. The conversion of HNO₃/NO₂ to NO and the oxidation of hydrocarbon residue to CO/CO₂ occurs at about 330 °C. PDD undergoes a solid-solid phase transition at 62 °C and melts at 126 °C without decomposition²³. Evolution of HNO₃(g) occurs at 280 °C followed by the oxidation-reduction products of HNO₃ and the alkylamine. MS investigation^{37,38} on the initial stages of thermal decomposition of BDD reveals the formation of the corresponding amine and HNO₃ at 160-180 °C and then HNO₃ is partially decomposed to NO₂.

The fast thermolysis pattern²² of pentaerythrityl tetrammonium tetranitrate (PTTN) exhibits the initial

Step -1



Step -3



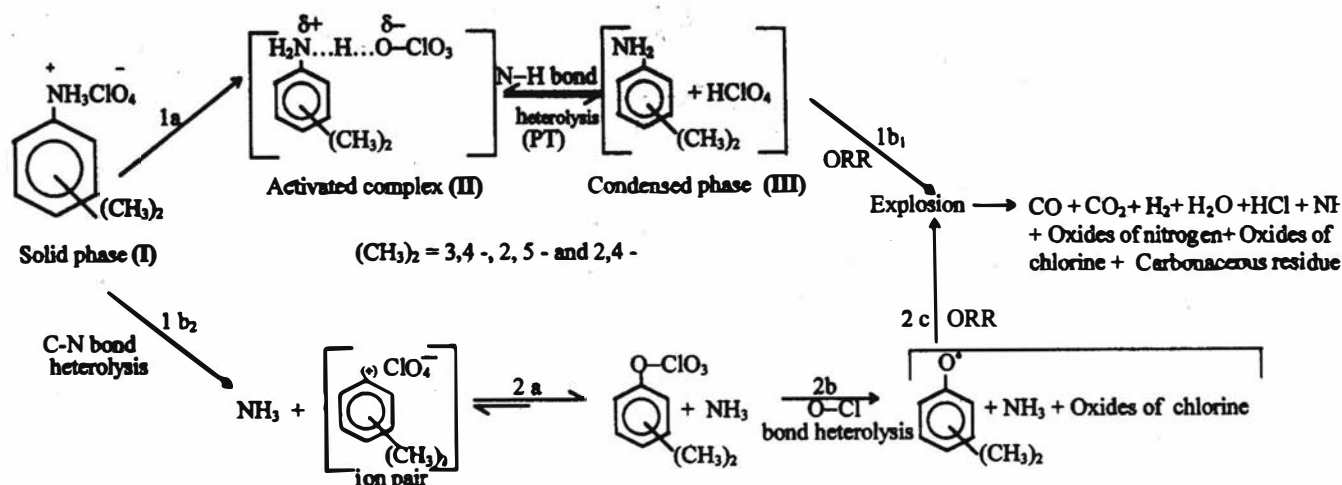
ORR – Oxidation Reduction Reactions

Scheme I—Schematic representation of the thermal decomposition pathways of ring substituted arylammonium perchlorates.

occurrence of the cleavage of N–H bond to form HNO₃. C–N bond cleavage also takes place producing NH₃ and NH₄NO₃(g). Partial oxidation of NH₃ by HNO₃ alongwith the decomposition of HNO₃ leads to the formation of NO₂, N₂O and H₂O. Piperazinium dinitrate (PIPZD) yields initially HNO₃ but then generates a significant amount of *N,N*-dinitrosopiperazine³⁹. Cubylammonium nitrate (CUBAN) and cubane-1, 4-diammonium dinitrate (CUBDAN) undergo thermal decomposition in the solid state without melting whereas, most of the other alkylammonium nitrates melt prior to

decomposition⁴⁰. CUBDAN is the only salt which was found to sublime during fast thermolysis.

