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Preparation, characterisation and thermal properties of some new hydrazinium carboxylates

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Abstract

Several hydrazinium (1 +) and dihydrazinium salts of aliphatic and aromatic carboxylic acids have been prepared by neutralisation of these acids with hydrazine hydrate in aqueous medium. They are hydrazinium hydrogendicarboxylates of malonic, succinic, glutaric and adipic acids, hydrazinium hydrogenphthalate monohydrate, hydrazinium carboxylates of benzoic, salicylic and *p*-hydroxybenzoic acids, and dihydrazinium dicarboxylates of succinic, phthalic, isophthalic and terephthalic acids. These salts have been characterised by analytical, IR spectral and thermal studies. IR spectra of all the salts show N–N stretching frequencies of the $N_2H_5^+$ ion in the region 960–990 cm^{-1}. Most of the salts undergo endothermic decomposition. Salts of benzoic acid and isophthalic acid show exothermic as well as endothermic decomposition whereas salt of terephthalic acid shows complete exothermic decomposition. All of them undergo complete decomposition to gaseous products.

Keywords: Carboxylate; Hydrazinium salt; IRS; TA

1. Introduction

Hydrazine is a diacidic base and forms salts with mineral as well as carboxylic acids. Hydrazine occurs as singly [hydrazinium (1+), $N_2H_5^+$] and doubly protonated [hydrazinium (2+), $N_2H_6^{2+}$] ionic salts. Hydrazinium (1 +) salts are the more common type and can be obtained with a variety of acids, whereas the hydrazinium (2+) salts are formed only with strong mineral acids [1–3]. The former salts have also been obtained by the reaction of solid ammonium salts [4–7] with hydrazine hydrate and

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the latter salts by double decomposition of hydrazine sulphate ($N_2H_6SO_4$), with the corresponding barium salts [3]. Some of these salts are used as flame retardants [8, 9] and proton conductors [10]. They have also been utilised for the preparation of metal hydrazinium/hydrazine complex [11–14].

In spite of the number of hydrazinium salts with mineral acids reported, there appears to be a limited number of hydrazinium salts of carboxylic acids reported in literature [15]. Even among them only a few salts, namely those of acetic [6], oxalic [16], EDTA [17] and formic [18] acids have been studied in detail. However, no systematic studies have been carried out on salts of aliphatic and aromatic carboxylic acids. We here report the preparation, spectral and thermal properties of these slats.

2. Experimental

All the salts reported here have been prepared by the neutralisation of the respective carboxylic acids in aqueous medium with hydrazine hydrate (99–100%) in appropriate molar ratios.

2.1. Preparation of hydrazinium hydrogendicarboxylates and hydrazinium carboxylates

To prepare hydrazinium hydrogenmalonate, the malonic acid (10.406 g, 0.1 mol dm^{-3}) was added to 50 ml distilled water and this was neutralised by hydrazine hydrate (5 ml, 0.1 mol dm^{-3}) diluted with 20 ml water. The resulting clear solution was concentrated on a hot water bath and kept in a vacuum desiccator for crystallisation. The colourless crystals obtained were separated, washed with alcohol and dried over P_2O_5.

The same procedure was repeated with a 1 : 1 molar ratio of the respective acids and hydrazine hydrate to prepare hydrazinium hydrogendicarboxylates of succinic, glutaric and adipic acids, hydrazinium hydrogenphthalate monohydrate and hydrazinium carboxylates of benzoic, salicylic and *p*-hydroxybenzoic acids.

2.2. Preparation of dihydrazinium dicarboxylates

These salts were prepared by mixing an aqueous solution of hydrazine hydrate (10 ml, 0.2 mol dm^{-3}) in 50 ml distilled water and the corresponding dicarboxylic acid, (e.g. succinic acid, 11.81 g, 0.1 mol dm^{-3}) in 50 ml water. The clear solutions obtained were concentrated and the salts isolated as before. In the case of dihydrazinium phthalate, the clear solution gave crystals only after keeping it at 7°C in a refrigerator for a month.

