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New hydrazinium salts of benzene tricarboxylic and tetracarboxylic acids—preparation and their thermal studies

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Abstract

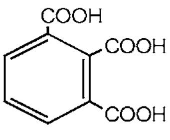
Some new hydrazinium salts of benzene tricarboxylic and tetracarboxylic acids have been prepared by neutralisation of these acids with hydrazine hydrate in aqueous medium and characterised by conductance measurement, IR spectral and thermal analyses. Hemimellitic acid (H_3hml) forms monohydrazinium salt, trimellitic acid (H_3tml) and trimesic acid (H_3tms), mono and dihydrazinium salts, and pyromellitic acid (H_4pml) all the four salts with hydrazine hydrate. Conductance study indicates their electrolytic nature. IR spectra of all the salts show N–N stretching frequencies of the $N_2H_5{}^+$ in the region of 960–990 cm^{-1}. The hemimellitate salt undergoes endothermic dehydrazination at 154 °C, trimellitates and pyromellitates in the range of 191–271 °C, and trimesates in the range of 267–332 °C. Trimesates decompose to give CO_2 around 337 °C. All the salts then undergo strong exothermic decomposition in the range of 517–595 °C via the formation of respective acid intermediates first, then arenes, yielding carbon residue. A comparison of the thermal behaviour of pure acids with that of their salts reveals the fact that the acids do not withstand high temperature like salts. They show sharp endotherms at their melting points and then they decompose exothermally before 400 °C to give carbon residue.

Keywords: Hemimelltic acid; Hydrazinium salts; IR; Thermal analysis; Trimellitic acid; Trimesic acid; Pyromellitic acid

1. Introduction

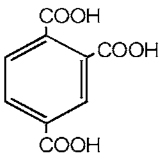
Hydrazine is the simplest diamine and forms salts with mineral and carboxylic acids. Hydrazine occurs as singly protonated hydrazinium ($N_2H_5{}^+$) and doubly protonated hydrazinium ($N_2H_6{}^{2+}$) ionic salts. The former salts are the common type and can be obtained with a variety of acids, whereas the latter are formed only with strong mineral acids [1,2]. The former salts have also been obtained by the reaction of solid ammonium salts [3–5] with hydrazinium hydrate and the latter salts by double decomposition of hydrazine sulphate ($N_2H_6SO_4$) with the corresponding barium salts [3]. Hydrazinium salts are used as the flame retardants [6,7] and proton conductors [8]. They have been utilised for the preparation of metal hydrazinium/hydrazine complexes [9–12].

Hydrazinium salts with carboxylic acids are quite known only recently. The thermal study of aromatic monocarboxylate and dicarboxylate has been reported [13]. A scarce literature about aromatic tricarboxylic and tetracarboxylic acid salts enthused us to study on hydrazinium salts with aromatic polycarboxylic acids such as hemimellitic, trimellitic, trimesic and pyromellitic acids and their thermal behaviour. The structures of acids and their designations used are shown below for clarity:



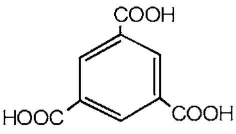
HEMIMELLITIC ACID

(H_3hml)



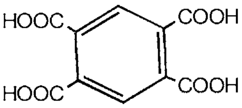
TRIMELLITIC ACID

(H_3tml)



TRIMESIC ACID

(H_3tms)



PYROMELLITIC ACID

(H_4pml)

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2. Experimental

All the salts reported have been prepared by the neutralisation of the respective carboxylic acids in aqueous medium with hydrazine hydrate (99–100%) in appropriate molar ratios. The acids of high purity were procured from Alrich Co. and used without further purification.

2.1. Preparation of monohydrazinium salts of tricarboxylic acids ($N_2H_5H_2hml{\cdot}2H_2O$, $N_2H_5H_2tml{\cdot}H_2O$, $N_2H_5H_2tms{\cdot}2H_2O$)

To a solution of the respective acid (1 mmol, e.g. 0.246 g of hemimellitic acid dihydrate) in water (40 ml) was added hydrazine hydrate (0.05 g; 1 mmol). The clear solution at specific pH (2.5, 2.5 and 4 for hemimellitic, trimellitic and trimesic acid solutions, respectively), was reduced to one third of its volume by heating over boiling water bath at which point white crystals of the product began to form. The reaction mixture was allowed to stand at room temperature for 2 days. The product formed was filtered, washed with ethyl alcohol and diethyl ether and dried over anhydrous calcium chloride in a desiccator. Hemimellitate is a shiny white flake like crystal and trimesate is needle shaped.

