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Thermolysis of hydrogen sulphate, nitrate and perchlorate salts of diphenylamine. Part LXVIII

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Abstract Hydrogen sulphate, nitrate and perchlorate salts of diphenylamine have been prepared and characterized by elemental, spectral and gravimetric analyses. Thermal decomposition of these salts has been evaluated by TG (static air) and DSC (inert atmosphere). The proton transfer reaction plays a major role during thermolysis of these salts. The diphenylammonium hydrogen sulphate under thermal and microwave irradiation forms 4-(phenylamino) benzenesulphonic acid by sulphonation process, whereas nitrate and perchlorate salts do not form corresponding nitro and perchloro derivatives, rather they ignite and explode, respectively, to form gaseous products along with a residual carbon .

Keywords Diphenylamine · Thermolysis · Proton transfer · Ignition/explosion

Introduction

Extensive studies have been made on preparation, characterization and thermolysis of ring substituted arylammonium sulphates [1–7], nitrates [8–11], perchlorates [12–15] salts. It has been observed that sulphate salts when heated under vacuum were found to form aminobenzenesulphonic acids, which find applications [16] in organic synthesis, dyestuffs, sulpha drugs and detergents.

The nitrate and perchlorate salts find applications in explosive and propellant formulations. Nitrates are powerful oxidizing agent and decompose at elevated temperatures to give oxygen as one of the major products [17–20]. Further, perchlorates are generally more violent in their explosive behavior as compared to nitrate salts [21–24]. The proton transfer process was considered as a primary and rate controlling step in the thermal decomposition of these salts.

Yet, a lot of work has been done on salts of mono and disubstituted arylamines, whose thermal stability depends upon the nature of substituted groups, but no work has so far been done on diphenylamine (a weak secondary amine). Based on our ongoing research programmes, we report here the preparation, characterization and thermolysis of hydrogen sulphate, nitrate and perchlorate salts of diphenylamine.

Experimental

Materials

Diphenylamine (s.d.fine) was purified by usual methods, conc. H_2SO_4 (Merck) 70% HNO_3 (Merck), 70% $HClO_4$ (Merck), silica gel of TLC grade (Ranbaxy), Iodine (s.d.fine) and Nitron (CDH) were used as received.

Preparation and characterization

The diphenylammonium hydrogen sulphate (DPAHS) was prepared by reacting diphenylamine with excess of conc. H_2SO_4 at room temperature (Scheme 1). Readily formed white leaflike crystals, after washing with diethylether to remove amine and excess of sulphuric acid were recrystallized under vacuum. The purity was checked by thin layer chromatography (TLC) and further characterized by elemental and spectral analyses.

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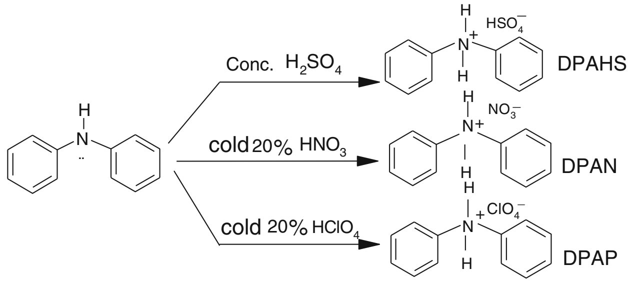


Scheme 1 Preparation of DPAHS, DPAN and DPAP from diphenylamine

Diphenylammonium nitrate (DPAN) and diphenylammonium perchlorate (DPAP) were prepared by the reaction of diphenylamine (in ether), with excess of cold 20% HNO_3 and 20% $HClO_4$, respectively (Scheme 1). Both nitrate and perchlorate salts were precipitated out after keeping the reaction mixture at room temperature for about 2 h. After washing with absolute alcohol, crystal were vacuum dried, Further their purity was checked by TLC and characterized by a gravimetric method using nitron reagent [25] (Table 1).