The fast thermolysis of primary alkanediammonium dinitrate salts such as [H₃N(CH₂)_{*n*}NH₃](NO₃)₂ [where *n* = 1-4 and 6] is very intriguing because H-bonding can cause intramolecular cyclization^{41,42} of longer chain diamines (*n* = 4, 6). The behaviour of *N*-methylethylenediammonium dinitrate (MEDD), *N,N,N',N'*-tetramethylethylenediammonium dinitrate (TMEDD), *N,N,N'*-trimethylethylenediammonium dinitrate (TRMEDD), *N,N'*-dimethylenediammonium dinitrate (s-DMEDD) and



ORR = Oxidation reduction reactions, PT = Proton Transfer

Scheme II—Schematic representation of the thermal decomposition pathways of dimethylanilinium perchlorates.

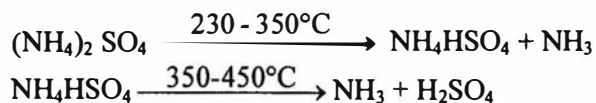
N, *N'*-dimethylethylenediammonium dinitrate (*u*-DMEDD) more closely resemble with the behaviour of alkylammonium mononitrate salt in terms of the temperatures at which HNO₃ is released⁴³. The first decomposition step of most primary and secondary alkylammonium nitrate salts is the production of HNO₃(g).

The thermal stability of some of the ring (mono)-substituted anilinium nitrates (RSAN) was investigated by Jain *et al.*⁴⁴. The decomposition temperature of *meta*- and *para*-RSAN was found to be linearly related to the Hammett substituent constant (σ). The activation energy for decomposition was found to increase with the increase in basicity of the corresponding arylamines. Recently Singh *et al.*^{45,46} have prepared and characterised a large number of RSAN. The thermolysis of these salts has also been investigated using TG, DTA, impact and friction sensitivity measurements. Although the kinetics of thermal decomposition of these salts was evaluated by fitting TG data in mechanism based kinetic equations but contracting envelopes ($n=2, 3$) and Avrami-Erofeev ($n=2, 3$) gave the best fits. The activation energy for decomposition, decomposition temperatures and impact sensitivity data were found to be linearly related to Hammett substituent constant (σ) and dissociation exponent (pK_a) of the corresponding arylamine. The mechanism of thermolysis of these salts has also been proposed based on the formation of reaction intermediates during decomposition. A reaction **Scheme III**, accounting for the products was also proposed that involves proton transfer leading to the formation of an

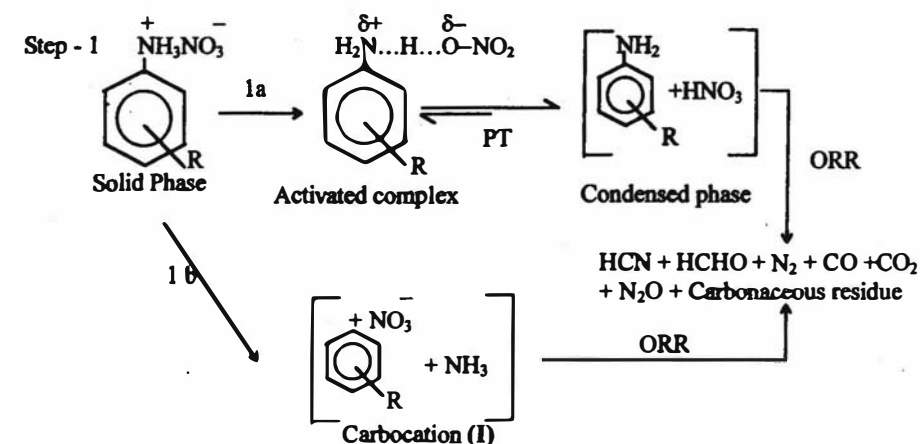
arylamine and HNO₃ and oxidation of the arylamines by decomposition products of HNO₃. The oxidation-reduction reactions near the surface of the thermolysing RSAN were reported to be responsible for the decomposition. The thermolysis of dimethylanilinium nitrates (DMAN) has also been carried out by TG, DTA, ignition delay, impact and friction sensitivity measurements⁴⁷. Thermolysis of DMAN involves complex reaction paths, and proton transfer seems to control the overall thermolysis. Electron donating groups ($-\text{CH}_3$) reduce the sensitivity of the energetic compounds within a class. A reaction **Scheme IV** has been proposed where an arylamine and HNO₃ are formed due to proton transfer. The evolution of NH₃ (C-N bond heterolysis) has also been suggested (**Scheme IV**) prior to the oxidation of aryl nucleus by NO₂, HNO₃ and/or its decomposition products, and ultimately gaseous products, are formed.

