Review

Studies on energetic compounds
Part 8 : Thermolysis of Salts of HNO$_3$ and HClO$_4$

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Abstract

The thermolysis of various substituted ammonium salts of nitric and perchloric acids has been reviewed in the present communication. The mechanistic aspects of thermal decomposition of these salts have been discussed critically. It has been observed that the proton transfer process do play a major role during thermolysis of these salts. The plausible decomposition pathways have also been described. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Energetic materials are the nucleus of modern warfare and one of the most intriguing classes of compounds, which can act as a source of high chemical energy. An energetic material [1,2] is a chemical substance or mixture of substances, when raised to a sufficient high temperature, whether by direct heating, friction, impact, shock, spark or flame, suddenly undergoes very rapid chemical transformations with the evolution of large amount of heat and gases, thereby exerting high pressure on the surroundings. In other words, it may be defined as a material that can undergo very rapid self propagative decomposition to release its potential energy and produces a sudden outburst of heat and volume of gases considerably greater than the original volume of the energetic material.

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Energetic material may be solid, liquid or gas and the products of explosion/ignition are gases or mixture of gases and solids. The thermal decomposition and explosivity of energetic materials, particularly in relation to their molecular structure, are of current interest. The explosive properties of any substance depend upon the presence of the following groups called explosophores:

1. $-NO_2$ and $-ONO_2$ in both inorganic and organic substances,
2. $-N=N-$ and $-N=N=N-$ in inorganic and organic azides,
3. $-NX_2$ (X — a halogen),
4. $-N=C$ in fulminates,
5. $-OClO_2$ and $-OClO_3$ in inorganic and organic chlorates and perchlorates, respectively,
6. $-O-O-$ and $-O-O-O-$ in inorganic and organic peroxides and ozonides, respectively,
7. $-C\equiv C-$ in acetylene and metal acetylides,
8. $M-C$ (metal bonded with carbon) in some organometallic compounds.

A further classification of explosives was also made on the basis of oxygen balance, "plosophoric" groups, auxoplosive groups and heat of explosion. A plosophore is a group capable of forming an explosive compound on introduction into a hydrocarbon and are divided into two classes, i.e., "primary" and "secondary". Primary plosophores include nitrate esters, aromatic and aliphatic nitro groups and the nitramine group. The secondary plosophores comprise groups, such as azo, azide, nitroso, peroxide, ozonide, perchlorate and nitrate, etc. Groups that do not themselves produce explosive properties, but may influence them, are called auxoplosive. The hydroxyl, carboxyl, chlorine, sulfur, ether, oxygen, amine, etc., are the examples of such groups.

2. Evaluation of structure–sensitivity relationship of energetic materials

Energetic materials are mostly employed in military, space, civil and mining. Both experimental and theoretical methods are available to evaluate the energy released and related parameters of energetic materials. Much information concerning any new energetic compound can be obtained for acceptance as a standard material and also to establish a structure–sensitivity relationship. The following are some of the important parameters (i–x) helpful to evaluate the energetic materials and give valuable information on the hazards associated with their preparation, handling, packing, transportation and uses.

(i) Heat of formation (ΔH_f): It is the heat evolved or absorbed when 1 mol of a compound is formed from its elements in their standard states at 298.16°K and zero pressure.

(ii) Oxygen balance (OB): It is defined as the oxygen content relative to the total oxygen required for the oxidation of all carbon, hydrogen and other easily oxidisable elements to CO_2, H_2O, etc.

(iii) Velocity of detonation (VOD): It is the steady value attained at a sufficiently long distance from the explosive (initiator) in a tube or charge diameter sufficiently large that further increase in length or diameter will not cause an increase in velocity.

(iv) Heat of explosion (H_E): It is an amount of energy in the form of heat, which is liberated in the process of explosion.

(v) Explosion pressure (P_E): Its direct measurement can not be made owing to its transient nature and exceedingly high magnitude. The P_E is accurately expressed by the hydrodynamic equation:

$$P_E = \rho Dw + p_1$$

where ρ = density, D = velocity of detonation, w = particle velocity and p_1 = pressure.

(vi) Explosion temperature (T_E): The explosion temperature is a very transient one and possibly maintains only on the charge exist at least in the same type of explosives. Its duration is of the order of microseconds or less.

(vii) Impact sensitivity ($h_{50\%}$): Drop tests were originally used as a measure of relative sensitivity of explosives using the minimum impact potential energy, i.e., mass–acceleration of gravity–height (mgh) and a go-on-go criteria for expressing the relative sensitivity. Even the relative sensitivity may differ considerably from one impact test to another and it depends on the physical state and size of the sample used. Thus, relative sensitivity may then be based on mgh for the 50% detonation, 50% failure and is expressed as $h_{50\%}$.

(viii) Friction sensitivity: It is an event of explosion when the material is subjected to friction. It is commonly measured by a device where explosive material is smeared on the surface of the rotating disc on which rests a known weight. The higher the speed and the greater the load before initiation of the explosive occurs, the lower will be the friction sensitivity of the material.

(ix) Shock sensitivity: Sensitiveness of explosives to mechanical shock is closely related to their chemical constituents but such relationships are frequently masked by difference in physical characteristics, which greatly modify the pressure developed by a blow of a certain intensity.

(x) Explosion delay (E_d): It is the time required for an explosive to detonate when thermal, impact or mechanical shocks are applied.
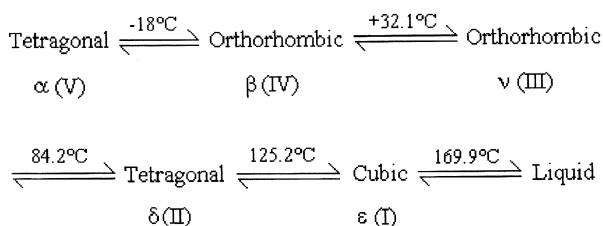
Correlation between the theoretical and experimental parameters leads to the classification of energetic materials. Several workers have studied the relationship between the structure of energetic materials and their sensitivity to impact [3–6]. Initially, Kamlet and Adolph studied a large number of polynitroaliphatic [3] and polynitroaromatic [4] compounds. They were able to identify a broad trend in which $\log h_{50\%}$ decreased with increasing OB. Mullay [5] reported a correlation between impact sensitivity and molecular electronegativities of energetic materials. Recently, Bliss et al. [6] have reported that impact sensitivity and OB relationship is excellent for polynitroaromatics containing nitro, amino and furoxan functional groups. However, groups, such as azide, diazonium, methyl and methylnitramino, are not giving good correlation due to dilution of OB. Jain [7] has suggested a simple approach involving the chemical valences of the fuel and oxidiser elements to evaluate the energetics related parameters. For fuel-rich compounds, a new valence-dependent parameter has also been derived, which is related with VOD, H_E and $h_{50\%}$.
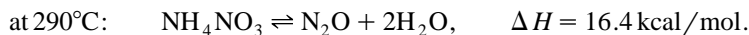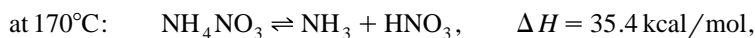
3. Thermolysis of salts of nitric acid

The nitrates (salts of nitric acid) demonstrate explosive properties and can act as readily available oxygen carriers. The chemistry and thermolysis of some of the nitrate salts are described below.

