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STUDIES ON ENERGETIC COMPOUNDS
IV. Thermal explosion of ring-substituted arylammonium perchlorates

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Abstract

Thermal and explosion characteristics of ring(mono) substituted arylammonium perchlorates (RSAP) are studied by DTA, impact and friction sensitivity measurements. Exothermic decomposition temperature (T_d) from DTA curves and impact sensitivity data ($h_{50\%}$) were found to be linearly related to the Hammett substituent constant (σ^+,σ^-) and pK_a values of the corresponding arylamines. A reaction scheme, based on the formation of reaction intermediates during decomposition and explosion, accounting for the products, is proposed which, involves proton transfer as the rate determining process and evolution of ammonia. It seems that oxidation-reduction reactions between the arylamine/substituted benzene and $HClO_4$ or its decomposition products cause explosion.

Keywords: arylammonium perchlorates, energetic compounds, thermal explosion

Introduction

The characteristics of thermal decomposition and explosion of energetic materials, particularly in relation to their molecular structure and composition, are of current interest [1–7]. The thermal decomposition of ammonium perchlorate (AP), ammonium nitrate (AN), alkyl ammonium derivatives of AP and AN have been investigated because of their deflagration and detonation characteristics [8, 9]. These salts find applications in pyrotechnics, explosive composition and propellant formulations [10–12].

Although, the perchlorates and nitrates of a number of aromatic amines are known [13–15], the detailed mechanism of thermal decomposition reactions leading to explosion are not yet reported. In our earlier paper [1], we have reported the preparation, characterisation and thermolysis of a number of ring(mono) substituted (having electron-withdrawing or donating substituents)

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arylammonium perchlorates. It has been found that the perchlorates having electron-withdrawing substituents are more sensitive to explosion than the perchlorates having electron-donating substituents.

In the present communication, detailed DTA, impact and friction sensitivity studies on ring(mono) substituted arylammonium perchlorates (RSAP) have been undertaken and the role of electron-withdrawing and electron-donating substituents on the thermal stability of these salts have been discussed. Exothermic decomposition temperatures (T_d) and impact sensitivity data ($h_{50\%}$) are found to be linearly related to Hammett substituent constant (σ^+,σ^-) and the pK_a of the corresponding arylamine. Mechanistic pathways leading to explosion have also been suggested.

Experimental

Materials

The following chemicals (obtained by the sources given in parentheses) were used after purification by usual methods: aniline (Ranbaxy); *p*-phenitidine, *m*-toluidine, *m*- and *p*-chloroaniline (Wilson, Bombay); *m*-and *p*-anisidine (Merck); *p*-toluidine (BDH); *p*-aminobenzoic acid (Thomas Baker); *p*-nitroaniline (CDH, Lucknow); *m*-nitroaniline (Robert Johnson); *m*-aminobenzoic acid (Sisco Research Lab.). Perchloric acid (AR, Qualigens), and Nitron (Loba) were used as received.

Preparation and characterisation of RSAP

All RSAP salts (caution! These are explosives of varying sensitivity and should be handled with appropriate precautions) were prepared by the same method as adopted earlier [1]. In addition to the perchlorates prepared earlier, *m*- and *p*-anisidinium and *m*-carboxylanilinium perchlorates have also been prepared. These perchlorates crystallized out when the volume of the reaction mixture was concentrated under reduced pressure at 60°C in a rotary vacuum evaporator (JSGW, Ambala), and then cooled. *m*-anisidinium perchlorate was recrystallized from 50% AcOH, whereas *p*-anisidinium and *m*-carboxylanilinium perchlorates were recrystallised from aqueous solution and then vacuum dried. The purity of all perchlorates were checked by thin-layer chromatography (TLC) and their composition were confirmed by gravimetric method using nitron reagent [16] as reported in our earlier publication [1].

DTA studies on RSAP

The DTA curves were recorded in static air using a micro DTA at High Energy Materiale Research Laboratory (HEMRL), Pune, at a heating rate of

10°C min^{-1} using a two-pen strip chart recorder. Sample (mass=5 mg, 100–200 mesh) was placed in sample crucible (Pt) and Al_2O_3 was taken as reference material. Pt–Pt (Rh 13%) thermocouple was used for recording ΔT. The DTA curves for all RSAP salts are presented in Fig. 1 and recorded decomposition temperatures (T_d) are reported in Table 1.

