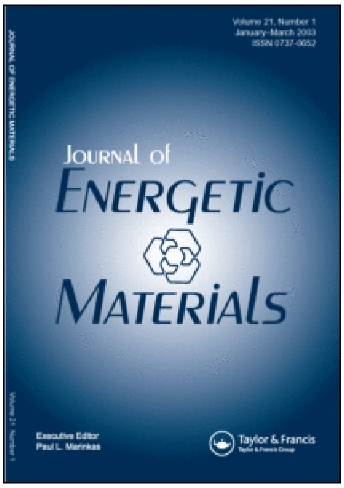

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Studies on energetic compounds part 5 dimethylanilinium perchlorates

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STUDIES ON ENERGETIC COMPOUNDS

PART 5 # DIMETHYLANILINIUM PERCHLORATES

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ABSTRACT

Dimethyl anilinium perchlorates (DMAP) have been prepared and characterised. Thermolysis of these salts induced by heat and drop-weight impact has been investigated by TG, DTA, explosion delay, explosion temperature, impact and friction sensitivity measurements. The explosion temperatures (ET & ET^*), explosion delay (D_E) and activation energy for explosion (E^*) have been found to be quite lower for 3,4-substituted perchlorate as compared to 2,5- and 2,4-substituted salts. However, 3,4-DMAP has been found to be less sensitive towards impact and friction. The role of substituents (methyl) have been discussed based on experimental results. The mechanism of early thermolysis reactions prior to explosion have also been suggested.

#Preceding papers: Refs.1 & 2

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INTRODUCTION

The preperation, characterisation and thermolysis of mono substituted anilinium perchlorates have been reported in our earlier papers.[1,2] Very recently, we have also undertaken studies on the mechanistic aspects of thermolysis of dimethylanilinium nitrates.[3] As a part of our ongoing programme to undertake investigations on energetic meterials,[1-10] we have prepared and characterised dimethylanilinium perchlorates (DMAP). The early reaction chemistry of DMAP induced by heat, drop-weight impact and friction has been investigated by TG, DTA, explosion delay (D_E), explosion temperatures (ET, ET^*), impact and friction sensitivity measurements. The decomposition pathways have also been suggested based on the experimental results.

EXPERIMENTAL

Materials

3,4-; 2,5- and 2,4-dimethylanilines (Merck); Perchloric acid (60% Qualigens); Nitron (Loba) and Benzene (Qualigens) were used as received.

Preperation and Characterisation of DMAP

The perchlorates of dimethylanilines were prepared by reacting 20% perchloric acid with corresponding dimethylaniline, in 1:1 molar ratio. The perchlorate of 2,5-dimethylaniline was obtained by cooling whereas, 2,4- and 3,4-DMAP crystallized out when the volume of the reaction mixture was concentrated under reduced pressure and then cooled. All these perchlorates were recrystallized from aqueous solution and their purity was checked by thin layer chromatography (TLC). The percentage of ClO_4^- was confirmed by a gravimetric method using nitron reagent,[11] as reported in our earlier publication.[1] The density of these salts were measured by pycnometric method,[12] by using benzene as the displacable liquid. The analytical and density data are given in Table 1.

Explosion Temperature Measurements on DMAP

The explosion temperature (ET) measurements were carried out in a deflagration temperature apparatus (Model 1960) at Explosives Research & Development Laboratory (ERDL), Pune at a heating rate of 5°C/min. The sample (wt = 50 mg, 100-200 mesh) was taken in a borosil test tube and inserted in the Wood's metal at 100°C. The temperatures corresponding to the physical changes in the sample and ET were noted from an electrically controlled thermometer. The observations are summerised in Table 1.

TG Studies on DMAP

Non-isothermal TG studies have been undertaken in static air (sample wt = 30 mg, 100-200 mesh) at a heating rate of 2°C/min, by using an indigenously fabricated TG apparatus in our laboratory[13] and the data are given in Table 2.