Alkyl and arylammonium sulphates

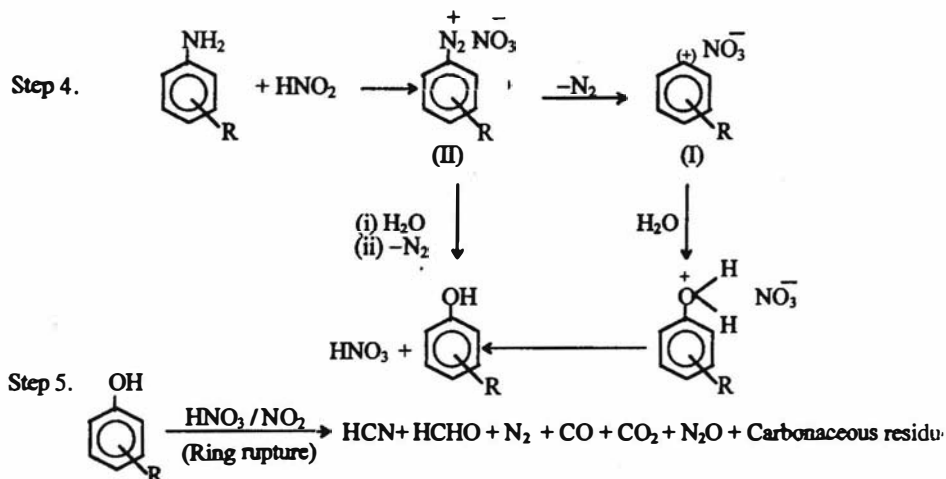
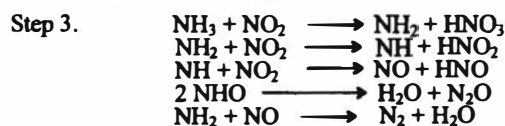
Erdey *et al.*² have reported that (NH₄)₂SO₄ decomposes in two steps and proton transfer was observed in each step.



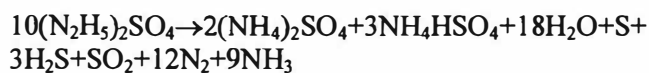
H₂SO₄ formed during the decomposition was reported to be very reactive. Dihydrazinium sulfate [(N₂H₅)₂SO₄] decomposition is reported to be quite complex and does not involve proton transfer reactions.



Where, R = H; *m*-CH₃, *p*-CH₃; *m*-NH₂, *p*-NH₂; *m*-Cl, *p*-Cl; *m*-NO₂, *p*-NO₂; *m*-COOH, *p*-COOH; *m*-OCH₃, *p*-OCH₃; *p*-OC₂H₅