2.2. Preparation of dihydrazinium salts of trimellitates and trimesates ($(N_2H_5)_2Html$ and $(N_2H_5)_2Htms{\cdot}2H_20$)

These salts were prepared by the above procedure by mixing the acid with the base in the molar ratio of 1:4. A hard white solid product was obtained at pH 7. It was filtered, washed with ethyl alcohol and diethyl ether and dried over anhydrous calcium chloride in a desiccator.

2.3. Preparation of hydrazinium salts of pyromellitic acid ($N_2H_5H_3pml$, $(N_2H_5)_2H_2pml$, $(N_2H_5)_3Hpml$ and $(N_2H_5)_4pml{\cdot}3H_2O$)

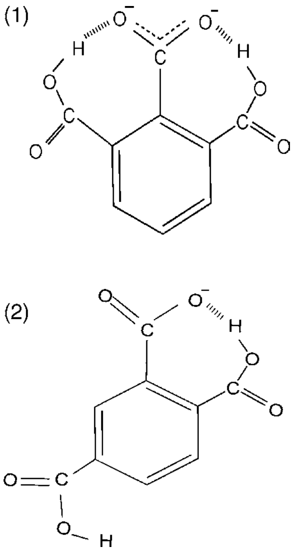
These salts were prepared by identical procedure using pyromellitic acid and hydrazine hydrate in the molar ratio 1:1, 1:2, 1:3 and 1:4. The crystals of the tetrahydrazinium salt were obtained at pH 8.5 after 10 days, whereas the other three salts were obtained at pH 2.5, 3.5 and 4.5, respectively, after 6 days. All the salts are dull yellow coloured crystals and are soluble in water.

The hydrazine content in all the salts was determined volumetrically using 0.025 M potassium iodate under Andrew's conditions [14]. Melting points were determined on Mettler FP 5 instrument and are uncorrected. Infrared spectra were recorded using KBr discs (4000–400 cm^{-1}) in a Shimadzu FTIR-8201 PC spectrophotometer. The simultaneous TG–DTA analysis was carried out using STA 1500 thermal analyser and NETZSCH-Geratebeau GmbH thermal analyser. The curves were obtained in air using platinum cups as sample holders with 5–10 mg of the samples at the heating rate of 10 °C min^{-1}.

3. Results and discussion

The analytical data of the salts (Table 1) were consistent with the proposed formulae for them. Hydrazinium hydrogentrimellitate, hydrazinium trihydrogenpyromellitate, hydrazinium dihydrogenpyromellitate and hydrazinium hydrogenpyromellitate are anhydrous salts whereas all other salts are hydrated. This has been confirmed by analytical, IR spectral and thermal studies. All of these salts are soluble in water.

It is significant to note that hemimellitic acid forms only monohydrazinium salt while trimellitic and trimesic acids form monohydrazinium and dihydrazinium salts. The reason for this observation cannot be generalised. A comparison of pK_a values indicates that though more distinct values noted for hemimellitic acid ($pK_{a_1} = 2.88$; $pK_{a_2} = 4.75$; $pK_{a_3} = 7.13$) may pave the way to the formation of three salts, it forms only one salt. The attempt to prepare dihydrazinium and trihydrazinium salts by neutralising hemimellitic acid with base in 1:2 and 1:3 ratio and even in higher pH ranges was unsuccessful. It may be perhaps due to strong internal hydrogen bonding formed between oxygen of deprotonated central carboxylate ion and hydrogens of adjacent carboxylic acids thereby stabilising the carboxylate ion (Fig. 1). The pK_a factor, to some extent, seems to be operating in the case of trimellitic acid ($pK_{a_1} = 2.52$; $pK_{a_2} = 3.84$; $pK_{a_3} = 5.20$) and trimesic acid ($pK_{a_1} = 2.12$; $pK_{a_2} = 4.10$; $pK_{a_3} = 5.18$); they form two salts. The dihydrazinium salts of these two acids are obtained only strenuously in the pH range of 7 upon careful prolonged heating. In the case of trimellitic acid, probably the hydrazine abstracts hydrogen ion from carboxyl groups present in the first and fourth carbon of the ring. Here also the internal hydrogen bonding formed between adjacent ionised and unionised carboxyl groups (Fig. 2) hinders the formation of trihydrazinium salt.