Hydrazinium hydrogenmalonate is slightly hygroscopic and dihydrazinium phthalate is low melting. Other salts are stable in air. Although hydrazinium(2+) formate, hydrazinium propionate and butyrate salts have been mentioned in the literature [15], our attempt to prepare these salts by the above method was not successful.

Hydrazine, in all the salts, was determined by titrating against standard KIO_3 solution (0.025 mol dm^{-3}) under Andrew's conditions [19]. The melting points were determined in capillaries and are uncorrected. Infrared spectra in the region 4000–400 cm^{-1} were recorded on pressed pellets of KBr using a Perkin-Elmer 597 spectrophotometer.

The DSC of the salts was carried out using a Perkin-Elmer DSC7 instrument. The TG curves of the salts were recorded on a Perkin-Elmer TGS-2 thermogravimetric system. Simultaneous TG–DTA studies were carried out using Shimadzu DT-40 and STA 1500 thermal analysers.

All the experiments were carried out in air using 5–10 mg of salts. Platinum cups were used as sample holders and alumina as reference. The heating rate employed was 10°C min^{-1}.

3. Results and discussion

All the hydrazinium and dihydrazinium salts prepared are white solids. The results of chemical analyses and the melting points are given in Table 1.

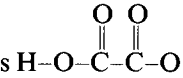
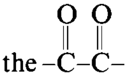
The analytical data agree well with the given formulae proposed for the salts. Hydrazinium hydrogenphthalate is monohydrated, $HOOC–C_6H_4–COON_2H_5 \cdot H_2O$, like other hydrated salts reported earlier [2, 6, 18]. This is supported by analytical, IR spectral and thermal data.

Table 1
Analytical and IR spectral data

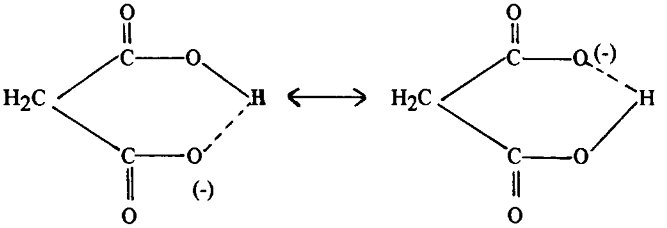
Compound	M.pt/°C	Hydrazine %		IR absorptions/cm^{-1}			
		Found	Calcd.	N–N str.	–COO– Asy. str	–COO– Sym. str	$\nu_{(C=O)}$ of COOH
$HOOCCH_2COON_2H_5$	235 (d)	23.90	23.54	965	1600	1370	1690
$HOOC(CH_2)_2COON_2H_5$	137	21.00	21.34	960	1600	1380	1690
$(CH_2COON_2H_5)_2$	115	34.90	35.18	960	1620	1390	–
$HOOC(CH_2)_3COON_2H_5$	60 (d)	19.80	19.52	960	1600	1410	1700
$HOOC(CH_2)_4COON_2H_5$	110	18.10	17.98	990	1610	1400	1690
$C_6H_5COON_2H_5$	112 (114.6) (r)	20.70	20.79	970	1585	1385	–
o-$HO–C_6H_4COON_2H_5$	110 (110.8) (r)	18.60	18.83	960	1590	1380	–
p-$HO–C_6H_4COON_2H_5$	175 (d)	18.40	18.83	980	1595	1390	
o-$HOOC–C_6H_4COON_2H_5 \cdot H_2O$	145 (d)	14.80	14.82	965	1600	1385	1685
o-$C_6H_4(COON_2H_5)_2$	50	27.60	27.84	960	1600	1380	–
m-$C_6H_4(COON_2H_5)_2$	82 (d)	28.00	27.84	975	1625	1395	–
p-$C_6H_4(COON_2H_5)_2$	105 (d)	27.70	27.84	975	1630	1390	–

Key: d, decomposes; r, reported value.

It is interesting to note that succinic acid forms both hydrazinium and dihydrazinium salts, whereas other aliphatic dicarboxylic acids form only hydrazinium salts. Of the aromatic dicarboxylic acids, phthalic acid forms both salts, whereas isophthalic and terephthalic acids form only dihydrazinium salts. The reasons are very difficult to generalise.