DTA studies on DMAP

DTA thermograms (Fig. 1) were recorded by using a DTA apparatus fabricated at ERDL, Pune. 10 mg of the sample (100-200 mesh) was taken in an open platinum (Pt) cup and heated at a heating rate of 10°C/min in static air in the temperature range 100-300°C Calcined alumina (10 mg) was taken as reference. A Pt-Pt (Rh 13%) thermocouple was used to record ΔT with the help of two-pen strip chart recorder and DTA peak temperatures are given in Table 1.

Explosion Delay Measurements on DMAP

The explosion delay (D_E) measurements were undertaken by tube furnace (TF) technique[1,9.10] in the temperature range 200-600°C. Each run was repeated three times and mean D_E values are reported in Table 3. The explosion temperature (ET^*) for these salts were taken at time explosion delay (t_{DE}) of 10 s. Explosion delay data were found to fit in the following equation[14,15]

$$\frac{1}{D_E} = A\ e^{E^*/RT}$$

where A is a constant. The activation energy for explosion (E^*) was assesed by the above equation. Typical plots are shown in Fig. 2. The values of E^*, ET^* and the correlation coefficient (r) are given in Table 3.

Impact and Friction Sensitivity Measurements on DMAP

Impact sensitivity measurements were carried out by an impact mechine for high explosives at ERDL, pune. The description of the device and the experimental procedure are already given in our earlier paper.[5] The $h_{50\%}$ data have been given in Table 1.

Friction sensitivity measurements were carried out by a friction sensitivity apparatus (Julius Peters, Berlin-21) at ERDL, Pune, to find out the friction insensitive limit in kg (Table 1) by the same procedure as adopted earlier.[5]

RESULTS AND DISCUSSION

The ET (Table 1), D_E, ET^* and E^* values reported in Table 3 are quiet lower for 3,4-DMAP as compared to 2,5- and 2,4-DMAP salts. It shows that 3,4-DMAP is most sensitive towards heat among the three perchlorates. The DTA thermograms (Fig. 1) in static air reveal that all DMAP gave sharp exothermic peaks prior to an audible explosion. During TG studies, all the salts exploded without undergoing appreciable weight losses (Table 2). A slight carbonaceous residue was found to be left over after the explosion. Melting of 2,5- and 2,4-DMAP was observed during ET measurements whereas, 3,4-DMAP undergoes decomposition without melting (Table 1). It has also been observed that all the DMAP are less sensitive towards heat as compared to mono substituted methylanilinium perchlorates reported in our earlier paper.[1]

In order to understand the role of PK_a towards thermal decomposition of DMAP, ET and ET^* were plotted against PK_a (Fig. 3a). Non linear plots were obtained, which clearly indicates that thermal behaviour of DMAP is not purely controlled by acidity constants of the respective amines. However, non-chemical parameters[16] seem to affect the thermolysis of 3,4-DMAP, which decomposes without melting (Table 1).

The performance of a new energetic compound can be determined by drop-weight impact and friction sensitivity measurements.[16,17] The friction sensitivity reported in Table 1, of all the DMAP salts is almost the same and their impact sensitivity is in the order 2,5->2,4->3,4-DMAP. log $h_{50\%}$ showed a very good linear relationship with pK_a (Fig. 3b), which clearly indicates the dependence of acidity on the impact behaviour of DMAP. Mullay[18] has reported that electron-donating groups ($-CH_3$) decrease the sensitivities within a class of compounds. It has also been observed that DMAP are less sensitive towards impact and friction as compared to monosubstituted anilinium perchlorates.[2] Moreover, DMAP are more sensitive towards heat, impact and friction, if we compare the data with corresponding nitrate salts.[3] This may be due to the existance of less electrostatic forces between the former than the latter and/or due to more oxidising nature of oxides of chlorine than the oxides of nitrogen (decomposition products of respective salts).