Figs. 1 and 2. Hydrogen bonding in hemimellitate and trimellitate anions.

Table 1
Analytical, IR and conductance data

Compound	M.Pt./ *D.Pt. (°C)	Yield (%)	Elemental analysis (observed (calculated)) (%)			Hydrazine (%) observed (calculated)	Conductance (ohm^{-1} cm^{2} mol^{-1})	IR data (cm^{-1})					
			Carbon	Hydrogen	Nitrogen			$\nu_{O–H}$	$\nu_{N–H}$	$\nu_{C=O}$ (free acid)	ν_{COO^-} (asym)	ν_{COO^-} (sym)	$\nu_{N–N}$
$N_2H_5(H_2hml)2H_2O$	240*	85	38.74 (38.84)	5.00 (5.04)	10.12 (10.07)	12.3 (11.51)	260	3500	3063	1706	1584	1384	978
$N_2H_5(H_2tml)H_2O$	>300	85	41.30 (41.54)	4.50 (4.62)	10.83 (10.77)	11.9 (12.30)	227	3400, 3500	3317	1697	1590	1373	978
$(N_2H_5)_2(Html)$	>300	85	39.30 (39.42)	5.01 (5.11)	20.34 (20.44)	23.5 (23.40)	240	–	3200,3360	1714	1580	1373	978
$(N_2H_5)(H_2tms)2H_2O$	270*	90	38.80 (38.84)	5.14 (5.04)	10.14 (10.07)	11.9 (11.51)	201	3482	3217	1681	1608	1428	972
$(N_2H_5)_2(Htms)2H_2O$	>300	85	34.90 (34.84)	5.70 (5.81)	18.16 (18.06)	21.0 (20.64)	240	3480	3300	1710	1624	1375	951
$N_2H_5(H_3pml)$	>300	90	41.80 (41.95)	3.48 (3.50)	9.82 (9.79)	12.3 (11.18)	235	–	3334	1680	1558	1355	972
$(N_2H_5)_2(H_2pml)$	>300	85	37.50 (37.73)	4.36 (4.40)	17.72 (17.61)	20.8 (20.10)	274	–	3334	1680	1558	1353	972
$(N_2H_5)_3(Hpml)$	>300	80	34.36 (34.29)	5.13 (5.14)	23.95 (24.00)	27.0 (27.40)	385	–	3334	1680	1558	1352	972
$(N_2H_5)_4(pml)3H_2O$	>300	90	27.32 (27.52)	6.38 (6.42)	25.74 (25.69)	29.1 (29.30)	455	∼3500	3347	–	1620	1373	955

Trimesic acid due to its poor solubility in water (owing to intermolecular hydrogen bonding) shows feeble acidity of the third carboxyl group towards hydrazine. But, surprisingly, pyromellitic acid ($pK_{a_1} = 1.70$; $pK_{a_2} = 3.12$; $pK_{a_3} = 4.92$; $pK_a = 6.23$) forms all the possible salts with hydrazine. Thus, the formation of various salts depends not only on pK_a values but also on other factors such as solubility, hydrogen bonding, electronic, resonance and substituent effects operating on aromatic systems.

4. Conductance data

The molar conductance values of salts and acids in aqueous medium (shown in Table 1) indicate their electrolytic behaviour.

Hemimellitic acid being a highly soluble substance, gives a value of 280 $ohm^{-1}\,cm^2\,mol^{-1}$ corresponding to its existence as 3:1 electrolyte. Its monohydrazinium salt solution shows a slightly less value of 260 $ohm^{-1}\,cm^2\,mol^{-1}$ due to hydrazinium ion in lieu of hydronium ion.

Trimellitic acid solution shows 270 $ohm^{-1}\,cm^2\,mol^{-1}$ whereas its monohydrazinium and dihydrazinium salt solutions show 220 and 240 $ohm^{-1}\,cm^2\,mol^{-1}$, respectively. These lower values are due to hydrazinium ions.