As reported [16], oxalic acid forms both salts. The hydrogenoxalate anion which is represented as  $H{-}O{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}O^-$ has a strong-I effect due to the  $-\overset{\overset{O}{\|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}O^-$ group which makes the O–H bond more labile. This leads to the formation of a dihydrazinium salt.

In the case of hydrogenmalonate anion, the O–H bond is stabilised by the formation of a six-membered ring anion due to strong intramolecular hydrogen bonding



Hence a proton cannot be abstracted by a weak base like N_2H_4, which prevents the formation of dihydrazinium salt.

In hydrogensuccinate anion, the intramolecular hydrogen bonding is not preferred due to an increase in size of the ring. Also the -I effect of the carboxylate group makes the O–H bond more labile. This helps to form the dihydrazinium salt.

In hydrogenglutarate and hydrogenadipate anions, the presence of more methylene groups makes the -I effect negligible on the O–H bond. Hence dihydrazinium salts are not formed.

In the case of aromatic dicarboxylic acids, the carboxyl groups are bonded to a rigid phenylene system and, hence, the pK_a values of the acids have been considered to explain the observed facts. The pK_a values of phthalic acid ($pK_{a_1} = 2.89$ and $pK_{a_2} = 5.51$) indicate that the carboxyl groups have quite different acidity and hence form both salts. The pK_a values of isophthalic acid ($pK_{a_1} = 3.54$ and $pK_{a_2} = 4.60$) and those of terephthalic acid ($pK_{a_1} = 3.51$ and $pK_{a_2} = 4.82$) indicate that the two carboxyl groups have almost the same acidity. This is the reason why the acid was not completely neutralised and soluble in a 1:1 molar aqueous mixture with hydrazine hydrate, even on heating. The filtrate of this mixture on crystallisation gave only dihydrazinium salts. Thus our attempt to prepare hydrazinium salts was not successful. Both carboxyl groups are neutralised almost simultaneously resulting in the formation of dihydrazinium salts only.

4. Infrared spectra

The important IR absorption bands along with their assignments are given in Table 1. The N–N stretching frequency of the free $N_2H_5^+$ ion is known [15] to occur in the 960–990 cm^{-1} region. The observed N–N stretching frequencies in the same region indicate the presence of $N_2H_5^+$ ion in these salts.

The hydrazinium hydrogendicarboxylates show IR absorption frequencies in the region 1680–1700 cm^{-1} due to carbonyl stretching of free carboxyl groups. All the salts show symmetric and asymmetric stretching frequencies of the carboxylate anions in the region 1360–1410 cm^{-1} and 1580–1630 cm^{-1}, respectively. The IR spectrum of hydrazinium hydrogenphthalate monohydrate shows a broad intense band in the region 3640–3030 cm^{-1} which is assigned to O–H stretching [20] of the water molecule.

5. Thermal studies

5.1. Hydrazinium hydrogenmalonate and hydrogenglutarate

The DSC/DTA and TG results are summarised in Table 2. The DSC and TG traces are given in Figs. 1(a), 1(d), 2(a) and 2(d). Both salts undergo direct decomposition without melting. While the former shows single-step decomposition in TG, the latter shows a two-step decomposition. These results are in accordance with the DSC showing an endotherm at 282 and 295°C as a doublet and two distinct endotherms at 90 and 266°C, respectively. The first endotherm at 90°C corresponds to the decomposition of the glutarate salt with the loss of N_2H_4, giving the acid as an intermediate which further decomposes endothermically at 266°C.

5.2. Hydrazinium hydrogensuccinate and hydrogenadipate

The DSC and TG traces of these salts are given in Figs. 1(b), 1(e), 2(b) and 2(e). These salts undergo melting followed by decomposition. While the former shows single-step decomposition in TG, the latter shows a two-step decomposition. These results are in accordance with the DSC traces. In succinate the DSC shows an endotherm at 138°C without weight loss, assigned to the melting temperature. The second broad endotherm with peak maximum at $\approx$ 165°C is assigned to the decomposition of the melt into gaseous products. For adipate, the DSC shows a sharp endothermic peak at 115°C corresponding to its melting point; the second endotherm near 170°C is attributed to dehydrazination of the melt to give the acid as an intermediate which further decomposes endothermically around 285°C to gaseous products.