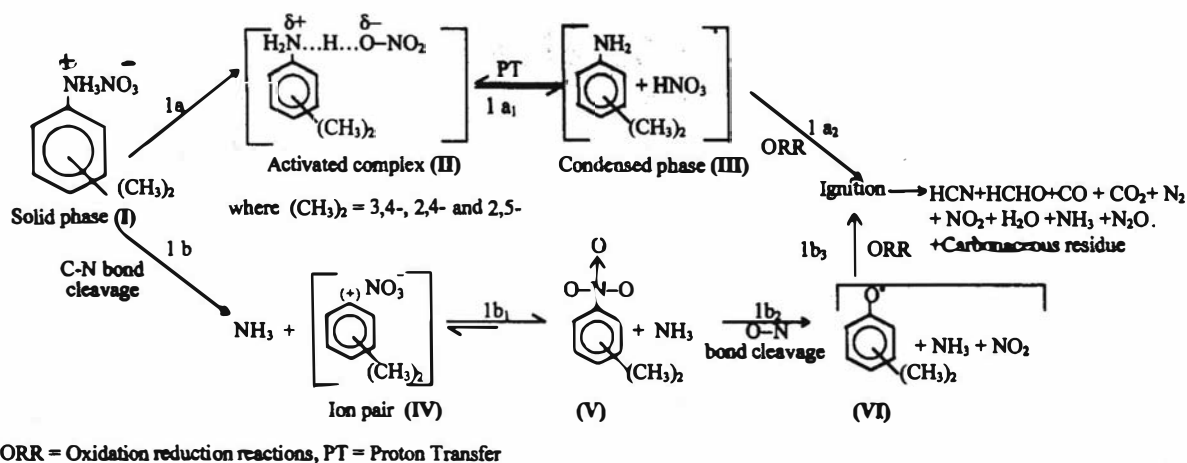
Scheme III—Schematic representation of the thermal decomposition pathways of dimethylanilinium nitrates.



The work on thermolysis of alkylammonium salts is not yet reported in literature. However, Jordanovsha and coworkers⁴⁸⁻⁵¹ have investigated the thermolysis of double sulfates of mono, di and trivalent metal cations with monovalent aliphatic ammonium cation. Proton transfer process seems to be involved in the decomposition of Co and Ni double sulfates⁵¹. Recently Singh *et al.*⁵²⁻⁵⁹ have done a lot of work in the thermolysis of arylammonium sulfates. It has been

found that dianilinium sulfate is formed when arylamine was reacted with H₂SO₄. Thermal decomposition of dianilinium sulfate⁵² gave sulfanilic acid by proton transfer and sulfonation process.

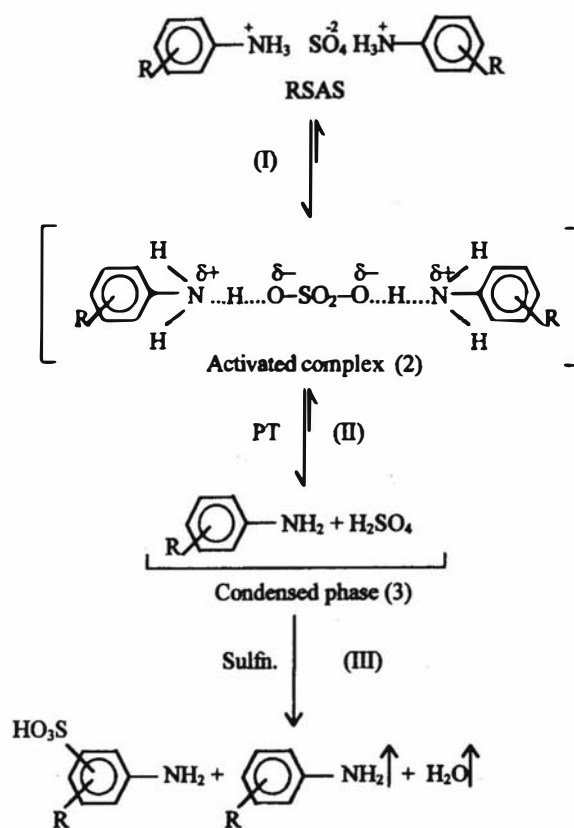
Thermal decomposition of *m*-ditoluidinium sulfate (*m*-DTS) gave 2-methylsulfonic acid⁵³. It has been suggested that phase boundary reactions occur during thermolysis of *m*-DTS. Reactive species such as *m*-toluidine and H₂SO₄ are formed *via* proton transfer process in adsorbed phase prior to sulfonation. *p*-Ditoluidinium sulfate (*p*-DTS) yields 2-amino-5-



Scheme IV—Schematic representation of the thermal decomposition pathways of ring substituted arylammonium nitrates.

methylbenzenesulfonic acid *via* solid state reaction induced by heat⁵⁴. Thus, large number of ring substituted arylammonium sulfates (RSAS) having electron donating or demanding substituents were prepared, characterised and their thermal decomposition was investigated by TG, DTG and DTA techniques⁵⁵. It has been found that thermal stability of these sulfate salts depends upon pK_a values of the corresponding amines. The overall decomposition pathway for RSAS is summarized in **Scheme V**.