The aqueous solution of trimesic acid shows relatively low value of 240 $ohm^{-1}\,cm^2\,mol^{-1}$ compared to that of other isomers. Its hydrazinium salts show lesser values, 200 and 240 $ohm^{-1}\,cm^2\,mol^{-1}$.

Pyromellitic acid dissociates completely in water and shows molar conductance value of 517 $ohm^{-1}\,cm^2\,mol^{-1}$ indicating its 4:1 electrolytic nature. Its monohydrazinium, dihydrazinium, trihydrazinium and tetrahydrazinium salt solutions have proportionately increased conductance values, 235, 274, 385 and 455 $ohm^{-1}\,cm^2\,mol^{-1}$ establishing the replacement of hydronium ions by hydrazinium ions.

The molar conductance values of the monohydrazinium salts mentioned above, in the range of 220–260 $ohm^{-1}\,cm^2\,mol^{-1}$ corresponding to 3:1 electrolytic nature cannot be attributed any reason except that they are undergoing hydrolysis in low concentrations. Poor solubility of trimesic acid in water may be the reason for less conductance values of its own and its salt solutions in water.

5. Infrared spectra

The important IR bands of the acids and their salts are listed in Table 1. The IR spectra of the hydrated salts of hydrazinium benzene tricarboxylates and hydrazinium pyromellitates display absorption bands in the range of 3400–3500 cm^{-1} due to O–H stretching of water molecule. The carbonyl stretching frequencies of the free carboxyl groups in monohydrazinium, dihydrazinium and trihydrazinium salts exhibit their appearance in the range of 1680–1714 cm^{-1} whereas they show around 1704 cm^{-1} in all acids. The bands in the region of 1370–1430 cm^{-1} and 1580–1625 cm^{-1} for these salts are assigned to symmetric and asymmetric stretching frequencies of the carboxylate ions, respectively. The N–N stretching frequencies in the range 950–978 cm^{-1} are the clear evidence of the presence of $N_2H_5^+$ ion in the salts [1].

6. Thermal analysis

The thermal data are summarised in Table 2. The thermograms of trimesic acid and their salts are shown as representative examples in Figs. 3–5.

6.1. $(N_2H_5)H_2hml\cdot 2H_2O$

The thermogram of this salt indicates that the decomposition of the salt takes place in two steps. In the first step, both dehydration and dehydrazination occur simultaneously showing a sharp endothermic peak at 154 °C. In the second step, the decomposition of acid intermediate begins slowly from its decomposition point 194 °C showing sharp endothermic peaks at 360 and 460 °C and a strong exothermic peak at 545 °C. Comparing the decomposition of acid intermediate with that of pure acid, the latter is found to decompose in a similar manner but the entire decomposition being over before 450 °C. The pure acid decomposes showing strong endothermic peaks at 187 and at 196 °C due to the formation of the anhydride and its melting, respectively. Subsequently, the decomposition of the anhydride also occurs exhibiting exothermic multiplets at 277, 405 and 445 °C. The final products are carbon residue which could not be further analysed, in both the cases.

6.2. $(N_2H_5)H_2tml\cdot H_2O$ and $(N_2H_5)_2Html$

The former salt undergoes decomposition in three steps, an endothermic dehydration at 109 °C, an endothermic dehydrazination at 213 °C and a complete decomposition showing an endothermic peak at 391 °C followed by a strong exothermic peak at 542 °C. The last step is probably due to the decomposition of the acid intermediate leading to the formation of trimellitic anhydride and its immediate oxidation.

The anhydrous dihydrazinium salt undergoes decomposition in two steps, dehydrazination showing endothermic doublet at 191 and 238 °C, and the decomposition of the intermediate showing an endothermic peak at 380 °C and a strong exotherm at 590 °C.

In order to confirm the acid intermediate, the thermal analysis of pure acid was carried out at the same rate of heating. The thermogram of the acid shows that it melts and decomposes at its decomposition point, 232 °C showing a sharp endothermic peak. During its decomposition it drives out a water molecule to form anhydride which decomposes immediately. But these decompositions are completed below 350 °C.