The sample of DPAHS was heated at 90 °C in a tube furnace [26] (TF) for 17 min under reduce pressure (400 mm Hg) and kept under 700 Watt for 3 min in a commercial household microwave oven (MS 1921 HE LG electronics private Ltd.,) gave a gray residue. The residue obtained then washed with double distilled water and dried under vacuum to get the gray amorphous solid and purity was checked by TLC. The residue then identified as 4-(phenylamino) benzenesulphonic acid [4-(PA) BSA] by physical parameters, TLC, elemental (Table 1) and spectral data (Table 2). Moreover, this acid gave effervescences with aq. $NaHCO_3$.

Elemental and spectral analyses

The C, H, N analyses were done with elemental Vario EL (II) Carlo Erba 1108 instrument. FT-IR spectra were taken with Perkin–Elmer RXI spectrometer in the range of 4,000–450 cm^{-1}. The FAB mass spectra were recorded on a Jeol SX 102/DA. NMR spectra were taken in Brucker 500 avance (field-500 MHz).

Thermal studies

Non-isothermal TG

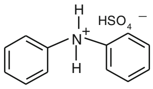
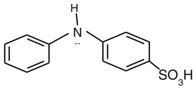
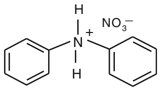
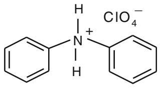
Non-isothermal TG of sulphate, nitrate and perchlorate salts (wt. 20 mg, 100–200 mesh) were undertaken in a static air at a heating rate of 5 °C min^{-1} using homemade TG apparatus [27]. The accuracy of the furnace was ±1 °C. A round bottom gold crucible was used as a sample holder. The fraction decomposition (α) has been plotted against temperature (°C) and thermograms are shown in Fig. 1.

Dynamic TG analyses on the salts has also been done by using Perkin Elmer instrument at a heating rate of 10 °C min^{-1} (wt. 10.5 mg, 100–200 mesh, under nitrogen atmosphere) and the thermograms are shown in Fig. 2.

Ignition delay (D_i)/explosion delay (D_E) measurements

The ignition delay (D_i) of DPAN and explosion delay (D_E) of DPAP were undertaken, in the temperature range

Table 1 Physical parameters, TLC, gravimetric analysis of hydrogen sulphate, nitrate and perchlorate salts of diphenylamine

Compound	Molecular weight	Structure	Colour	MP/°C	TLC	Spot colour	R_f	Nitrate and perchlorate/%	
								Experimental	Theoretical
DPAHS	267		White amorphous	120	a:b:c	Yellow	0.84	–	–
4(PA) BSA	250		Gray	80	a:b:c	Yellow	0.93	–	–
DPAN	169		White amorphous	52 (d)	a:b:d	Yellow	0.72	0.1610	0.1616
DPAP	232		White amorphous	82 (d)	a:b:d	Gray	0.62	0.1521	0.1530

Eluent: a = H_2O, b = $CHCl_3$, c = n BuOH, d = Et_2O; locating reagent: iodine

Table 2 Elemental and spectral parameters for DPAHS and 4-(PA) BSA

Compound	% Observed (calculated)			IR/cm^{-1}	m/z	Chemical shift/δ
	C	H	N			^{1}HNMR
DPAHS	53.9 (5.29)	4.86 (4.82)	5.24 (5.2)	3,433 νN–H str, 2,890 (m) C–H str, 1,322 C–H bend, 1,592 (C=C), 616 (s) HSO_4^-	169.8, 335, 92.2	6.5–7.5, 2.5 (–NH_2)
4-(PA) BSA	57.6 (56.8)	4.8 (5.5)	5.6 (4.9)	3,435 (s) νN–H str, 3,023 (m) C–H str, 1,522 (s) C–H bend, 750 (v,s) C–H, 1,300 (s) C–N, 1,196 (s) and 601.4 (s) SO_3H	170.3, 128	6.5–7.2, 5.3, 2.5 (–NH_2)