3.1. Ammonium nitrate (AN)

AN is the most readily available and cheapest salt of nitric acid. Generally, AN is prepared by the neutralisation of nitric acid with ammonia. AN exists in the form of five crystalline modifications distinguished by the transition temperatures as shown below:

$$\text{Tetragonal} \underset{}{\overset{-18^{\circ}\text{C}}{\rightleftharpoons}} \text{Orthorhombic} \underset{}{\overset{+32.1^{\circ}\text{C}}{\rightleftharpoons}} \text{Orthorhombic}$$
$$\alpha\ (\text{V}) \qquad\qquad \beta\ (\text{IV}) \qquad\qquad \nu\ (\text{III})$$

$$\underset{}{\overset{84.2^{\circ}\text{C}}{\rightleftharpoons}} \text{Tetragonal} \underset{}{\overset{125.2^{\circ}\text{C}}{\rightleftharpoons}} \text{Cubic} \underset{}{\overset{169.9^{\circ}\text{C}}{\rightleftharpoons}} \text{Liquid}$$
$$\delta\,(\text{II}) \qquad\qquad \varepsilon\ (\text{I})$$

Recently, Kestila et al. [8,9] have also investigated all the five phase transitions of AN by DSC and Raman studies. The disadvantages of AN, which limits its application, are phase transitions and its hygroscopicity. Numerous experiments have been carried out in search of a method for crystallographic stabilisation of AN and to protect it against caking during storage. Manufacturing granulated AN having uniform size minimises the contact surface of granules with moisture. Putting "inert coating" of fuel oil on AN or adding organic substance are quite effective. Very recently, Highsmith et al. [10] used metal dinitramide salts for the phase stabilisation of AN against IV and III phase transitions, which restrict the undesired volume changes. AN decomposes upto 98% in between 210°C and 260°C into nitrous oxide and water. This decomposition often takes place explosively above 300°C and the products are also different.

at 170°C: $\quad NH_4NO_3 \rightleftharpoons NH_3 + HNO_3, \qquad \Delta H = 35.4\,\text{kcal/mol},$

at 290°C: $\quad NH_4NO_3 \rightleftharpoons N_2O + 2H_2O, \qquad \Delta H = 16.4\,\text{kcal/mol}.$

The thermal decomposition of AN in the temperature range 40–200°C under reduced pressure has been found to be strongly temperature-dependent [11]. Brill and Russell [12] have studied its thermal decomposition by rapid-scan FTIR/thermal profiling technique and detected $HNO_3(g)$ and $NH_3(g)$, above 180°C, which is formed by proton transfer process. Shortly thereafter, AN begins to be detected in the gas phase, probably as a result of the recombination of $HNO_3(g)$ and $NH_3(g)$:

$$NH_4NO_3(s) \rightarrow (HNO_3 + NH_3)_{\text{adsorbed}} \rightarrow HNO_3(g) + NH_3(g) \rightarrow NH_4NO_3(g).$$
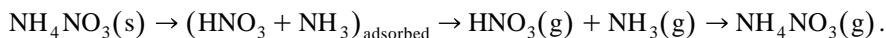
Thermal decomposition studies [13–15] of bulk AN conducted over the past several years revealed the difficulty to distinguish between reactions in the gas and condensed phase. Recent studies [16,17] on the thermal stability of AN mixtures with variety of organic explosives suggest that AN or its decomposition products desensitise them. The sensitiveness of AN towards impact and friction is relatively low.

3.2. Hydrazinium nitrate (HN)

HN exists in two crystalline forms: the stable form melts at 70.7°C, while the labile melts at 62.1°C. HN is practically stable at 75°C and slightly less hygroscopic than AN. The significant difference of HN compared to other nitrate salts is the formation of NH_3, which enhances the explosive sensitivity and the toxicity [12]. HN is sensitive to impact and friction resembling tetryl.

3.3. Guanidinium nitrate (GN)

GN exists as crystals melting at 215–216°C. It represents the most important intermediate product for the commercial manufacture of both nitro-and amino guanidines. Moreover, GN can be used as an ingredient of propellants and also a component of fusible mixtures containing AN. High rate thermolysis [18] of 1,2,3-triaminoguanidinium nitrate (TAGN) liberates predominantly $HNO_3(g)$ and $NH_3(g)$ as the initial products. The second-stage decomposition products are NO_2, N_2O and HCN, which are then followed by third stage products CO_2, H_2O, NO and probably NO_2. The crystal structure of TAGN was established by X-ray [19] and neutron [20] diffraction studies.

3.4. Urea and thiourea nitrates [21]

Urea nitrate (UN) can be prepared by treating urea with dilute nitric acid (34%). Due to its instability, its practical applications are limited. UN decomposes into CO_2, N_2O, AN and urea at 140°C and, at 180°C its decomposition is rather violent. UN is impact and friction insensitive. Thiourea nitrate was prepared by the action of dilute nitric acid on thiourea at 5–10°C and is reported as a weak explosive.

3.5. Alkyl and arylammonium nitrates

Methylammonium nitrates are used as an ingredient of fusible explosives. Jain et al. [22] have prepared mono-, di- and trimethylammonium nitrates by neutralising the aqueous solution of the corresponding amine with nitric acid. Monomethylammonium nitrate (MAN) showed a structural transformation at 85°C; whereas trimethylammonium nitrate showed two transformations, one at 86°C and the other at 136°C. The decomposition temperature of these compounds increases in the order: $CH_3NH_3NO_3 > (CH_3)_2NH_2NO_3 > (CH_3)_3NHNO_3$. The mass spectrometric investigation suggested