Table 2
Thermal analysis

Compound	DTA (°C)	Thermogravimetry			Nature of decomposition
		Temperature range (°C)	Mass loss (%)		
			Observed	Calculated	
H_3hml2H_2O	95(+)	64–163	14.4	14.6	Dehydration
	187(+)	167–195	7.0	7.3	Melting and dehydration leading to anhydride
	196(+)	195–198	–	–	Melting of anhydride
	277(−)				Decomposition to carbon residue
	405(−)	198–320	89	–	
	442(−)				
$N_2H_5(H_2hml)2H_2O$	154(+)	128–195	24.10	24.46	Dehydration and dehydrazination
	360(−)				
	460(−)	195–650	92.73	–	Decomposition to carbon residue
	545(−)				
H_3tml	232(+)	210–235	8.7	8.6	Dehydration to give anhydride
	274(−)	235–350	78.0	–	Decomposition to carbon residue
$N_2H_5(H_2tml)H_2O$	109(+)	95–174	6.3	6.9	Dehydration
	213(+)	174–359	18.8	19.0	Dehydrazination
	391(+)	359–700	89.4	–	Decomposition to carbon residue
	542(−)				
$(N_2H_5)_2(Html)$	191(+)	140–283	22.5	23.4	Dehydrazination
	238(+)				
	381(+)	283–700	85.3	–	Decomposition to carbon residue
	590(−)				
H_3tms	290(+)	280–345	4.5	4.5	Dehydration to give anhydride
	368(+)	345–700	99.0	–	Decomposition to carbon residue
	500(−)				
$(N_2H_5)(H_2tms)2H_2O$	283(+)	261–315	13.3	12.9	Dehydration
	337(+)	315–376	29.7	27.3	Dehydrazination and decarboxylation
	522(−)	376–650	89.8	–	Decomposition to carbon residue
	583(−)				
$(N_2H_5)_2(Htms)2H_2O$	68(+)	60–150	6.0	5.8	Dehydration
	95(+)				
	179(+)	150–200	12.0	11.6	Dehydration
	267(+)	200–290	23.8	21.9	Dehydrazination
	332(+)	290–400	46.3	46.1	Dehydrazination and decarboxylation
	517(−)	400–650	77.8	–	Decomposition to carbon residue
H_4pml	96(+)	51–250	3.0	–	Removal of moisture
	261(+)				
	286(+)	250–330	90	–	Complete decomposition to carbon residue
	314(+)				
	325(−)				
$N_2H_5(H_3pml)$	223(+)	185–255	12.5	11.2	Dehydrazination
	250(+)				
	496(−)	255–610	90.0	–	Decomposition to carbon residue
	594(−)				
$(N_2H_5)_2(H_2pml)$	270(+)	208–319	21.0	20.1	Dehydrazination
	513(−)	319–650	92.5	–	Decomposition to carbon residue
	595(−)				
$(N_2H_5)_3(Hpml)$	271(+)	308–369	26.0	27.4	Dehydrazination
	500(−)	369–650	91.9	–	Decomposition to carbon residue
	582(−)				
$(N_2H_5)_4(pml)3H_2O$	87(+)	63–151	8.5	8.3	Dehydration
	197(+)	151–219	20.5	19.8	Dehydration and dehydrazination
	263(+)	219–371	39.5	41.8	Dehydrazination
	505(−)	371–600	89.9	–	Decomposition to carbon residue
	583(−)				

(+): endotherm; (−): exotherm.

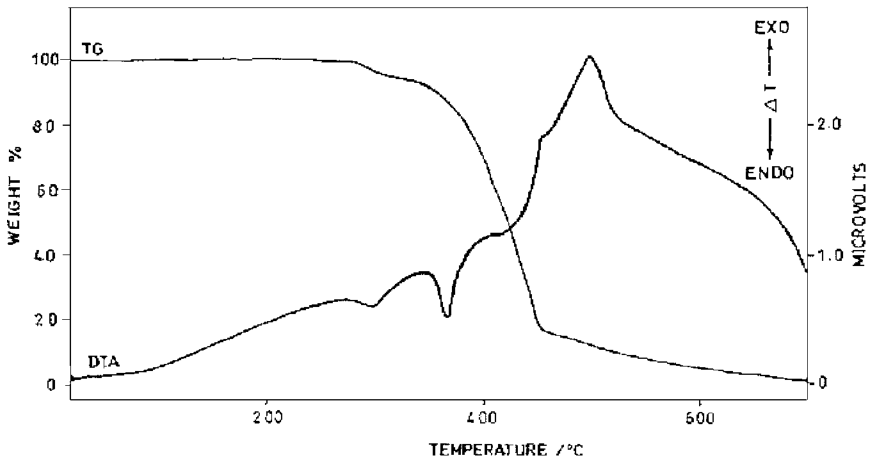


Fig. 3. TG–DTA curves of trimesic acid.