5.3. Hydrazinium hydrogenphthalate monohydrate

The simultaneous TG and DTA traces of this salt are given in Fig. 6. It undergoes decomposition without melting. The TG shows a three-step decomposition in accordance with DTA showing three endotherms. The first endotherm at 47°C is due to loss of the water molecule and is supported by the weight loss in TG (found; 7.90%; calcd; 8.33%). The second endotherm at 175°C is assigned to dehydrazination to form phthalic acid as the intermediate. This intermediate undergoes endothermic decompo-

Table 2
Thermal data

Compound	DSC/DTA peak Temperature/°C	Thermogravimetry (TG)			Phenomenon
		Temp. range/°C	Weight loss %		
			Found	Calcd.	
$HOOCCH_2COON_2H_5$	$\left.\begin{array}{l}282(+)\\295(+)\end{array}\right\}$ d	240–420	98.00	100.00	Complete decomposition
$HOOC(CH_2)_2COON_2H_5$	138(+)	–	–	–	Melting
	165(+)	135–440	98.00	100.0	Complete decomposition
$(CH_2COON_2H_5)_2$	118(+)	–	–	–	Melting
	170(+)	130–250	35.00	35.18	Loss of two N_2H_4 molecules
	285(+)	250–420	99.00	100.00	Complete decomposition
$HOOC(CH_2)_3COON_2H_5$	90(+)	60–120	19.00	19.52	Loss of N_2H_4 molecule
	266(+)	180–320	98.00	100.00	Complete decomposition
$HOOC(CH_2)_4COON_2H_5$	115(+)	–	–	–	Melting
	170(+)	130–190	18.00	17.98	Loss of N_2H_4 molecule
	285(+)	190–425	99.00	100.00	Complete decomposition

$C_6H_5COON_2H_5$	113(+)	–	–	–	Melting
	150–200(+) (b) 215(−)	130–275	95.00	100.00	Decomposition
	340(+)	320–375	–	–	Tar decomposition
o-HO-$C_6H_4COON_2H_5$	108(+)	–	–	–	Melting
	205(+)	150–260	95.00	100.00	Decomposition
	340(+)	320–370	–	–	Tar decomposition
p-HO-$C_6H_4COON_2H_5$	210(+) 235(+) d	180–260	95.00	100.00	Decomposition
	325(+)	285–400	–	–	Tar decomposition
o-HOOC-$C_6H_4COON_2H_5 \cdot H_2O$	47(+)	35–70	7.90	8.33	Dehydration
	175(+)	150–205	23.50	23.16	Loss of N_2H_4 molecule
	328(+)	205–355	97.00	100.00	Complete decomposition
o-$C_6H_4(COON_2H_5)_2$	52(+)	–	–	–	Melting
	170(+) 190(+) d	140–200	28.00	27.84	Loss of two N_2H_4 molecules
	340(+)	200–350	98.00	100.00	Complete decomposition
m-$C_6H_4(COON_2H_5)_2$	120(−)	85–145	13.50	13.92	Loss of N_2H_4 molecule
	150(+) 195(+) d	145–205	27.20	27.84	Loss of two N_2H_4 molecules
	340(+)	205–355	96.00	100.00	Complete decomposition
p-$C_6H_4(COON_2H_5)_2$	169(−)	110–170	13.89	13.92	Loss of N_2H_4 molecule
	220(−)	170–228	27.78	27.84	Loss of two N_2H_4 molecules
	350(−)	228–360	100.00	100.00	Complete decomposition

Key: (+), endotherm; (−), exotherm; d, doublet; b, broad.