that the extent of decomposition increases with increasing substitution on the nitrogen atom. The dissociation involving proton transfer and the overall decomposition can be shown as:
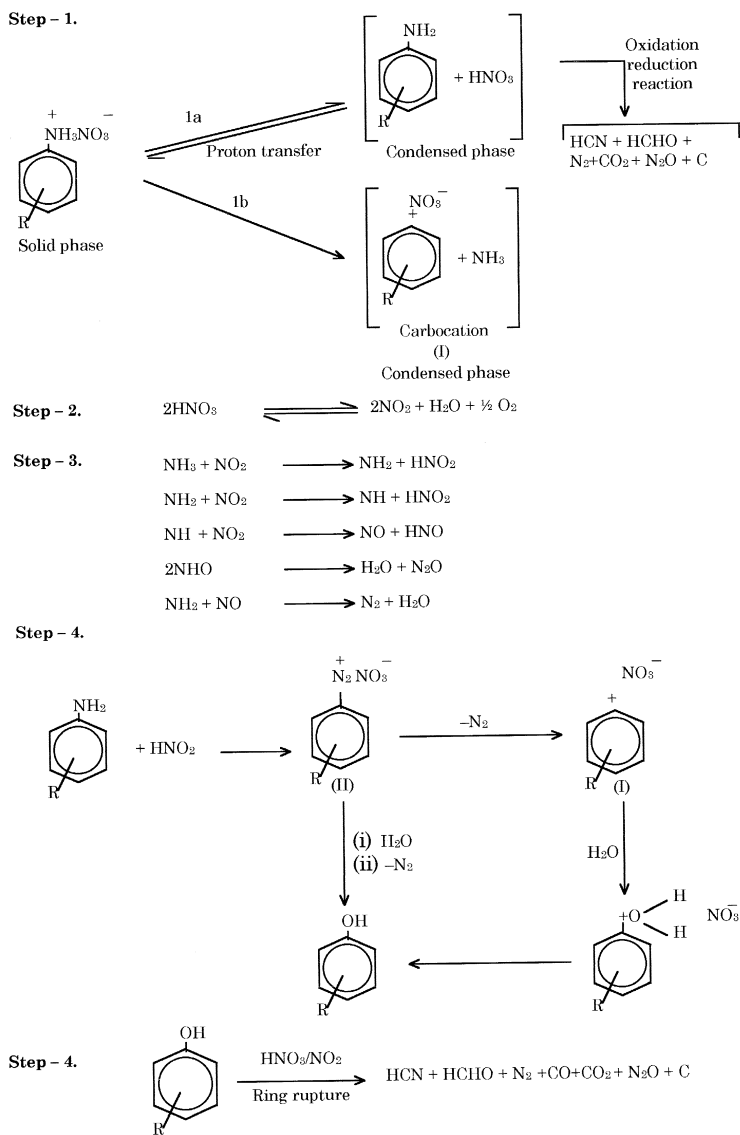
$$(CH_3)_n NH_{4-n} NO_3 \rightarrow (CH_3)_n NH_{3-n} + HNO_3 \rightarrow Products.$$
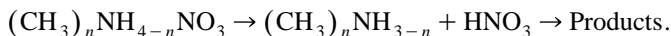
The chief decomposition products are N_2, NO, NO_2 and H_2O. However, MAN also yields CH_3NH_2 and NH_3 by methyl group transfer.

$$CH_3NH_3NO_3 \nearrow CH_3NH_2 + HNO_3$$
$$\searrow NH_3 + CH_3ONO_2$$
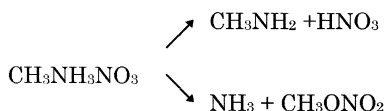
Tetramethylammonium nitrate (TMAN) [23] has no explosive properties. However, it is being used as an ingredient of explosive mixtures blended with cyclonite or incorporated in fusible mixture with AN. TMAN undergoes decomposition as follows:

$$(CH_3)_4 NNO_3 \rightarrow (CH_3)_3 N + CH_3NO_3 \rightarrow Products.$$

Methylnitrate was found to decompose above 200°C forming formaldehyde, methanol, water, carbon monoxide, nitric oxide and nitrogen dioxide. Jain et al. [23] have also prepared TMAN by treating equimolar solutions of $AgNO_3$ and tetramethylammonium iodide. The decomposition proceeds via dissociation of TMAN into trimethylamine and methyl nitrate involving a methyl group transfer. The activation energy for decomposition has been determined by isothermal TG and formation of triethylamine was monitored by spectrometer. The thermal stability of ring (mono)-substituted anilinium nitrates (RSAN) was investigated by Jain et al. [24]. 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 obtained by isothermal TG, increases with the increasing basicity of the corresponding arylamine. The primary step in the decomposition of RSAN salts is proton abstraction by the nitrate anion from the anilinium ion. Very recently, Singh et al. [25–27] have also prepared and characterised a large number of RSAN. TG, DTA, impact and friction sensitivity techniques were applied to investigate their thermolysis. It has been observed that activation energy for decomposition, decomposition temperatures and impact sensitivity data are linearly related to Hammett substituent constant (σ) and dissociation exponent (pK_a) of the corresponding amines. The mechanism of the thermolysis of the salts has been proposed in Scheme 1. Thermolysis of dimethylanilinium nitrates (DMAN) has also been investigated by TG, DTA, ignition delay, impact and friction sensitivity measurement [27]. It has been observed that thermolysis of DMAN involves complex and competitive reaction paths and proton transfer seems to control the overall decomposition (Scheme 2).

Step – 1.

Step – 2. $2HNO_3 \rightleftharpoons 2NO_2 + H_2O + \frac{1}{2} O_2$

Step – 3.

$NH_3 + NO_2 \longrightarrow NH_2 + HNO_2$

$NH_2 + NO_2 \longrightarrow NH + HNO_2$

$NH + NO_2 \longrightarrow NO + HNO$

$2NHO \longrightarrow H_2O + N_2O$

$NH_2 + NO \longrightarrow N_2 + H_2O$

Step – 4.

Step – 4.

Scheme 1.

3.6. Polyammonium nitrates

Polyammonium nitrate have been used as a component of explosives for many years. Recently, Mckenny et al. [28] have synthesised a series of selected organo di- and polyammonium nitrate salts and characterised by ^{1}H NMR, DTA, DSC, FTIR and mass spectrometry. These salts (Table 1) were prepared by reacting the base with 70% nitric

Scheme 2.

ORR – Oxidation reduction reaction
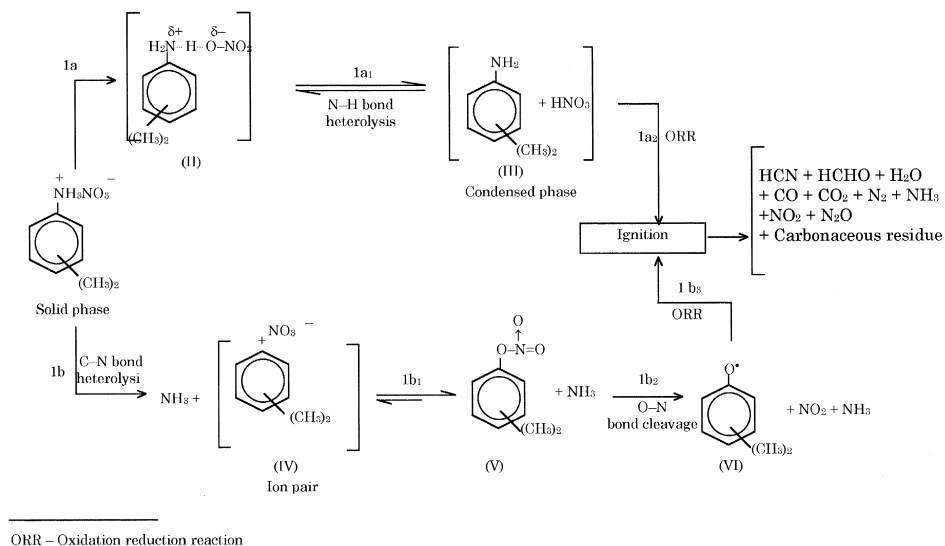
acid in cold 95% ethanol. The acid was added dropwise to the cold ethanolic solution of the respective amine with stirring, and the low temperature minimises the formation of ethyl nitrate. Impact sensitivity of these nitrates was found to be related to OB. The thermolysis of these salts has been reported to be quite complex.