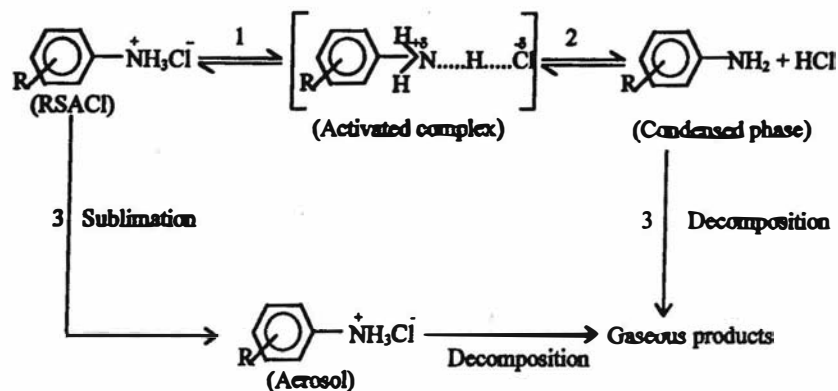
Singh *et al.*⁵⁶ have also investigated the thermal decomposition of di-*m*-chloroanilinium sulfate (di-*m*-CIAS) in solid state and found two isomeric chloroaminobenzenesulfonic acids as intermediate products. The decomposition of di-*m*-CIAS involves proton transfer process as a primary step. Singh *et al.*⁵⁷ have also prepared and characterised tetramethyldianilinium sulfates (TMDAS). The activation energy for decomposition has been found to be related to pK_a of the corresponding arylamines. The N-H bond heterolysis seems to be the primary step during decomposition of these salts. Five sulfate salts of *ortho*-substituted amines (*o*-RSAS) were prepared and characterized^{58,59} by elemental, gravimetric and spectral analyses. *o*-RSAS are also reported to yield the corresponding ring substituted aminobenzenesulfonic acids when the former were subjected to thermal energy. Thermal decomposition of these salts was investigated by thermoanalytical techniques. Parabolic law (α^2) was found to fit the TG data. It has been observed that most of *o*-RSAS undergo transformation to substituted aminobenzenesulfonic acids in solid state *via* proton transfer reaction^{58,59}.



Where, $R = H, m\text{-Cl}, p\text{-Cl}; m\text{-CH}_3, p\text{-CH}_3; m\text{-OCH}_3; m\text{-NO}_2 \text{ \& } p\text{-NO}_2$

PT = Proton transfer
Sulfn. = Sulfonation
↑ = Given off

Scheme V—Schematic representation of the thermal decomposition pathways of ring substituted arylammonium sulfates.



Scheme VI—Schematic representation of the thermal decomposition pathways of ring substituted arylammonium chlorides.

Alkyl and arylammonium chlorides

Erdey and coworkers¹⁻³ have investigated the thermal decomposition of various ammonium salts. NH_4Cl has been reported to sublime above 200°C prior to dissociation to NH_3 and HCl molecules. The studies on alkylammonium salts do not seem to be reported in literature. Singh and coworkers⁶⁰ have prepared and characterised a large number of ring substituted arylammonium chlorides (RSACl). The thermal decomposition of RSACl has also been investigated using TG and DSC techniques, and decomposition pathways for these salts have been proposed. It has been reported that overall decomposition process (Scheme VI) seems to commence by the transfer of proton through an activated complex from arylammonium ion to chloride ion forming amine and HCl molecules in the condensed phase. Two routes of decomposition have been proposed. In first route, amine and HCl may form aerosol via sublimation prior to decomposition into gaseous products. In the second route, decomposition may involve deamination and ring rupture and gaseous products are formed. It has also been reported that simultaneous sublimation/decomposition processes are involved during the thermolysis of RSACl.