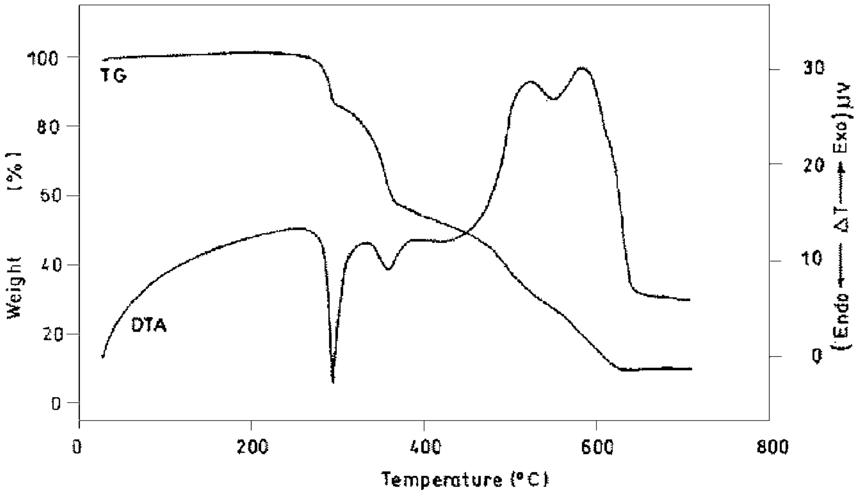


Fig. 4. TG–DTA curves of $N_2H_5H_2tms \cdot 2H_2O$.

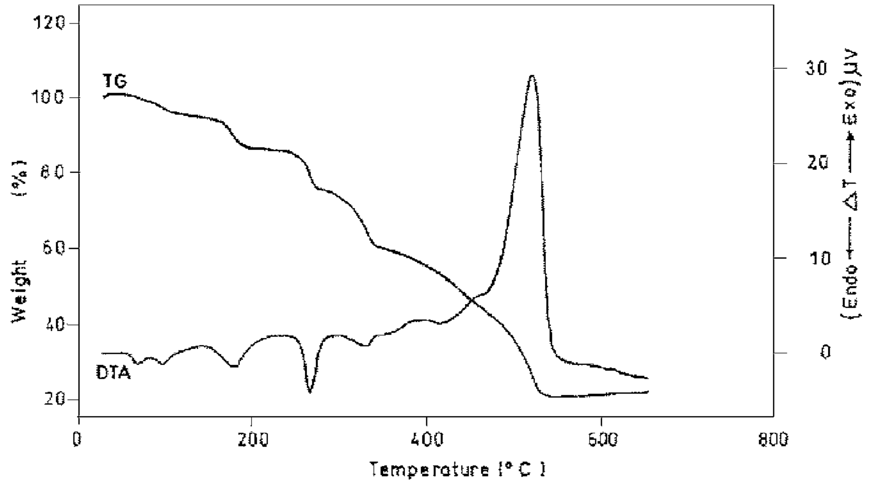


Fig. 5. TG–DTA curves of $(N_2H_5)_2Htms \cdot 2H_2O$.

6.3. $N_2H_5H_2tms{\cdot}2H_2O$ and $(N_2H_5)_2Htms{\cdot}2H_2O$

These trimesic acid salts follow a different type of degradation path unlike its isomeric salts. The monohydrazinum salt shows a high temperature dehydration in its first step of decomposition, displaying an endothermic peak at 283 °C corresponding to two water molecules. This may be due to the strong holding of water molecules by carboxyl groups through intermolecular hydrogen bonding. Hydrazine molecule accompanied by carbon dioxide, is liberated from the compound and this is inferred from the endothermic peak at 337 °C in its DTA. Finally it undergoes oxidative decomposition at 522 and 583 °C.