Fast thermolysis patterns and pre-ignition reactions of ethylenediammonium dinitrate (EDD), 1,3-propanediammonium dinitrate (PDD), 1,4-butanediammonium dinitrate (BDD), 1,6-hexanediammonium dinitrate (HDD) (Table 1) and methanediammonium dinitrate (MDD) have been described by Russell and Brill [29]. EDD decomposes to HNO_3 and NO_2 at about 275°C and NH_3 appears at about 300°C as a result of C−N bond fission and proton transfer. The reaction of HNO_3 with NH_3 in the gas phase produces NH_4NO_3 aerosol at about 310°C. The reduction of HNO_3/NO_2 to NO and the oxidation of hydrocarbon residue to CO/CO_2 occurs at about 330°C.

PDD undergoes a solid–solid phase transition at 62°C and melts at 126°C without decomposition [30]. Evolution of $HNO_3(g)$ occurs at 280°C followed by the oxidation–reduction products of HNO_3 and the alkylamine. Mass spectrometric investigations [31,32] on the initial stages of thermal decomposition of HDD reveal the formation of the corresponding amine and nitric acid at 160–180°C. The nitric acid partially decomposes to produce nitrogen dioxide.

The fast thermolysis patterns [33] of pentaerythrityltetraammonium tetranitrate (PTTN) exhibit the initial occurrence of the cleavage of N−H bond to form HNO_3. Some C−N bond cleavage also takes place producing NH_3 and $NH_4NO_3(g)$. Partial oxidation of NH_3 by HNO_3 along with the decomposition of HNO_3 leads to the formation of NO_2, N_2O and H_2O. Piperazinium dinitrate (PIPZD) yields initially HNO_3, but then generates a significant amount of N,N'-dinitrosopiperazine [34]. Cubylammonium nitrate (CUBAN) and cubane-1,4-diammonium dinitrate (CUBDAN) undergo thermal decom-

Table 1

Molecular formula, OB and melting point of organodi and polyammonium nitrate salts

Compound name	Acronym	Molecular formula	OB	Melting point (°C)
Homologues of EDD				
(1) Ethylenediammonium dinitrate	EDD	$C_2H_{10}N_4O_6$	−1.07	188
(2) 1,3-Propanediammonium dinitrate	PDD	$C_3H_{12}N_4O_6$	−3.00	126
(3) 1,4-Butanediammonium dinitrate	BDD	$C_4H_{14}N_4O_6$	−4.67	139
(4) 1,6-Hexanediammonium dinitrate	HDD	$C_6H_{18}N_4O_6$	−7.43	109
N-substituted EDD				
(5) *N*-methylethylenediammonium dinitrate	MEDD	$C_3H_{12}N_4O_6$	−3.00	78
(6) *N*-ethylethylenediammonium dinitrate	EEDD	$C_4H_{14}N_4O_6$	−4.67	86
(7) *N*-isopropylethylenediammonium dinitrate	IPEDD	$C_5H_{16}N_4O_6$	−6.25	94
N,N′-substituted EDD				
(8) *N,N′*-dimethylethylenediammonium dinitrate	s-IMEDD	$C_4H_{14}N_4O_6$	−4.67	130
(9) *N,N′*-dimethylethylenediammonium dinitrate	u-DMEDD	$C_4H_{14}N_4O_6$	−4.67	52
(10) *N,N′*-dimethylethylenediammonium dinitrate	s-DEEDD	$C_6H_{18}N_4O_6$	−7.43	193
N,N,N′-substituted EDD				
(11) *N,N,N′*-trimethylethylenediammonium dinitrate	TRMEDD	$C_5H_{16}N_4O_6$	−6.13	93
(12) *N,N*-dimethyl-*N′*-ethylethylenediammonium dinitrate	DMEEDD	$C_6H_{18}N_4O_6$	−7.43	101
(13) *N,N,N′*-triethylethylenediammonium dinitrate	TREEDD	$C_8H_{22}N_4O_6$	−9.62	86
N,N,N′,N′-substituted EDD				
(14) *N,N,N′,N′*-tetramethylethylenediammonium dinitrate	TMEDD	$C_6H_{18}N_4O_6$	−7.43	228
(15) *N,N,N′,N′*-tetraethylethylenediammonium dinitrate	TEEDD	$C_{10}H_{26}N_4O_6$	−11.40	140
Miscellaneous				
(16) Diethylenediammonium trinitrate	DETN	$C_4H_{16}N_6O_9$	−2.05	150
(17) Triethylenetetrammonium tetranitrate	TETN	$C_6H_{22}N_8O_{12}$	−2.51	229
(18) Tetraethylenepentammonium pentanitrate	TEPP	$C_{18}H_{28}N_{10}O_{15}$	−2.78	196
(19) Piperazinium dinitrate	PIPZD	$C_6H_{12}N_4O_6$	−3.77	224

position in the solid state without melting whereas, most of the other alkylammonium nitrate salts melt prior to decomposition [35]. CUBDAN is the only alkyldiammonium dinitrate salt found to sublime during fast thermolysis.

(CUBAN)   (CUBDAN)
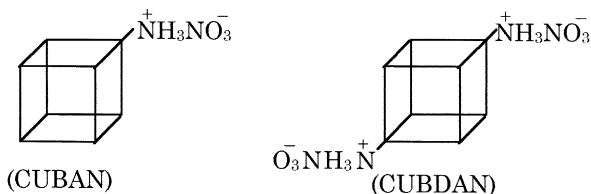
The fast thermolysis of primary alkanediammonium dinitrate salts $[H_3N(CH_2)_nNH_3]$-$(NO_3)_2$, where $n = 1$–4 and 6, is potentially intriguing because hydrogen bonding can

cause intramolecular cyclisation [36], of the longer chain diamines ($n = 4,6$). The behaviour of N-methylethylenediammonium dinitrate (MEDD); N,N,N',N'-tetramethyl-ethylene diammonium dinitrate (TMEDD); N,N,N'-trimethylethylenediammonium dini-trate (TRMEDD), N,N'-dimethylethanediammonium dinitrate (s-DMEDD) and N,N'-dimethylethanediammonium dinitrate (u-DMEDD) are more closely resemble the be-haviour of alkylammonium mononitrate salts in terms of the temperature at which HNO_3 is released [37] (Table 1). The first decomposition step of most primary and secondary alkylammonium nitrate salts is the production of $HNO_3(g)$.

4. Thermolysis of salts of perchloric acid

All the perchlorates (salts of perchloric acid) find technological application in explosives, pyrotechnics, and propellants. Most of the perchlorates are in the form of ammonium salt, which serve as an ideal solid oxidiser than any other commercially available compounds. Some of the important perchlorates are described below.
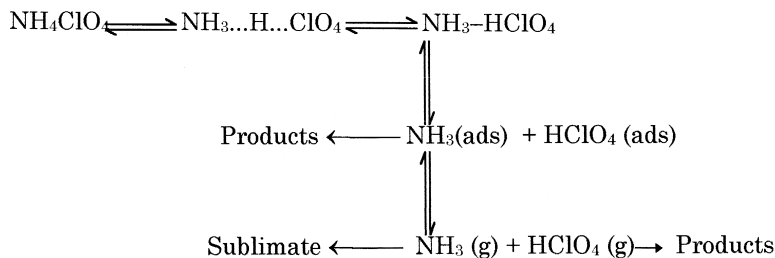
4.1. Ammonium perchlorates (AP)

AP can be regarded as the most important perchlorate salt, due to its key role in the composite solid propellants. Generally, AP is being prepared by double displacement reaction between sodium perchlorate and ammonium chloride and is crystallised from water as an anhydrous salt. The intensive thermal decomposition studies on AP have been undertaken during the past several years resulting in the accumulation of vast literature [38–44]. AP is a white crystalline solid, which undergoes a reversible crystallographic transition from orthorhombic to a cubic at 240°C. This phase transition is endothermic and is accompanied by a significant amount of decomposition with concomitant heat generation.