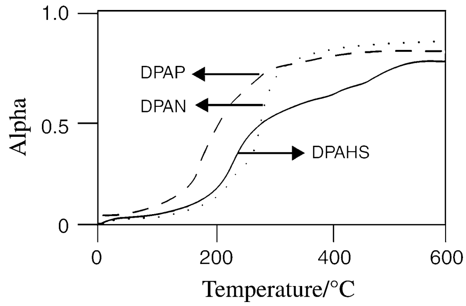


Fig. 1 Nonisothermal TG of diphenylammonium salts

230–330 °C by taking the sample in an ignition tube (4.5 cm length and 0.4 cm diameter) and the time interval between the insertion of the ignition tube into the TF and the moment of an ignition/explosion noted with the help of a stopwatch, gave the value of ignition delay (D_i) Similarly moment of an audible explosion gave the value of explosion delay (D_E). Each run was repeated three times and mean values are reported in Table 3. The D_i or D_E data were found to fit separately in following equation [28–31]

$$D = A\ \exp(E_a/RT)$$

$D = D_i$ for nitrate and D_E for perchlorate

where E_a is the activation energy for thermal ignition/explosion, A the preexponential factor and T the absolute temperature. E_a assessed by above equation along with the correlation coefficient (r) are given in Table 3. Plots of D vs. $1/T$ are presented in Fig. 3.

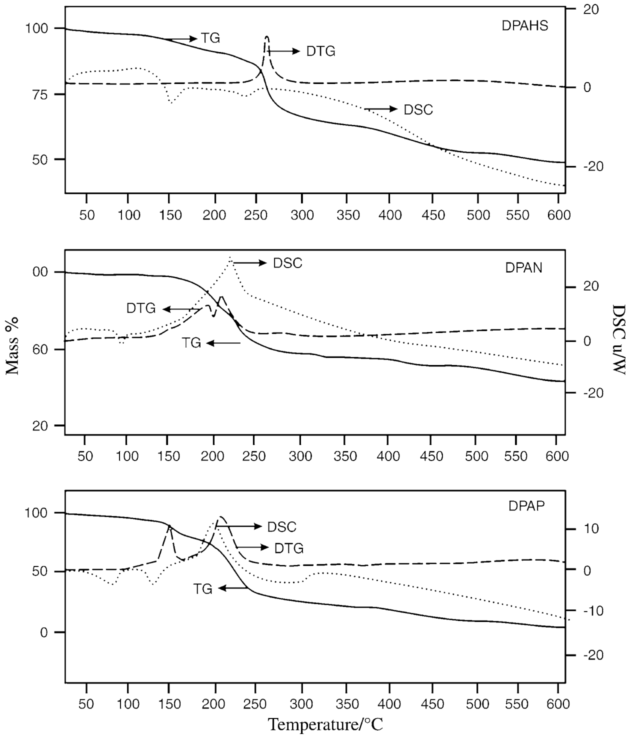


Fig. 2 TG, DTG and DSC curves of DPAHS, DPAN and DPAP salts

Results and discussion

The C, H, N data (Table 2) confirms beyond doubt the formation of DPAHS. The IR data (Table 2) shows the bands in the region 3433.97 cm^{-1} νN–H str, 2,890 (m) for C–H str, 1,322 (w) C–H bending and 616 (s) ν HSO_4^-; MS, m/z 169.8 = 170, 333.5, and 92 are due to $(C_6H_5)_2\ ^+NH_2$, $(C_6H_5N)_2$, and $^+$NH-Ph species respectively; ^{1}HNMR (DMSO) δ 6.8–7.6 is due to the three types of interacting H nuclei. A peak at δ 2.5 is due to some nondeuterated DMSO molecules. The observed and experimental value by nitron estimation for nitrate and perchlorate are characterized within experimental error (Table 1). Non isothermal TG of DPAHS in static and inert atmosphere shows that mass loss occurs in two steps. Step I is the solid state decomposition of salts to form corresponding sulphonic acid and step II is concerned with the decomposition of acid. In DPAHS, there is 13% weight loss due to evolution of water of crystallization and a water molecule during sulphonation. The plateau in region 200–250 °C shows the stability of acid in that particular temperature range. The DSC shows two endotherms at 149 °C (elimination of a molecule of water) and at 241 °C (due to sulphonation). It has been observed that heating DPAHS in air at high temperature gave bluish black product which contain 4-(PA) BSA. This is presumably due to formation of quinonoid like material arising from hydroxylation,