Based upon our observations, the overall process of decomposition of DMAP is reported in Fig. 4. It seems that transfer of proton[1-5,19-21] (N—H bond heterolysis) from dimethylanilinium ion of DMAP (I) to ClO_4^- (step 1a) takes place through an activated complex (II) to form the corresponding dimethylamine and $HClO_4$ molecules in the adsorbed phase (III). It is reported[22,23] that the basicity of anion (ClO_4^-) increases with rise in temperature until, it reaches the base strength of arylamine. At this temperature, the proton would be removed from the arylammonium ion by the anion base to form the corresponding arylamine and $HClO_4$ molecules. Subsequently, the oxidation-reduction reactions between amines and $HClO_4$ (step 1b) or its decomposition products would lead to explosion and gaseous products are generated.

Since, the evolution of NH_3 (confirmed qualitatively) was observed during thermal decomposition of these salts, the second possible mode of decompostion may be through the C—N bond heterolysis (step 2) to form an ion pair (IV) and NH_3. Theoretically, ammonia is the expected product of decomposition of these salts since, their O/H ratio is less than one.[24,25] Evolution of NH_3 during decomposition of methylammonium perchlorate has also been reported by Nambiar et al.[26]

The carbocation (IV) may form the ester of perchloric acid [dimethyl benzene perchlorate (V)] as shown in step 2a. Ester of perchloric acid may decompose (step 2b, O–Cl bond heterolysis) via free radical mechanism (the ester of HNO_3 are reported to decompose via same mechanism[3,27]) leading to explosion (step 2c). It may be noted that the above intermediates at higher temperatures are transitory prior to explosion.

Summarizing the data it can be concluded that thermolysis of DMAP involves competitive decomposition reaction paths. The proton transfer seems to control the decomposition of these salts induced by impact (step 1) and free radicals are predominantly involved in thermal reactions induced by heat energy.

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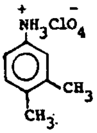
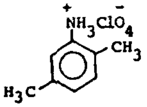
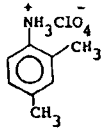
TABLE-1

Analytical, Impact, Friction and Thermolysis Data for Dimethylanilinium Perchlorates

Compound	 (3,4-DMAP)	 (2,5-DMAP)	 (2,4-DMAP)
% of ClO_4^- Exp.(Theor.)	40.38(40.58)	40.08(40.58)	40.59(40.58)
Density (gm cm^{-3})	1.280	1.186	1.251
DTA Peak Temp. (°C)	200	220	216
Impact Sensitivity $h_{50\%}$ (cm)	107	88	95
Friction Insensitive Limit (kg)	21.6	21.6	19.2
Physical Changes Observed			
Starting Temp. (°C)	100	100	100
Change in Colour (°C)	135	145	180
Melting (°C)	-[a]	218	233
Boiling (°C)	-[a]	262	335
Explosion, ET (°C)	228	280	340

a - Did not melt and boil

TABLE - 2

Non-isothermal TGA on DMAP in Static Air at a Heating Rate of 2°C/min.

Temperature (°C)	% weight loss		
	3,4-DMAP	2,5-DMAP	2,4-DMAP
60	0.0	4.0	0.0
80	0.0	9.3	0.0
100	0.0	–[a]	1.3
120	1.3	10.6	–
140	2.7	12.0	2.7
160	4.0	13.3	–
180	5.3	–	4.0
200	–	–	–
220	–	–	–
240	6.7	14.7	5.3
260	Explosion	17.3	6.7
288		Explosion	8.0
306			Explosion

a - Indicates no weight loss

TABLE-3

Explosion Delay (D_E), Explosion Temperature (ET^*) and Kinetic Parameters for Dimethylanilinium Perchlorates

Compound	Explosion Delay (s) at							ET^*	E^*	r
	200°C	250°C	300°C	350°C	400°C	500°C	600°C	(°C)	(kJ mol^{-1})	
3,4-DMAP	67.9±4.5	42.0±2.8	32.6±0.6	22.7±0.7	16.9±0.4	12.5±0.4	8.0±0.2	482	18.3	0.9618
2,5-DMAP	DNE	67.3±2.2	44.8±1.1	29.1±1.0	22.1±1.0	13.9±0.6	8.7±0.3	564	22.5	0.9989
2,4-DMAP	DNE	91.5±4.4	56.5±1.5	37.1±1.6	30.3±0.5	17.7±0.3	11.7±0.3	666	22.5	0.9984