AP is stable at room temperature but decomposes at measurable rates over a wide temperature range 200–440°C and its behaviour changes with the increase of tempera-ture. It undergoes an autocatalytic decomposition between 200°C and 300°C, which is limited to about 30% decomposition and is usually called low-temperature decomposi-tion (LTD). At 300–430°C, the high-temperature decomposition (HTD) occurs and this reaction is not autocatalytic. Concurrently, with these decomposition reactions, AP also undergoes dissociative sublimation both in the LTD and HTD regions. At about 400°C, AP decomposes very fast and suddenly explodes after a very small induction period.

The comprehensive studies on the thermal decomposition of AP suggested the following three pathways:

1. An electron transfer process from the perchlorate anion to the ammonium cation;
2. A proton transfer reaction, accompanied by the formation of perchloric acid and ammonia; and
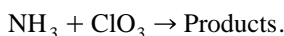3. The thermal breakdown of the perchlorate anion.

Both electron transfer and proton transfer mechanisms have been reported for the LTD of AP. The decomposition products in the electron transfer processes are Cl_2, O_2, N_2O and H_2O with minor amounts of N_2, ClO_2, $HClO_4$ and HCl. The proton transfer has been reported to be the rate determining process in LTD and this is followed by the oxidation of the gaseous ammonia by the decomposition products of perchloric acid.

$$NH_4ClO \rightleftharpoons NH_3...H...ClO_4 \rightleftharpoons NH_3-HClO_4$$

$$Products \longleftarrow NH_3(ads) + HClO_4 (ads)$$

$$Sublimate \longleftarrow NH_3 (g) + HClO_4 (g) \longrightarrow Products$$

At LTD, the decomposition is faster than the sublimation. NH_3 and $HClO_4$ remain adsorbed on the solid AP surface, where they decompose or react with each other. The $HClO_4$ presumably decomposes in a bimolecular process giving the following products:

$$2HClO_4 \rightleftharpoons H_2O + ClO_3 + ClO_4,$$

$$2HClO_4 \rightleftharpoons ClO_3^+ + ClO_4^- + H_2O.$$
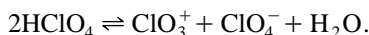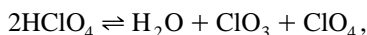
The adsorbed NH_3 is oxidised by the chlorine oxide:

$$NH_3 + ClO_3 \rightarrow Products.$$

The explosive decomposition of AP can be represented as follows:

$$2NH_4ClO_4 \rightarrow N_2 + 3H_2O + 2HCl + 5/2O_2 + 266\,kcal/kg.$$
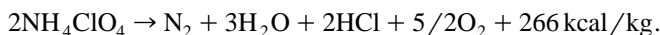
The heat of formation ΔH_f is 79.7 kcal/mol. Recently, Galway and Mohammed [39] have proved the formation of nitronium perchlorate (NO_2ClO_4) as an intermediate during the LTD of AP:

$$NO_2^+ ClO_4^- \rightarrow O_2 NO-ClO_3 \rightarrow O_2 + NO^+ + ClO_3^-.$$

The activation energies for thermolysis of AP are reported in the range 10–44 kcal/mol, by using various kinetic models [38,40]. The stability of AP is found to be extremely sensitive to the presence of various additives [40–48] (catalyst as well as inhibitors). Depending on their structure and chemical properties, these additives effect the rate of LTD, HTD, ignition temperature and rate of deflagration of AP.

Mechanistic aspects of thermolysis of AP have been extensively carried out in our laboratory for the last 20 years. The combustion of solid propellants is a complex phenomenon, which involves several physicochemical process taking place in different phases. The thermolysis and deflagrating rate of AP and solid propellants can be accelerated or suppressed by (i) changing the fuel binder ratio, (ii) the addition of small amount of various additive (modifier) and (iii) changing AP molecular structure.

A comparative study of combustion of polystyrene and oxygen styrene copolymer/AP composite propellants has been taken by Rastogi et al. [49,50] in order to investigate the role of peroxide linkage in the latter and to study the role of surface reactions in combustion. AP decomposition was investigated by DSC and enthalpy changes were estimated [51]. The combustion of composite solid propellants was studied using large number of catalysts and inhibitors as burning rate modifiers [52–60]. Burning rate were considerably enhanced by catalysts, such as basic copper carbonate [44,54], chromium carbonate [44,54], CuO [54,55], Cr_2O_3 [54,56], copper chromite [40,56] and carboxylates of copper [58]. Considerable decrease in decomposition and burning rate were observed when CaO and $CaCO_3$ were used [42,43,59]. Moreover, carbonates of Ca, Ba, Sr, Cd and CaO acted as thermolysis and burning rate inhibitors [59] for AP based propellants.

## 4.2. Nitryl or nitronium perchlorate

Nitronium perchlorate is the simplest inorganic perchlorate, which has the highest OB for using as oxidiser in propellants. Initially, it was prepared by reacting nitric and perchloric acid or by mixing ClO_2 with O_3 and NO_2 or by treating dry N_2O_5 with anhydrous $HClO_4$ at $-80°C$. The thermal decomposition of nitronium perchlorate takes place via nitrosonium perchlorate ($NOClO_4$) formation and following are the decomposition reactions:

$$NO_2ClO_4 \rightarrow NOClO_4 + 1/2O_2,$$

$$2NOClO_4 \rightarrow NO_2ClO_4 + ClO_2 + NO_2,$$

$$NO_2ClO_4 \rightarrow NO_2 + O_2 + ClO_2.$$

The kinetic analysis of TG data showed the involvement of branching-nuclei mechanism and ion pair evaporation. Nitronium perchlorate reacts violently with many organic compounds causing ignition or explosion and hence restricts its use in propellants. When it is dissolved in nitromethane, it can be used as a nitrating agent.

4.3. Nitrosyl or nitronium perchlorate

Nitrosonium perchlorates is a strong endothermic compound and was prepared by passing a mixture of NO and NO_2 into 72% $HClO_4$. The LTD and HTD of nitrosonium perchlorate is as follows:

at $< 100°C$: $2NOClO_4 \rightarrow 2ClO_2 + N_2O_5 + 1/2O_2,$

at $> 100°C$: $2NOClO_4 \rightarrow Cl_2 + N_2O_4 + 3O_2.$
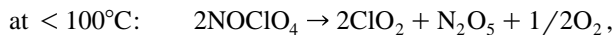
The overall decomposition is given below:

$$4NOClO_4 \rightarrow 4NO_2 + 3ClO_2 + 1/2Cl_2 + 3O_2.$$

$NOClO_4$ undergoes ignition/explosion with ethanol, acetone, dry ether and primary amines.