Table 3 Ignition delay (D_i), explosion delay (D_E) and activation energy (E_a) for thermal ignition/explosion for DPAN and DPAP (D_i or D_E/s at temperature ±1 °C)

Compound	230 °C	250 °C	270 °C	290 °C	310 °C	330 °C	E_a/kJ mol^{-1}	*r*
DPAN	DNI	92	78	57	45	36	31.8	0.9951
DPAP	DNE	DNE	52	35	29	24	36.7	0.9922

DNI Did not ignite, *DNE* did not explode, *r* correlation coefficient

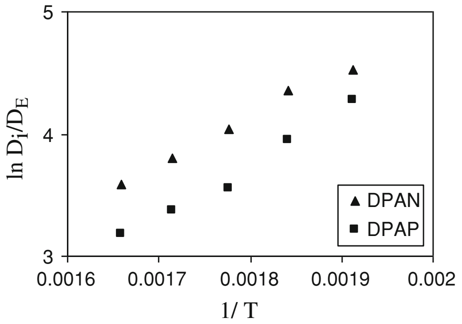
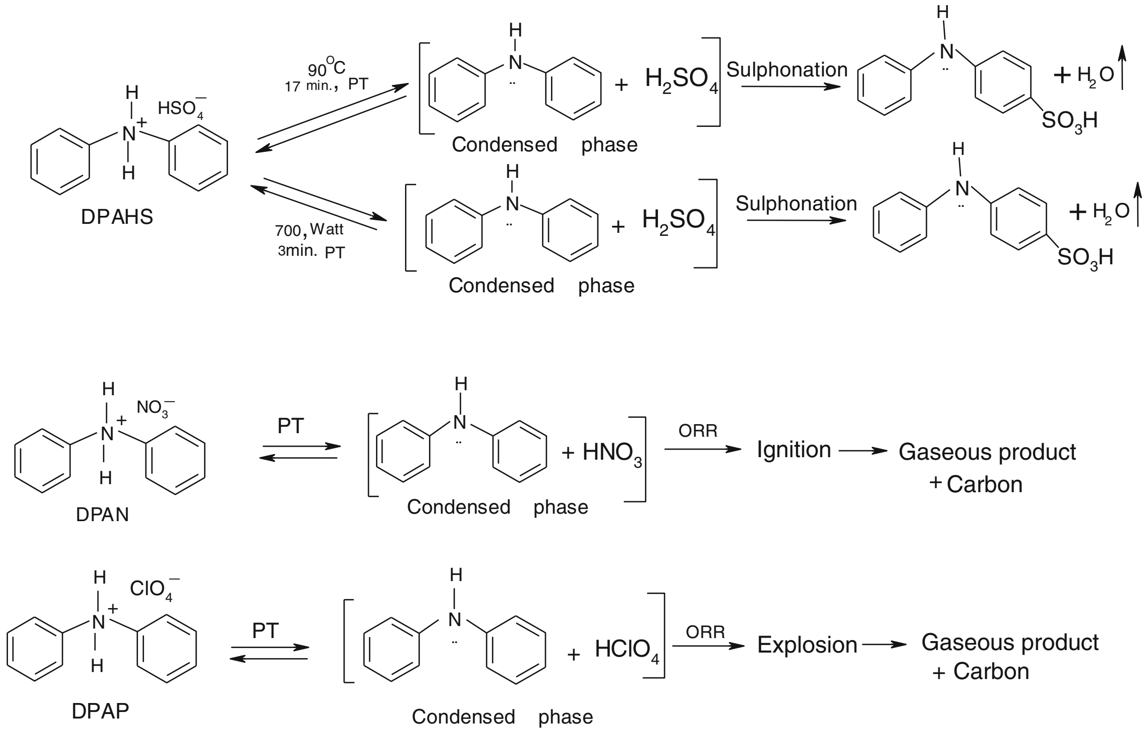