Impact sensitivity measurements on RSAP

Impact sensitivity measurements on RSAP were carried out by an impact machine for high explosives fabricated at HEMRL, Pune, similar to the Picatinny Arsenal impact sensitivity apparatus [17]. It consists of 1 inch long striker and a 1 inch long anvil machined to 1.5 cm diameter and hardened to the base. A conical heap, comprising about 10 mg of the sample (100–200 mesh) is centered on the anvil over a piece of aluminium foil (thickness 0.005–0.01 mm) and the sample was also covered with foil to avoid spilling. The striker is then hit by a 2 kg weight dropped from heights, which are varied according to the Bruceton 'staire case' method [18, 19] i.e., the height being decreased if the previous event was an explosion, or increased if it was otherwise. This design permits the calculation of height from which drops will cause 50% explosions. The results of the event, explosion or otherwise was determined by a combination of sound, smell and visual observations. The $h_{50\%}$ data, reported in Table 1 was determined from 20 shot sequences.

Friction sensitivity measurements on RSAP

Friction sensitivity measurements on RSAP were carried out by friction sensitive apparatus for high explosives (Julius Peters, Berlin-21) at HEMRL. Pune, to find out the friction insensitive limit in kg which, was confirmed by five runs. The sample (mass=5 mg, 100–200 mesh) was placed over the ceramic friction plate (hardness 7–9 mho's scale, Roughness profile=12.3 mμ). The pre-determined weight was applied over the sample through the friction pin and the sample was subjected to friction. The result of the event was noted by visual observation and sound. The friction insensitivity data are given in Table 1.

Results and discussion

The DTA curves reported in Fig. 1 show only exotherms prior to an audible explosion for all the RSAP salts, which proves the involvement of exothermal decomposition reactions. Substituents like *m*-COOH, *p*-OC_2H_5, *m*-NO_2, *p*-NO_2, *p*-OCH_3, *m*-Cl and *p*-CH_3 generated sharp exothermic peaks, whereas medium intensity exotherms were obtained for *p*-COOH, *p*-Cl and anilinium perchlorate. Very small exotherms were observed for *m*-OCH_3 and *m*-CH_3 substituted salts. The exothermic decomposition temperature (T_d°C) for all the sub-

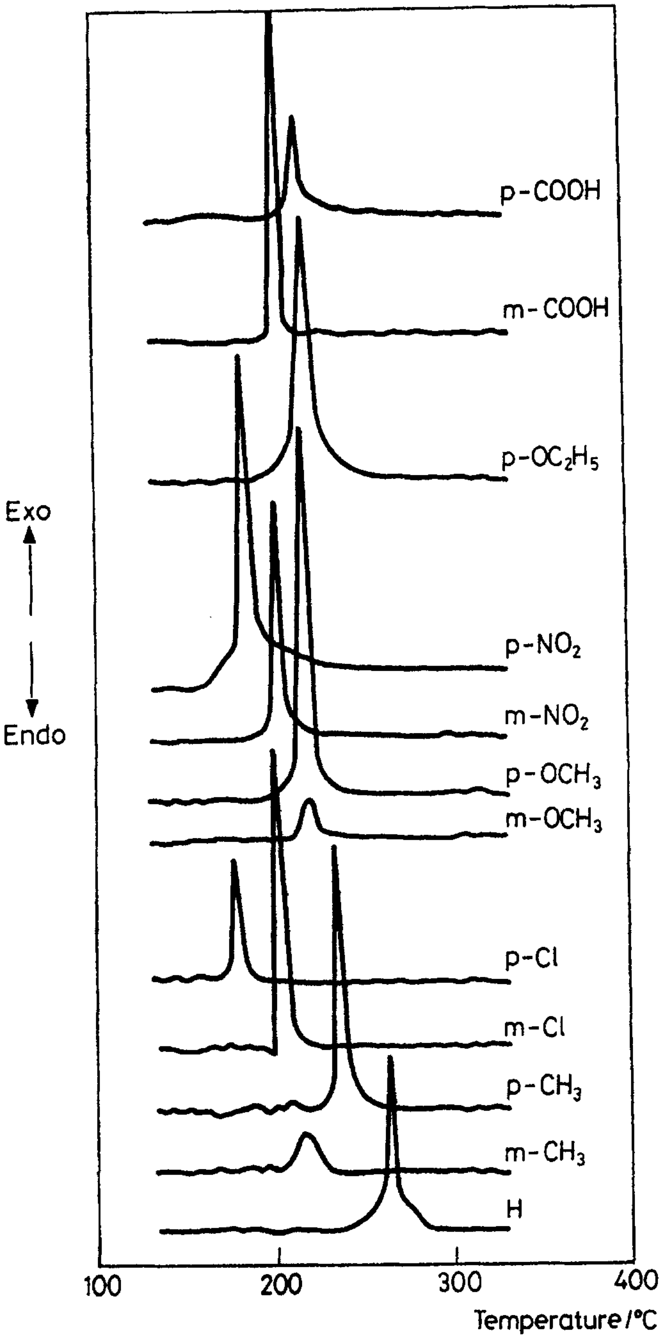
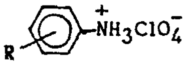