DNE - Did not explode

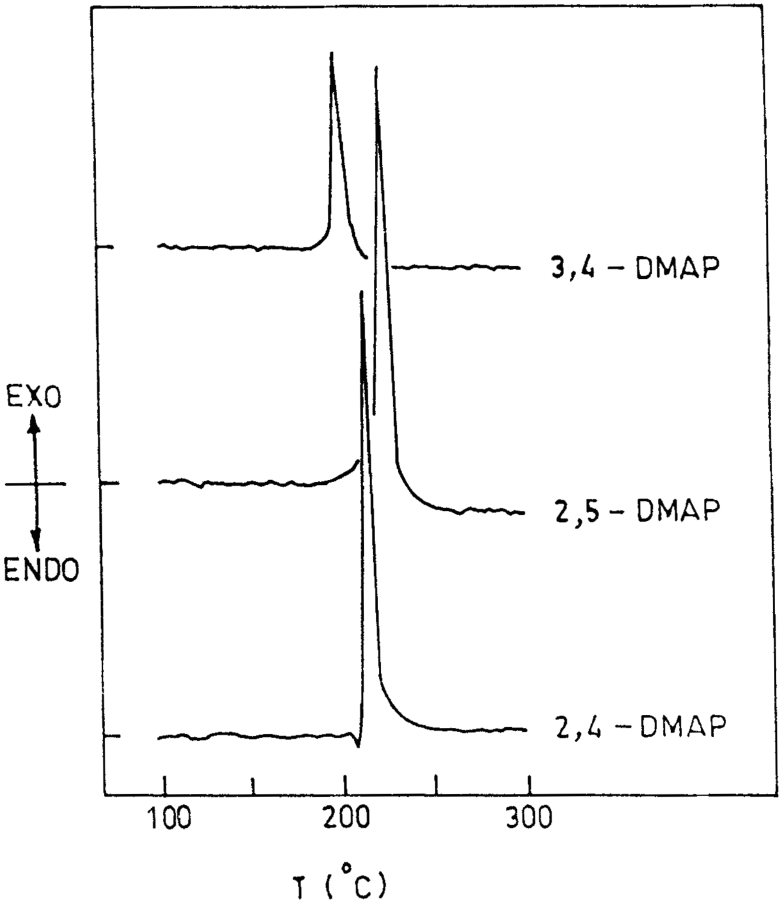


FIGURE 1

DTA thermograms of dimethylanilinium perchlorates in static air.