The dihydrazinium salt undergoes an endothermic dehydration showing peaks in its DTA, at 68 and 95 °C as a doublet, corresponding to elimination of one water molecule, and at 179 °C of another water molecule. Subsequently an endothermic dehydrazination occurs at 267 and 332 °C in which the latter shows elimination of hydrazine accompanied by carbon dioxide. The dicarboxylic acid formed as the intermediate decomposes continuously, showing an exothermic decomposition at 517 °C (Fig. 5).

The thermogram of trimesic acid shows that the acid liberates a water molecule at 290 °C forming intermolecular anhydride and a continuous decomposition occurs from 344 °C showing endothermic peaks at 368 °C and a strong exotherm at 500 °C. Above 300 °C, the pure acid and the acid intermediate show similar decomposition behaviour resulting carbon residue.

6.4. Pyromellitic acid salts

Pyromellitic acid salts show similar mode of decomposition in their thermograms which imply that they are identical in their thermal behaviour. All the salts lose hydrazine in the temperature range of 223–271 °C and they are completely decomposed in the range of 496–595 °C to give carbon residue, which could not be further investigated. Pure acid undergoes a two-step decomposition showing large endothermic maximum at 96 °C in the first step, corresponding to the removal of moisture and an endothermic triplet at 261, 286 and 314 °C due to slow melting and decomposing of acid to form pyromellitic anhydride and its immediate decomposition, in the second step. A broad exotherm is observed at 325 °C after which there is no significant mass loss.

6.4.1. $N_2H_5(H_3pml)$

This salt shows two doublet peaks in its DTA, an endothermic at 223 and 250 °C corresponding to the elimination of N_2H_4 molecule and an exothermic peaks at 496 and 594 °C leading to the oxidative degradation.

6.4.2. $(N_2H_5)_2(H_2pml)$ and $(N_2H_5)_3(Hpml)$

The thermograms of these salts show similarity in their thermal decomposition behaviour. They show two peaks in their DTA, endothermic peak in the range of 270–271 °C corresponding to the elimination of two hydrazine molecules and exothermic multiplets in the range of 500–595 °C implying their oxidative decomposition.

6.4.3. $(N_2H_5)_4\ (pml){\cdot}3H_2O$

This undergoes decomposition in three steps. First step shows an endothermic peak at 87 °C corresponding to the liberation of two water molecules. Second step shows an endothermic peak at 197 °C due to the elimination of one molecule each of hydrazine and water. Third step is a dehydrazination step at 263 °C where three molecules of hydrazine are eliminated. Finally at 505 and 583 °C oxidative decomposition occurs.

The thermogravimetry of all tricarboxylates and tetracarboxylates show a meta-stable step at about 450 and 496 °C and this may be attributed to the formation of benzene and its immediate oxidation.

7. Conclusions

Among benzene tricarboxylic acids, hemimellitic acid forms only monohydrazinium salt while other two isomers, trimellitic and trimesic acids form monohydrazinium and dihydrazinium salts. Pyromellitic acid (benzene 1,2,4,5-tetracarboxylic acid) forms all the possible salts, viz. monohydrazinium, dihydrazinium, trihydrazinium and tetrahydrazinium salts. The salt formation is highly dependent on pH of the reaction mixture. The existence of oxidation states of the various anions of pyromellitic acids has been established through their formation of metal carboxylates [15]. The same trend is noted with hydrazinium salts also.

All the salts undergo dehydrazination endothermally and oxidative decomposition exothermally via the respective acid intermediates. This is somewhat similar to the observation of our earlier work on pyridine dicarboxylic acids [16]. While comparing the thermal decomposition of pure acids at the same rate of heating, with that of acid intermediates, it is understood that acids, except trimesic acid, undergo complete decomposition exothermally at lower temperature region (below 400 °C) whereas the intermediates decompose exothermally at higher temperature above 300 °C slowly. Further, the intermediates of the decomposition of pure acids could not be made out because of their fast reaction in the narrow temperature region. Brzyska and co-workers have reported that benzene tricarboxylates decompose with a strong exothermic effect [17,18]. In this work it is found that irrespective of the number of carboxyl groups, the salts give strong exothermic decomposition in the temperature range 517–583 °C. Their thermal behaviour appears to be same near 480–520 °C. This may be probably due to same thermal degradation path via the formation of arene intermediates.

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