Fig. 1 DTA traces of ring(mono) substituted arylammonium perchlorates

Table 1 Molecular formula, molecular weight, pK_a of corresponding arylamine, Hammett substituent constant (σ^+, σ^-), DTA peak temperature (T_d°C), impact ($h_{50\%}$) and friction sensitivity of ring(mono) substituted arylammonium perchlorates

Compound 	Molecular weight	pK_a	σ^+, σ^-	T_d/°C	$h_{50\%}$	Friction insensitive limit/kg
R						
H	193.6	4.60	0	265	61	12.0
m–CH$_3$	207.6	4.71	–0.07	214	84	9.6
p–CH$_3$	207.6	5.08	–0.31	234	64	12.0
m–Cl	228.0	3.52	0.37	202	59	8.0
p–Cl	228.0	3.99	0.12	176	62	6.4
m–NO$_2$	238.6	2.45	0.71	204	46	12.0
p–NO$_2$	238.6	1.01	1.27	185	30	9.6
m–COOH	237.6	3.07	0.36	209	142	19.2
p–COOH	237.6	2.41	0.73	207	55	16.0
m–OCH$_3$	223.6	4.20	0.12	218	88	19.2
p–OCH$_3$	223.6	5.18	–0.78	221	160	25.2
p–OC$_2$H$_5$	237.6	5.25	–	221	78	16.0

stituted salts was found to be lowered as compared to anilinium perchlorate (Table 1). However, *p*-Cl causes lowering of T_d to a large extent. A black residue (carbonaceous) was also observed in the sample cup for each RSAP sample at the expiry of DTA runs. The lowering of T_d was much higher for perchlorates having electron-withdrawing substituents as compared to those having electron-donating substituents.

An understanding of structure/sensitivity relationship is essential for the systematic scientific formulation of appropriate targets or synthesis of potential new energetic materials. The performance of a potential new energetic material can be determined by drop-weight impact and friction sensitivity tests [20–22]. Impact sensitivities [23] of organic high explosives are primarily functions of the rates of the thermal decomposition process taking place in the temperature regions generated under the impact hammer. Bowden and Yofee [24] and Copp *et al.* [25] suggested that the initiation of explosion by impact is due to the formation of hot spots in the explosive mass. Kamlet and Adolph [20, 21] have reported that if a compound contains structural features of more than one sensitivity, then its impact behaviour should be confirmed more closely with the more sensitive feature. Moreover, it is well known that both impact and friction sensitivities depend on nonchemical parameters, primarily they depend on the chemical structure of the explosive molecule [22] and hence impact and friction sensitivities of RSAP salts were measured.

It is very clear from the Table 1 that the perchlorates having substituents like *m*-Cl, *m*-NO_2, *p*-NO_2 and *p*-COOH showed lower values of $h_{50\%}$ as compared to anilinium perchlorate. Amongst these, *m*- and *p*-NO_2 groups impart greater sensitivity to impact and this may be attributed to the intramolecular oxygen supply by the nitro group [26]. The same effect of -NO_2 group has also been observed in our earlier publication [3] on ring(mono) substituted arylammonium nitrates (RSAN). The *p*-methoxyanilinium perchlorate showed a very high value of $h_{50\%}$. Friction sensitivity data showed that *m*-CH_3, *m*-Cl, *p*-Cl and *p*-NO_2 substituted perchlorate salts are more sensitive to friction as compared to unsubstituted one, and are twice more sensitive than *p*-$OCH_3C_6H_4NH_3ClO_4$. It has been observed that all RSAP are more sensitive to impact and friction than corresponding RSAN [3].