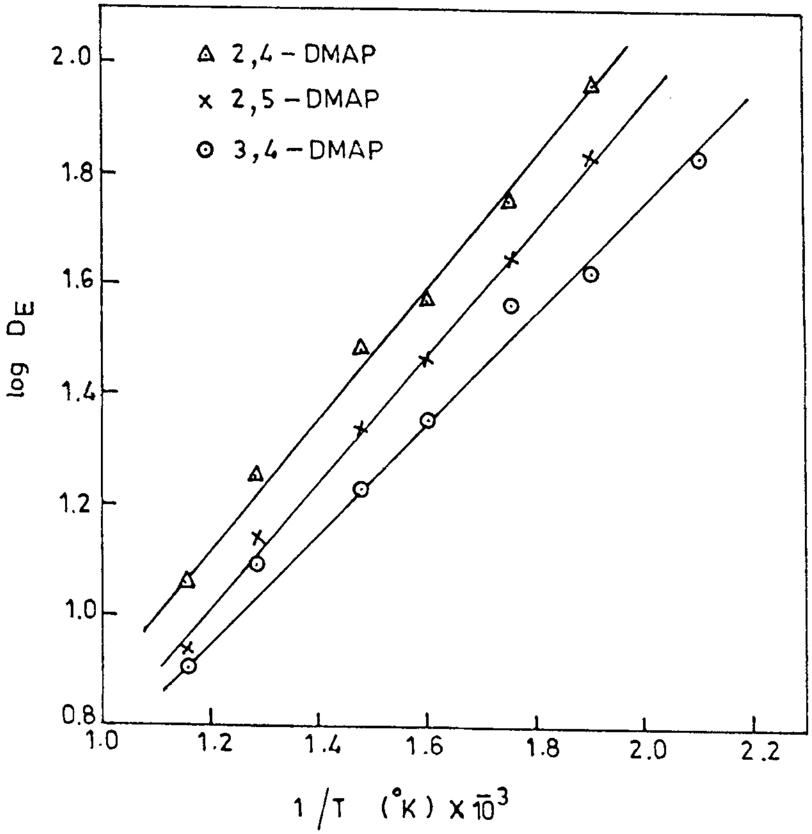


FIGURE 2

Plots of log D_E versus 1/T (°K) for dimethylanilinium perchlorates

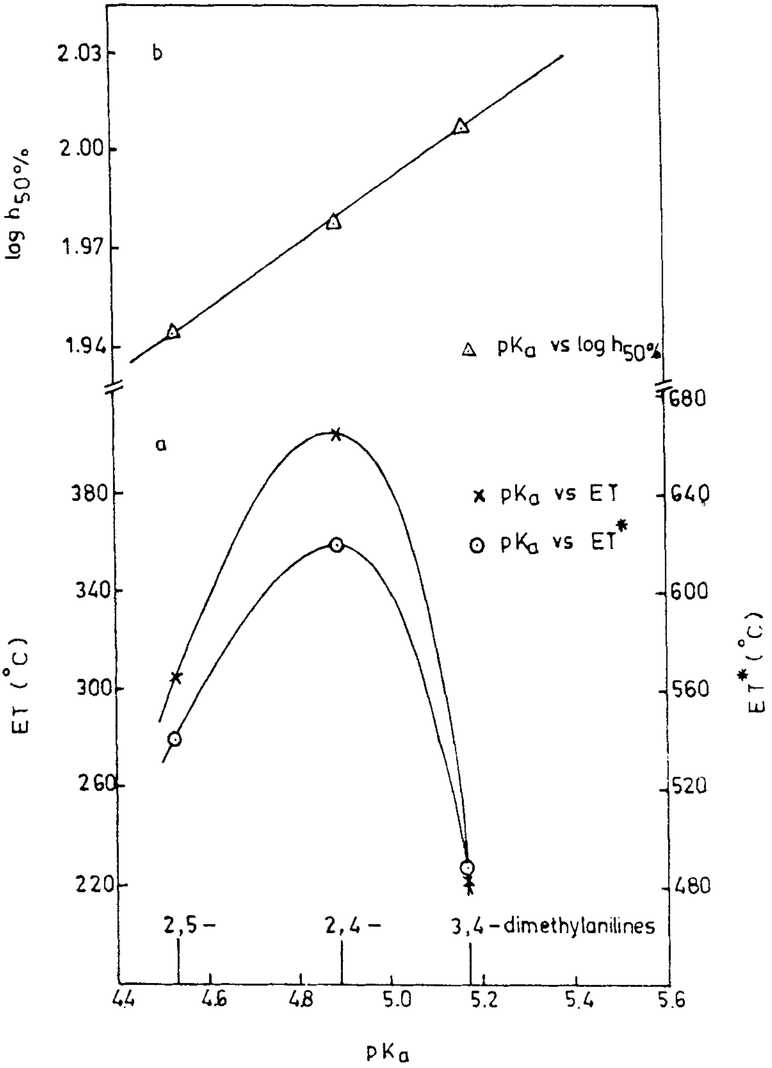


FIGURE 3

(a) Plots of explosion temperatures (ET & ET*) versus pKa

(b) Plot of log $h_{50\%}$ versus pK_a for dimethylanilinium perchlorates.