General conclusions

The proton transfer seems to be the primary and rate controlling step in the thermolysis of alkyl and arylammonium salts having perchlorate, nitrate, sulphate and chloride anions.

These salts have been found to dissociate to parent arylamines and acid molecules (HClO_4 , HNO_3 , H_2SO_4 , HCl) in the condensed phase. H_2SO_4 formed

during decomposition of RSAS, sulphonates the arylamines in solid state to form aminobenzene-sulphonic acids. On the other hand, HNO_3 and HClO_4 formed during thermolysis of RSAN and RSAP respectively have been reported to oxidise the arylamines to gaseous products. Simultaneous sublimation / decomposition processes predominate in the thermal decomposition of chloride salts of arylamines (RSACl).

Acknowledgement

Thanks are due to the Head, Chemistry Department, DDU Gorakhpur University, Gorakhpur for laboratory and library facilities. Financial support by DST is also acknowledged.

References

- 1 Erdey L & Gal S, *Talanta*, 10, 1963, 23.
- 2 Erdey L, Gal S & Liptay G, *Talanta*, 11, 1964, 913.
- 3 Erdey L, *Periodica Polytech*, 1, 1957, 91.
- 4 Duval C, *Inorganic Thermogravimetric Analysis*, 2nd edn (Elsevier, Amsterdam), 1963.
- 5 Urbanski T, *Chemistry and Technology of Explosives*, Vol II (Pergamon Press, London) 1961.
- 6 Solymosi F, *Structure and Stability of Salts of Halogen Oxyacids in the Solid Phase* (John Wiley and Sons, New York) 1977.
- 7 Singh G, Kapoor I P S & Mannan S M, *Chemistry of Materials*, (Communicated, 1998).
- 8 Jacobs, P W M & Whitehead H M, *Chem Rev*, 69, 1969, 551.
- 9 Kapoor I P S, *Studies on Energetic Compounds and Dianilinium Sulphate*, (Ph.D Thesis, Gorakhpur University, Gorakhpur) 1992.
- 10 Mannan S M, *Studies on Energetic Materials*, (Ph.D. Thesis, Gorakhpur University, Gorakhpur) 1995.
- 11 Schumaker J C, *Perchlorates: Their Properties, Manufacture and Uses*, (Reinhold, New York), 1960.
- 12 Burton A & Praill P F G, *Analyst*, 80, 1955, 4.
- 13 Guillory W A & King M, *J Phys Chem*, 73, 1969, 4367.