4.4. Hydrazinium mono and diperchlorates

Hydrazinium monoperchlorate (HP-1) is a crystalline solid, has a monoclinic structure and can be prepared by titrating 85% hydrazine hydrate with 48% $HClO_4$ untill a pH of 3.2 was reached and then precipitated it by pouring into 2-propanol at 0°C .The thermal decomposition of HP-1 involves proton transfer mechanism and the overall decomposition has been suggested as given below:

$$2N_2H_5ClO_4 \rightarrow 0.8NH_4ClO_4 + 0.7O_2 + 1.6N_2 + 0.6Cl_2 + 3.4H_2O,$$
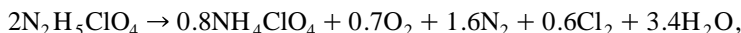
Later Pai Verneker et al. [60] have proposed the following reaction:
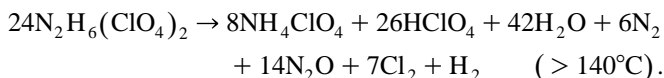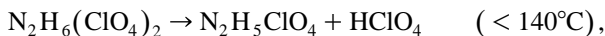
$$5N_2H_5ClO_4 = 4NH_4ClO_4 + HCl + 3N_2 + 4H_2O.$$

HP-1 has been found more sensitive to shock and less sensitive to impact.

Hydrazinium diperchlorate HP-2 was prepared by adding 72% $HClO_4$ to 85% hydrazine at 5°C. The decomposition of HP-2 showed long induction period (77 hours at 120°C) after which the reaction suddenly accelerates and the compound completely decomposes within a few seconds as follows:

$$12N_2H_6(ClO_4)_2 \rightarrow 4NH_4ClO_4 + 12HClO_4 + 22H_2O + 10N_2 + 5O_2 + 4Cl_2.$$

Decomposition of $HClO_4$ was postulated as the rate-determining step. The LTD and HTD of HP-2 can be represented [61] as:

$$N_2H_6(ClO_4)_2 \rightarrow N_2H_5ClO_4 + HClO_4 \qquad (< 140°C),$$

$$24N_2H_6(ClO_4)_2 \rightarrow 8NH_4ClO_4 + 26HClO_4 + 42H_2O + 6N_2$$
$$+ 14N_2O + 7Cl_2 + H_2 \qquad (> 140°C).$$

4.5. Guanidinium and nitroguanidinium perchlorates

Guanidinium perchlorate (GP) has the advantage of being stable, nonhygroscopic, moderately sensitive to shock and is capable of producing violent explosion. Crystallographic modification of GP occurs at 180°C from orthorhombic to cubic. It can be prepared by fusing dicyanamide with AP at 150–160°C. The major products of decomposition are HCl, CO, CO_2, N_2, NH_3, O_2 and H_2O as given below:

$$2CH_5N_3HClO_4 \rightarrow 2HCl + 5H_2O + CO + CO_2 + 3N_2,$$

$$2CH_5N_3HClO_4 \rightarrow 2HCl + 2NH_3 + 2CO_2 + O_2 + 2N_2 + 2H_2O.$$
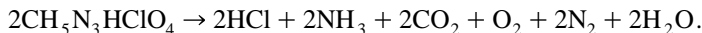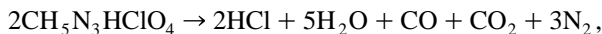
Generally, later reaction predominates and more pronounced with increasing temperature. Udupa [62] has confirmed these reactions by TG, DTA, mass spectrometry and X-ray diffractometry. Nitroguanidinium perchlorate (NGP) was prepared from a mixture of nitroguanidine and $HClO_4$. The thermal decomposition of NGP begins in the solid phase and proceeds as follows:

$$2H_2N\text{-}\underset{\underset{\text{NH-NO}_2}{|}}{C}=NH \cdot HClO_4 \longrightarrow CH_5N_3 \cdot HClO_4 + NH_4ClO_4 + CO_2 + NO_2 + 3/2N_2$$

NGP has been reported to be more unstable as compared to GP.

4.6. Alkyl and aryl ammonium perchlorates

A large number of substituted ammonium perchlorates have been used in solid propellants as oxidisers. These compounds have been reported to sublimate and decompose at lower temperatures and are found to explode readily at higher temperatures. These are generally much more violent in their explosive behaviour as compared to nitrate salts. Some of them even explode on slight shock or friction. These compounds can be prepared by reacting $HClO_4$ with appropriate amine [63,64]. Amine perchlorates have both the combustible (fuel part) and the oxidiser part in the same molecule.

Monomethylammonium perchlorate (MAP), dimethylammonium perchlorate (DMAP) and trimethylammonium perchlorate (TMAP) were prepared by titrating aqueous solution of methyl-substituted amines against 70% $HClO_4$ using methyl red indicator. It has been suggested that MAP, DMAP and TMAP decompose principally to the corresponding methyl-substituted amine and $HClO_4$ by proton transfer.
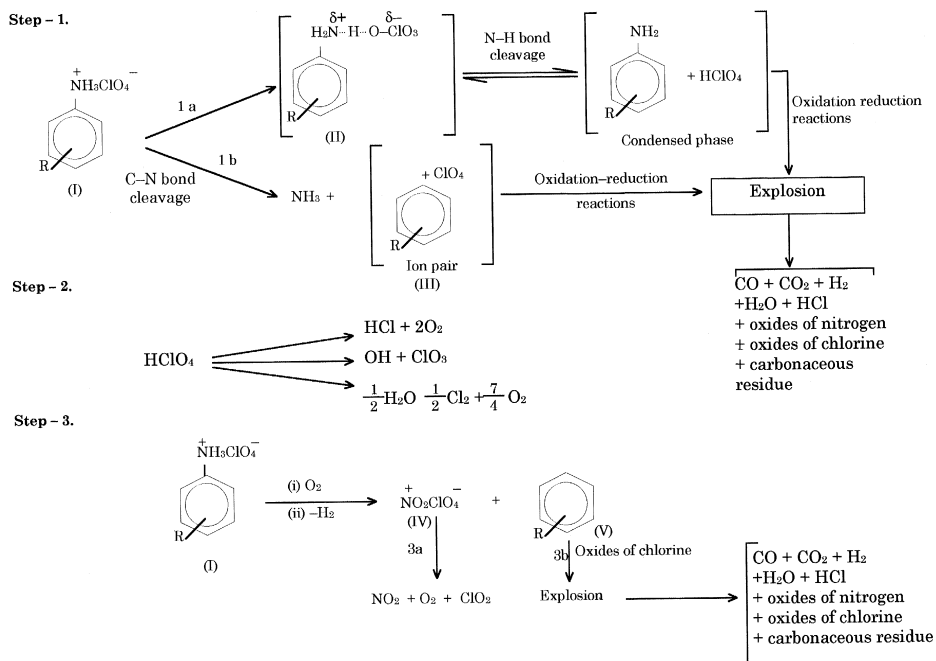
$$(CH_3)_n NH_{4-n} ClO_4 \rightarrow (CH_3)_n NH_{3-n} + HClO_4 \qquad (n = 1-3).$$
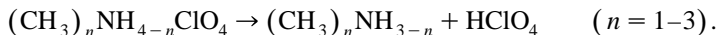
In each case, there is an additional mode of decomposition giving rise to small contributions of HCl, NO_2, H_2O, O_2, N_2 and N_2O. The thermal stability of these salts, increases with the increase in the number of methyl groups. During thermal decomposition of methylammonium perchlorates, in addition to proton transfer mechanism, occurrence of methyl group transfer is also reported [63]. The thermal sensitivity of these salts [64] as compared to AP is in the following order:

$$NH_4ClO_4 < CH_3NH_3ClO_4 < (CH_3)_2NH_2ClO_4 < (CH_3)_3NHClO_4$$
$$< (CH_3)_4NClO_4.$$
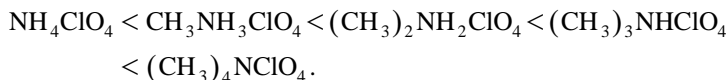
Jain et al. [65] have studied the thermal and explosive characteristics of ring (mono)-substituted anilinium perchlorate (RSAP) by DTA, explosion delay and impact sensitivity measurements. The decomposition temperature and activation energy for explosion have been found to increase with increasing basicity of the corresponding arylamine. The proton transfer from anilinium ion to perchlorate ion was observed during decomposition and explosion of these salts. Very recently, Singh et al. [66–68] have prepared and characterised a large number of RSAP. The thermolysis of these salts was undertaken by thermoanalytical techniques, explosion delay, impact and friction sensitivity measurement. The explosion temperatures, activation energies and impact sensitivity data ($h_{50\%}$) were found to be linearly related to pK_a values of the Hammett substituent constant (σ^+/σ^-). The proton transfer process has been proposed as rate determining steps. It seems that oxidation reaction between arylamines and $HClO_4$ and/or its decomposition products cause explosion. A reaction Scheme 3 has been proposed based on the formation of reaction intermediates during decomposition and explosion.

Dimethylanilinium perchlorates (DMAP) have been prepared, characterised and their thermolysis was investigated using TG, DTA, explosion delay, explosion temperature, impact and friction measurements [68]. DMAP have been reported to involve competitive decomposition reaction. The proton transfer seems to be the rate controlling step during decomposition induced by heat and impact as reported in Scheme 4.

Step – 1.

Step – 2.

$$HClO_4 \Big\langle \begin{array}{l} HCl + 2O_2 \\ OH + ClO_3 \\ \tfrac{1}{2}H_2O \ \tfrac{1}{2}Cl_2 + \tfrac{7}{4}O_2 \end{array}$$

Step – 3.

Scheme 3.

House et al. [69] prepared tetraethylammonium perchlorate (TEAP) by treating aqueous solution of tetraethylammonium bromide with 70% $HClO_4$. TEAP undergoes phase transition [70] at 98°C and explode at 298°C. The fragmentation occurs through three routes namely, perchlorate anion and its disintegration products, tetraethyl-

ORR – Oxidation reduction reaction

Scheme 4.

ammonium cation and its products following the Hofmann dealkylation mechanism and the oxidation of the organic group by the perchlorate.

Ethylenediammonium perchlorate (EDP) was prepared [71] by neutralising 1:1 aqueous ethylenediamine by 20% aqueous $HClO_4$. Its decomposition involves four stages and proton transfer takes place in the temperature range 275–310°C and 320–365°C and the whole material is oxidised to gaseous products. Triethylenediammonium diperchlorate (TED) can also be prepared [72] by neutralising aqueous solution of triethylenediamine with 40% $HClO_4$. TED undergoes decomposition by proton transfer process. Udupa [72] identified the formation of N-methyl-N′-ethylpiperzine and N,N′-diethylpiperzine in addition to usual decomposition products. Diphenylammonium perchlorate (DPP) also undergoes thermal decomposition by proton transfer mechanism[73].

Propyl-1,3-diammonium perchlorate (PDP) [30] 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 about 280°C, forming HCl, CO, CO_2 and H_2O as thermodynamically stable products. Pentaerthrityltetrammonium perchlorate (PTTP) [33] undergoes decomposition in a complicated fashion. The decomposition products HCl, CO_2, ClO_2 and H_2O were detected but the expected nitrogen containing products were not traceable, which suggests that the N_2 may be a product and/or it is retained as part of the condensed phase residue.

5. Conclusion

The thermal decomposition of energetic compounds is a very complex process even in a simple case expressed by the stoichiometric equation:

$$A(s) \rightarrow B(s) + C(g).$$

This process takes place in several stages, e.g., the chemical act of breaking of bonds; destruction of initial crystal lattice; formation of crystal lattice of the solid product (B), consisting of the formation of crystallisation centres and the growth of these centres; adsorption/desorption of gaseous products C; diffusion of C and heat transfer. The

Scheme 5.

thermolysis of ammonium salts of $HClO_4$ and HNO_3 has been reviewed here. The proton transfer process seems to be the primary and rate controlling step for these salts. Thus, a unified decomposition mechanism can be suggested (Scheme 5).

These salts have been found to dissociate to adsorbed amines and acids ($HClO_4$ or HNO_3) on the surface of these salts. Since the low-temperature decomposition (LTD) of these salts would be faster than their sublimation; and, hence, the adsorbed species, such as RNH_2(a) and HX(a), must be involved in the decomposition reaction. It seems that low temperature reaction is initiated on the surface, although it may be completed in gas phase. Since the reaction is catalysed by HX and retarded by RNH_2, it has been proposed that decomposition proceeds via bimolecular reaction of the adsorbed $HClO_4$ or HNO_3 molecules followed by the rapid decomposition to unstable species, which oxidise amines (RNH_2) and the reaction commences in the adsorbed phase. Sublimation also seems to play a major role during the decomposition of these salts.

Acknowledgements

References

[1] F. Solymosi, Structure and Stability of Salts of Halogen Oxyacids in the Solid Phase, Wiley, London, 1977.
[2] L. Marinkas, Organic Energetic Compounds, Nova Science Publishers, New York, 1996.
[3] M.J. Kamlet, The relationship of impact sensitivity with structure of organic high explosive, 1, Polynitroaliphatic explosives, Proc. 6th Int. Symp. Detonation, San Diego, California (1976) 312–322.
[4] M.J. Kamlet, H.G. Adolph, Propellants Explos. 4 (1979) 30.
[5] J. Mullay, Propellants, Explos., Pyrotech. 12 (1987) 60.
[6] D.E. Bliss, S.L. Christian, W.S. Wilson, J. Energ. Mater. 9 (1991) 319.
[7] S.R. Jain, Propellants, Explos., Pyrotech. 12 (1993) 188.
[8] E. Kestila, M.E.E. Harju, J. Valkonen, Thermochim. Acta 214 (1993) 67.
[9] E. Kestila, J. Valkonen, Thermochim. Acta 214 (1993) 305.
[10] T.K. Highsmith, C.J. Hinshaw, R.B. Wardle, US Pat., 5,292,387, 1994.
[11] S.K. Adhya, S.K. Mukerjee, B.K. Banerjee, J. Indian Chem. Soc. 62 (1980) 321.
[12] T.B. Brill, T.P. Russell, Combust. Flame 76 (1989) 393.
[13] K.R. Brower, J.C. Oxley, M. Tewari, J. Phys. Chem. 93 (1989) 4029.
[14] D.G. Patil, S.R. Jain, T.B. Brill, Propellants, Explos., Pyrotech. 17 (1992) 99.
[15] T.B. Brill, P.J. Brush, D.G. Patil, Combust. Flame 92 (1993) 178.
[16] J.C. Oxley, J. Phys. Chem. 98 (1994) 3893.
[17] W. Engel, K. Menhe, Def. Sci. J. 46 (1996) 311.
[18] Y. Oyumi, T.B. Brill, J. Phys. Chem. 89 (1985) 4325.
[19] A.J. Bracuti, Acta Crystallogr. B 35 (1979) 760.
[20] C.S. Choi, E. Prince, Acta Crystallogr. B 35 (1979) 761.
[21] T. Urbanki, Chemistry and Technology of Explosives Vol. II Pergamon, New York, 1965.
[22] S.R. Jain, M.V. Rao, V.R. Pai Verneker, Propellants Explos. 3 (1978) 83.
[23] S.R. Jain, M.V. Rao, V.R. Pai Verneker, Kinetics and mechanism of thermal decomposition of tetraethylammonium nitrate, Proc. - Indian Acad. Sci. 87A (1978) 31.