In order to investigate the influence of the substituents on the explosive sensitivity of RSAP, $\log h_{50\%}$ and T_d have been plotted against the Hammett substituent constant (σ^+,σ^-) [27–29] (Table 1) and a linear plot (Fig. 2) was obtained which, clearly indicates that the electronic effects exerted by electron-withdrawing substituents, cause decrease in the T_d and $h_{50\%}$ values. A linear plot was also observed (Fig. 3), when $\log h_{50\%}$ and T_d were plotted against pK_a of the corresponding arylamines [30]. Although, the inductive and resonance effects as- sociated with the perchlorate salts produce a net synergistic effect, it appears that the acidity of arylammonium ion causes a dominant effect

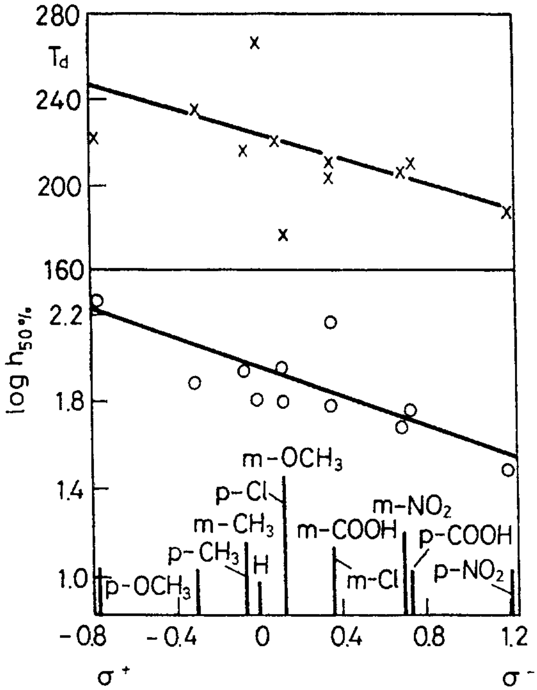
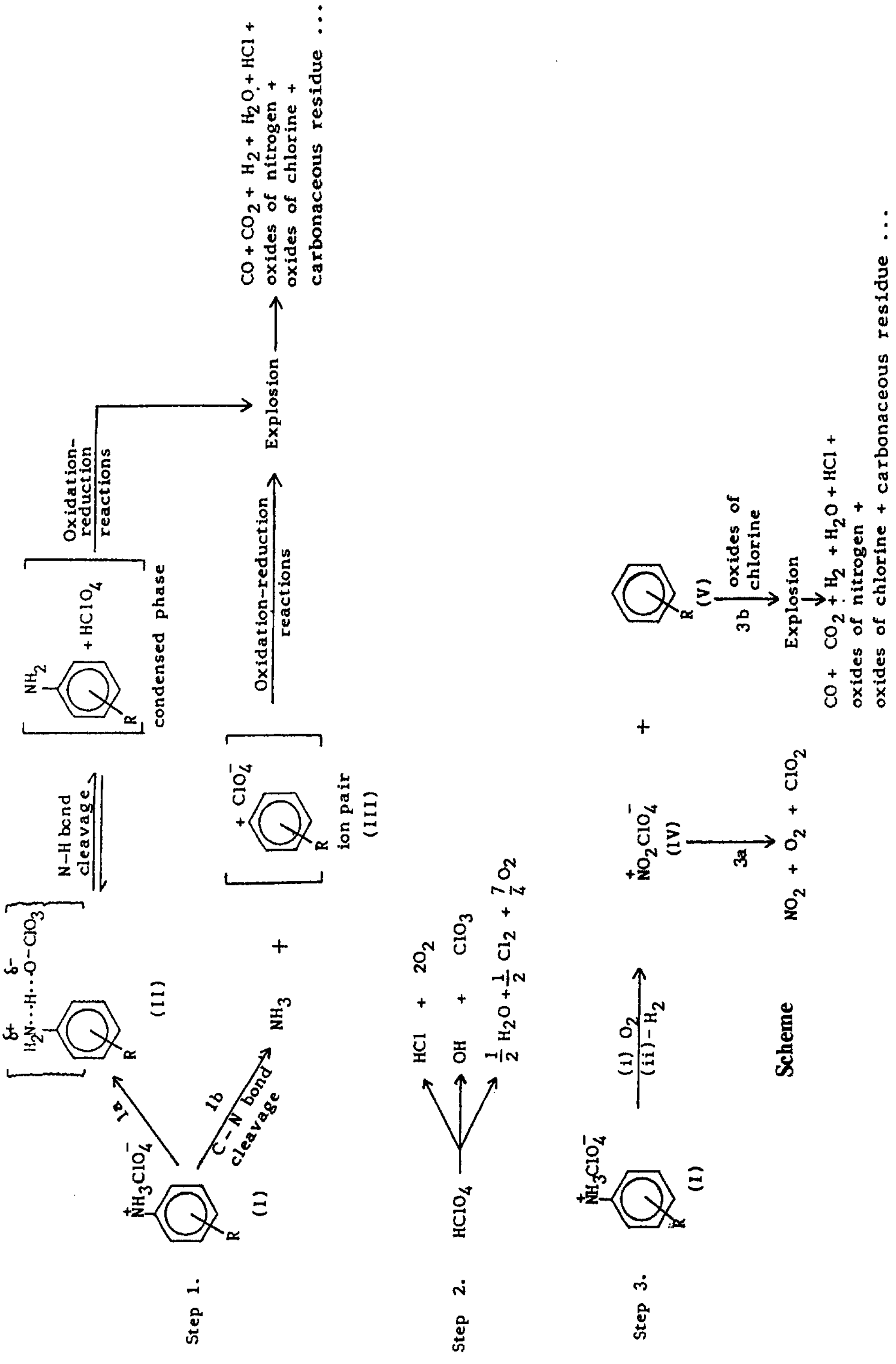