- 14 Nambiar P R, Verneker V R Pai & Jain S R, *J Therm Anal*, 8, 1975, 15.
- 15 Stammel M, Bluenner R, Schmidt W & Orcult D, *Advance X-ray Anal*, 9, 1966, 170.
- 16 Nambiar P R, Verneker V R Pai & Jain S R, *J Therm Anal*, 7, 1975, 587.
- 17 Udupa M R, *Propell Explos Pyrotech*, 7, 1982, 155.
- 18 Hesse M, Weller W & Schmid H, *Helv Chem Acta*, 48, 1965, 674.
- 19 Udupa M R, *Thermochim Acta*, 42, 1980, 383.
- 20 Udupa M R, *Thermochim Acta*, 58, 1982, 379.
- 21 Udupa M R, *Thermochim Acta*, 71, 1983, 219.
- 22 Oyumi Y, Brill T B Rheingold A L & Lowe-Ma C, *J Phys Chem*, 89, 1985, 2309.
- 23 Chen R, Russell T P, Rheingold A L & Brill T B, *J Cryst Spect Res*, 21, 1971, 167.
- 24 Jain S R, Rao M V & Verneker V R Pai, *Combust Flame*, 35, 1979, 289.
- 25 Singh G & Kapoor I P S, *J Phys Chem*, 96, 1992, 1215.
- 26 Singh G, Kapoor I P S & Mannan, S M, *J Therm Anal*, 46, 1996, 1751.
- 27 Singh G, Kapoor I P S & Mannan S M, *J Energ Mat*, 13, 1995, 141.
- 28 Jain S R, Rao M V & Verneker V R Pai, *Propell Explos*, 3, 1978, 83.
- 29 Jain S R, Nambiar P R & Verneker V R Pai, *Proc Indian AcadSci*, 87A, 1978, 31.
- 30 Breisacher P, Tabimoto H H, Denault G S & Hichs W A, *Combust Flame*, 14, 1970, 393.
- 31 Stenhagen E, Abrahamson S & McLafferty F W, *Registry of Mass Spectral Data*, (John Wiley, New York) 1, 1974, 12.
- 32 Appin A, Todes O & Khantor Yu, *J Phys Chem*, (USSR) 8, 1936, 866.
- 33 Nambiar P R & Jain S R, *Thermochim Acta*, 9, 1974, 295.
- 34 McKenney R L Jr, Struch S R, Hildreth R A & Fryling J A, *J Energ Mat*, 5, 1987, 1.
- 35 Russell T P & Brill T B, *Combust Flame*, 15, 1990, 77.
- 36 Russell T P & Brill T B, *Combust Flame*, 76, 1989, 393.
- 37 Quishe, J M E, Fu J, Hardy K A, Sheldon J W, Doolite F G & McKenney R L Jr, *Propell Explos Pyrotech*, 14, 1989, 76.
- 38 Mehenny R L Jr, Struchs S R, Ellison D S, Maegelein S D & Climino R, *J Energ Mat*, 8, 1990, 205.
- 39 Russell T P, Brill T B, Rheingold A L & Haggerty B S, *Propell Explos Pyrotech*, 15, 1990, 81.
- 40 Russell T P & Brill T B, *Propell Explos Pyrotech*, 16, 1991, 27.
- 41 Yamdangm R & Kebale P, *J Am Chem Soc*, 95, 1973, 3504.
- 42 Ane D H, Webb H M & Bowers M T, *J Am Chem Soc*, 95, 1973, 2699.
- 43 Russell T P & Brill T B, *Propell Explos Pyrotech*, 15, 1990, 123.
- 44 Jain S R, Rao M V & Verneker V R Pai, *J Chem Soc Perkin II*, 1979, 406.
- 45 Singh G & Kapoor I P S, *Combust Flame*, 92, 1993, 283.
- 46 Singh G & Kapoor I P S, Mannan S M & Agrawal J P, *Combust Flame*, 97, 1994, 355.
- 47 Singh G, Kapoor I P S & Mannan S M, *Thermochim Acta*, 262, 1995, 117.
- 48 Jordanovsha V, *J Therm Anal*, 35, 1989, 1331.
- 49 Jordanosha V & Siftar J, *J Therm Anal*, 31, 1986, 1049.
- 50 Jordanosha V & Siftar J, *J Therm Anal*, 37, 1991, 73.
- 51 Jordanosha V, Aleksovska S & Siftar J, *J Therm Anal*, 38, 1992, 1563.
- 52 Singh G & Kapoor I P S, *J Chem Soc Perkin Trans II*, 1989, 2155.
- 53 Singh G, Kapoor I P S & Jain M, *J Chem Soc Perkin Trans*, 2, 1993, 1521.
- 54 Singh G, Kapoor I P S & Jain M, *Indian J Chem*, 356B, 1996, 369.
- 55 Singh G, Kapoor I P S & Jain M, *Thermochim Acta*, 292, 1997, 135.
- 56 Singh G, Kapoor I P S & Singh J, *Indian J Engg & Tech*, 5, 1998, 300.
- 57 Singh G, Kapoor I P S & Singh J, *Indian J Chem*, 36B, 1997, 590.
- 58 Singh G, Kapoor I P S & Singh J, *Indian J Chem*, (Communicated).
- 59 Singh G, Kapoor I P S & Singh J, *Thermochim Acta*, 335, 1999, 11..
- 60 Singh G, Kapoor IPS & Kaur J, *Indian J Chem*, 38B, 1999, 56.