Fig. 3 Graph of ln D_i vs. 1/*T* (DPAN) and ln D_E vs. 1/*T* (DPAP)

oxidation and polymerization of amino compounds. In order to prepare the 4-(PA) BSA in pure form, it was thought best to heat the DPAHS under low pressure. Thus, the sample of DPAHS heated at 90 °C for 17 min at 400 mm Hg pressure, was found to contain 4-(PA) BSA and a water molecule (confirmed by Karl Fisher Reagent). Moreover, DPAHS under microwave irradiation for 3 min yields too 4-(PA) BSA. The acid was confirmed by TLC, elemental, chemical and spectral analyses (Table 2) and C, H, N data are within experimental error; IR (cm^{-1}) peaks at 3,433 (s) νN–H str, 3,023 (m) C–H str, 1,522 (s) C–H bending, 750 (v, s) C–H, 1,300 (s) C–N, 1,196 (s) and 601.4 (s) for SO_3H; *m*/*z* at 170 and 128 are due to respectively diphenylammonium ion and a dimer (5-cyclopentadienyl-1,3-cyclopentadiene); ^{1}HNMR (DMSO); δ 2.5 is may be due to two aromatic protons ortho with the –CSO_3H moiety and 6.6–7.2 ppm is due to another four interacting H nuclei.

The TG data taken in inert and static air (Figs. 1, 2) reveals that nitrate and perchlorate both show incomplete mass loss as they are highly fuel rich and a black residue remains in the crucible after completion of decomposition followed by ignition or explosion. During TG the DPAN were found to ignite while DPAP explodes; DSC of nitrate



Scheme 2 Thermolytic pathways of diphenylammonium hydrogen sulphate, nitrate and perchlorate salts. *PT* Proton transfer, *ORR* oxidation–reduction reactions

show one endotherm at 98 °C (phase transition) and one exotherm at 225 °C; while perchlorate show two endotherm at 75 °C (melting) and 120 °C (phase transition) and one exotherm at 200 °C. The exotherms may be due to oxidation reduction reactions between oxidizer part (NO_3^- or ClO_4^-) and fuel part (diphenylamine) leading to ignition/explosion to produce gaseous products along with a residual carbon.

The thermolysis of diphenylammonium hydrogen sulphate, nitrate and perchlorate may be illustrated in Scheme 2. The overall decomposition process of these salts seems to commence by the transfer of a proton from diphenylammonium ion to SO_4^-, NO_3^- and ClO_4^- ions forming diphenylamine and respectively, H_2SO_4, HNO_3 and $HClO_4$ molecule in the condensed phase prior to sulphonation (DPAHS), ignition (DPAN) and explosion (DPAP). A molecule of water will be given off as vapour at higher temperature in the case of sulphates along with the formation of solid 4-(PA) BSA, whereas nitrate and perchlorate, respectively get ignite and explode at higher temperatures.

Oyumi and Brill et al. [32] have also reported that salts with $O/H < 1$ release NH_3 (g) while those with $O/H > 1$ do not release NH_3 (g). Nambier et al. [33] have also reported the evaluation of NH_3 as a dissociation product of methylammonium perchlorates. Since for DPAHS, DPAN and DPAP $O/H < 1$ hence ammonia may be one of the decomposition products.

It is inferred that proton transfer is the rate determining step and thermal stability of diphenylammonium salts depends upon the tendency of diphenylammonium cation to release a proton to corresponding anion. In the case of NO_3^- and ClO_4^-, further, weak bonds are broken, and groups of atoms are produced. These charged and uncharged groups of various stabilities have different lifetimes and thus can be considered as intermediates possessing enhanced reactivity. Because of this, they propagate solid-phase interactions to chain-like or even branching chain-like process having strongly exothermic reactions which may cause an ignition/explosion.

Conclusions

The proton transfer seems to be a primary and rate controlling step in the thermolysis of hydrogen sulphate, nitrate and perchlorate salts of diphenylamine. These salts have been found to dissociate by proton transfer to form diphenylamine and acid molecule (H_2SO_4, HNO_3, $HClO_4$) in the condensed phase. Sulphate in solid state under thermal and microwave irradiation, forms aminobenzenesulphonic acid, whereas nitrate and perchlorate oxidize the fuel (diphenylamine) leading to ignition/explosion to form various gaseous products and a residual carbon.

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