Fig. 2 Plots of impact sensitivity ($h_{50\%}$) and decomposition temperature (T_d) *vs.* Hammett substituent constant (σ^+,σ^-) for ring(mono) substituted arylammonium perchlorates

on proton transfer. Thus a general trend was observed that explosive sensitivity of perchlorate salts is enhanced by electron-withdrawing substituents whereas, the opposite trend was observed for electron-donating substituents.

Chemical analysis of the intermediate products during decomposition was also carried out in order to know the mechanism of thermal decomposition of RSAP salts. The mechanistic pathways given in Scheme have been suggested based on the formation of compounds in situ and the gaseous products evolved. It seems that the overall decomposition process takes place by the transfer of proton (N–H bond cleavage) from arylammonium ion in (I) to perchlorate ion (step 1a), to form the corresponding amine and the perchloric acid molecule in condensed phase prior to explosion. However, the proton transfer from anilinium ion to ClO_4^- seems to occur through an activated complex (II). The nitrogen atom in (II) must bear a substantial partial positive charge at the transition state and moreover the activated complex (II) is destabilized by electron-donating substituents. It is reported [31, 32] that the basicity of anion (ClO_4^-) increases with rise in temperature until it reaches the base strength of arylamine. At this temperature, the anion base (ClO_4^-) removes the proton from the arylammonium ion to form corresponding arylamine and $HClO_4$ molecules in condensed phase. The proton transfer process is quickly joined by the other


Step 1.
$\overset{+}{N}H_3ClO_4^-$
R
(I)
1a
1b
C–N bond cleavage
$\delta+$ $H_2N\cdots H\cdots O{-}ClO_3$ $\delta-$
(II)
N–H bond cleavage
NH_2
$+HClO_4$
R
condensed phase
Oxidation-reduction reactions
Explosion
$CO + CO_2 + H_2 + H_2O + HCl +$
oxides of nitrogen +
oxides of chlorine +
carbonaceous residue ...
NH_3
+
$+ ClO_4^-$
R
ion pair
(III)
Oxidation-reduction reactions
Step 2.
$HClO_4$
$HCl + 2O_2$
$OH + ClO_3$
$\frac{1}{2}H_2O + \frac{1}{2}Cl_2 + \frac{7}{4}O_2$
Step 3.
$\overset{+}{N}H_3ClO_4^-$
R
(I)
(i) O_2
(ii) $-H_2$
$\overset{+}{N}O_2ClO_4^-$
(IV)
+
R
(V)
3a
$NO_2 + O_2 + ClO_2$
3b
oxides of chlorine
Explosion
$CO + CO_2 + H_2 + H_2O + HCl +$
oxides of nitrogen +
oxides of chlorine + carbonaceous residue ...