[24] S.R. Jain, M.V. Rao, V.R. Pai Verneker, J. Chem. Soc., Perkin. Trans 2 (1979) 406.
[25] G. Singh, I.P.S. Kapoor, Combust. Flame 92 (1993) 283.
[26] G. Singh, I.P.S. Kapoor, S.M. Mannan, Combust. Flame 97 (1994) 355.
[27] G. Singh, I.P.S. Kapoor, S.M. Mannan, Thermochim. Acta 262 (1995) 117.
[28] R.L. Mckenny Jr., S.R. Struck, R.A. Hildreth, J.A. Fryling, J. Energ. Mater. 5 (1987) 1.
[29] T.P. Rusell, T.B. Brill, Propellants, Explos., Pyrotech. 15 (1990) 77.
[30] R. Chen, T.P. Russell, A.L. Rheingold, T.B. Brill, J. Crystallogr. Spectrosc. Res. 21 (1991) 167.
[31] J.M.E. Qurike, J. Fu, K.A. Hardy, J.W. Sheldon, F.G. Doolite, R.L. Mckenny Jr., Propellants, Explos., Pyrotech. 14 (1989) 76.
[32] R.L. Mckenny Jr., S.R. Struck, D.S. Ellison, S.D. Maegerlein, R. Climino, J. Energ. Mater. 8 (1990) 205.
[33] Y. Oyumi, T.B. Brill, A.L. Rheingold, C. Lowe-Ma, J. Phys. Chem. 89 (1985) 2309.
[34] T.P. Russell, T.B. Brill, A.L Reingold, B.S. Haggerty, Propellants, Explos., Pyrotech. 15 (1990) 81.
[35] T.P. Russell, T.B. Brill, Propellants, Explos., Pyrotech. 16 (1991) 27.
[36] R. Yamadengni, P. Kebarle, J. Am. Chem. Soc. 95 (1973) 3504.
[37] T.P. Russell, T.B. Brill, Propellants, Explos., Pyrotech. 15 (1990) 123.
[38] A.G. Kennan, R.F. Siegmund, J. Solid State Chem. 4 (1972) 362.
[39] A.K. Galway, M.A. Mohammed, J. Chem. Soc. Commun. (1984) 1197.
[40] B.L. Dubey, G. Singh, C.S. Shukla, Fuel 61 (1982) 129.
[41] G. Singh, J. Sci. Ind. Res. 37 (1978) 79.
[42] R.P. Rastogi, G. Singh, R.R. Singh, J. Appl. Chem. Biotechnol. 28 (1978) 889.
[43] G. Singh, I.P.S. Kapoor, J. Energ. Mater. 11 (1993) 293.
[44] G. Singh, R.R. Singh, Indian J. Chem. 16A (1978) 406.
[45] R. Sundararajan, S.R. Jain, J. Therm. Anal. 27 (1983) 43.
[46] V.G. Dedgaonker, D.B. Sarvade, J. Therm. Anal. 35 (1989) 2305.
[47] V.G. Dedgaonker, D.B. Sarvade, J. Therm. Anal. 36 (1990) 223.
[48] F. Shadman-Yazidi, E.E. Peterson, Combust. Sci. Technol. 5 (1972) 61.
[49] R.P. Rastogi, K. Kishore, G. Singh, AIAA. J. 12 (1974) 9.
[50] R.P. Rastogi, G. Singh, J. Sci. Ind. Res. 34 (1975) 547.
[51] R.P. Rastogi, K. Kishore, G. Singh, Thermochim. Acta 12 (1975) 89.
[52] R.P. Rastogi, B.L. Gupta, G. Singh, Combust. Sci. Technol. 11 (1975) 85.
[53] T.L. Boggs, D.E. Zurn, H.F. Cordes, J. Covino, J. Propul. 4 (1988) 27.
[54] R.P. Rastogi, G. Singh, R.R. Singh, Combust. Flame 30 (1977) 1177.
[55] R.P. Rastogi, G. Singh, R.R. Singh, Combust. Flame 33 (1978) 305.
[56] G. Singh, S.K. Vasudeva, I.P.S. Kapoor, Indian J. Technol. 29 (1991) 589.
[57] R.P. Rastogi, G. Singh, B.L. Dubey, C.S. Shukla, J. Catal. 65 (1980) 25.
[58] G. Singh, R.R. Singh, A.P. Rai, I.P.S. Kapoor, J. Therm. Anal. 36 (1990) 2539.
[59] R.P. Rastogi, G. Singh, R.R. Singh, Indian J. Chem. 15A (1977) 845.
[60] V.R. Pai Verneker, A.N. Sharma, S.R. Jain, J. Therm. Anal. 11 (1977) 277.
[61] V.R. Pai Verneker, A.N. Sharma, S.R. Jain, Propellants Explos. 1 (1976) 107.
[62] M.R. Udupa, Propellants, Explos., Pyrotech. 8 (1983) 109.
[63] R.R. Nambiar, V.R. Pai Verneker, S.R. Jain, J. Therm. Anal. 7 (1975) 587.
[64] R.R. Nambiar, V.R. Pai Verneker, S.R. Jain, J. Therm. Anal. 8 (1975) 15.
[65] S.R. Jain, M.V. Rao, V.R. Pai Verneker, Combust. Flame 35 (1979) 289.
[66] G. Singh, I.P.S. Kapoor, J. Phys. Chem. 96 (1992) 1215.
[67] G. Singh, I.P.S. Kapoor, S.M. Mannan, J. Therm. Anal. 46 (1996) 1751.
[68] G. Singh, I.P.S. Kapoor, S.M. Mannan, J. Energ. Mater. 13 (1995) 141.
[69] H.O. House, E. Feng, N.P. Peet, J. Org. Chem. 36 (1971) 2371.
[70] M.R. Udupa, Propellants, Explos., Pyrotech. 7 (1982) 155.
[71] M.R. Udupa, Thermochim. Acta 42 (1980) 383.
[72] M.R. Udupa, Thermochim. Acta 71 (1983) 219.
[73] M.R. Udupa, Thermochim. Acta 58 (1982) 379.