Scheme

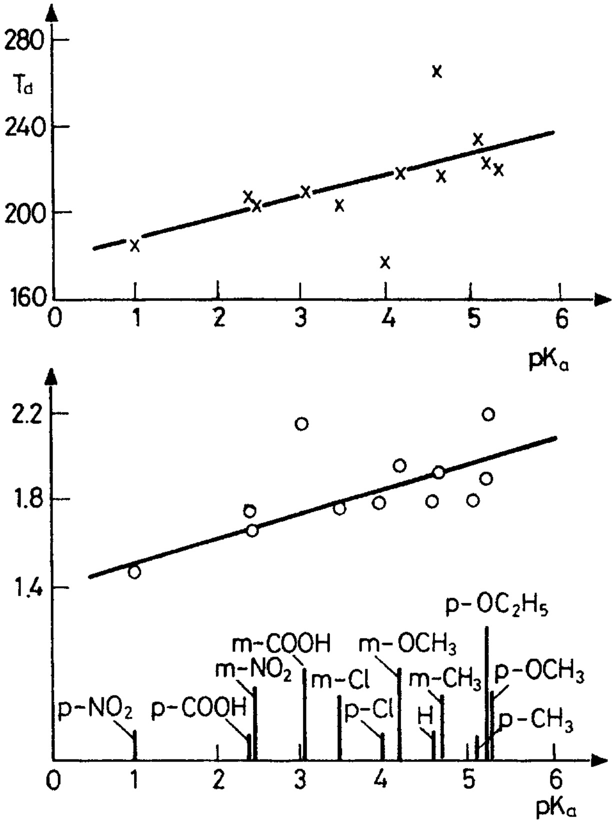


Fig. 3 Plots of impact sensitivity ($h_{50\%}$) and decomposition temperature (T_d) *vs.* pK_a for ring(mono) substituted arylammonium perchlorates

definable degradation reactions. The $HClO_4$ or the dissociation products of $HClO_4$ may also rapidly react with the aryl backbone to cause explosion on account of which secondary oxidation and reduction products of carbon, nitrogen and chlorine are generated, along with the carbonaceous residue.

RSAP may also be decomposed by C–N bond cleavage (step 1b), forming an ion pair (III) and NH_3 (confirmed by chemical analysis). Ammonia is the expected product of decomposition of RSAP since, O/H ratio for all perchlorate salts is less than 1. It is reported [3, 33, 34] that salts with $O/H<1$ have been found to release NH_3 (g) while those with $O/H\geq1$ do not. Nambiar *et al.* [35] have also reported the evolution of NH_3 as a dissociation product of methylammonium perchlorates. The carbonium ion has been found to be formed in the reaction of phenyl-*p*-biphenyl-α-napthylmethylthioglycolic acid with $HClO_4$ [36]. It has been observed that the perchlorates having electron-withdrawing substituents give off ammonia at a slower rate than the perchlorates having electron-donating substituents. This may be due to the fact that the electron-withdrawing substituents, by induction or resonance, cause weakening of the C–N bond. Moreover, the electron-withdrawing substituents increase the intensity of the positive charge on carbonium ion in (III) and this favour the increase in reaction rates.

Step 2 involves the decomposition pathways of $HClO_4$ in the temperature range 150–350°C as reported by many workers. Heath and Majer [37] confirmed the formation of HCl and O_2 during heterogeneous decomposition of $HClO_4$ in the vapour phase. Levy [38] reported the cleavage of $HO-ClO_3$ bond to form OH and ClO_3 radicals. However, decomposition reaction suggested by Sibbett and Lobato [39] involves the formation of water, chlorine and oxygen molecules.

RSAP (I) may react (step 3) with the oxygen (decomposition products of $HClO_4$) and eliminate hydrogen to form nitronium perchlorate (IV) and substituted benzene derivative (V) (confirmed by chemical analysis). The dissociation of nitronium perchlorate seems to take place via step 3a as reported by Galway and Mohamed [40]. The evolution of NO_2 (confirmed by chemical analysis) seems to occur by the decomposition of nitronium perchlorate as reported by Goddard *et al.* [41]. Further ring rupture of substituted benzene (V) by oxides of chlorine/NO_2 may lead to explosion, to form gaseous products (3b). The formation of ClO_2, N_2 and O_2 has also been proved by Oyumi *et al.* [42] during thermolysis of $[C(CH_2NH_3)_4](ClO_4)_4$. Due to the highly energetic nature of RSAP, a very small amount (in mg) of the samples were taken for qualitative analyses and hence quantitative investigation of the intermediates was quite difficult. Moreover, all the reaction intermediates at higher temperature are transitory prior to explosion.

Conclusion

The thermal explosion of RSAP seems to involve many decomposition routes and proton transfer from anilinium ion to ClO_4^- ion is the primary rate controlling step. Exothermic decomposition temperature (T_d) and impact sensitivity ($h_{50\%}$) of these salts gave a linear relationship with the Hammett substituent constant (σ^+,σ^-) and pK_a of the corresponding arylamine.

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