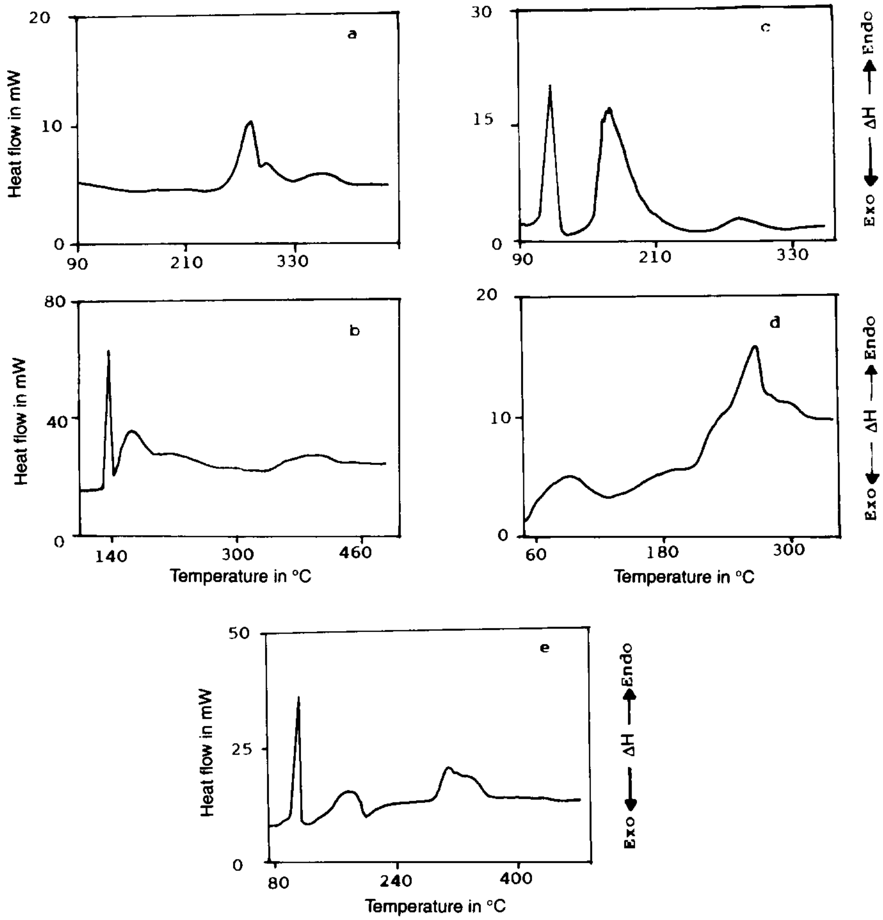


Fig. 1 DSC of: (a) hydrazinium hydrogenmalonate; (b) hydrazinium hydrogensuccinate; (c) dihydrazinium succinate; (d) hydrazinium hydrogenglutarate; (e) hydrazinium hydrogenadipate.

sition at 328°C corresponding to the temperature range 205–355°C in TG. This is in good agreement with the decomposition temperature, 211°C, of the free acid [21].

5.4. *Hydrazinium benzoate, salicylate and* p*-hydroxybenzoate*

The simultaneous TG and DTA traces of these salts are given in Figs. 3, 4 and 5, respectively. These salts show a single-step decomposition in TG. Benzoate and salicylate salts undergo decomposition after melting, whereas *p*-hydroxybenzoate undergoes decomposition without melting. The endotherms at 113 and 108°C, respectively, for benzoate and salicylate salts correspond to the melting points which are in agreement with the values reported [22]. For benzoate, the broad endotherm in the range 150–200°C and sharp exotherm at 215°C are assigned to 95% decomposition of

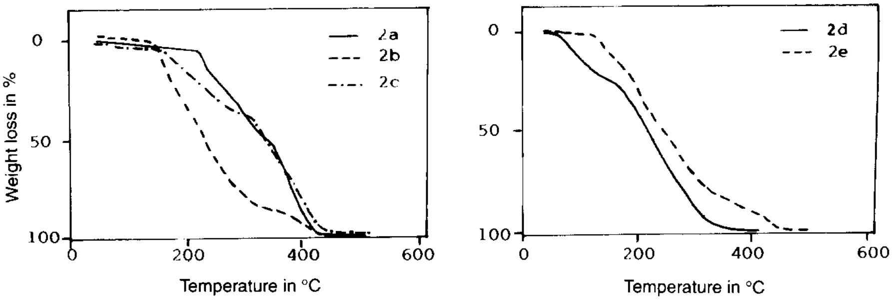
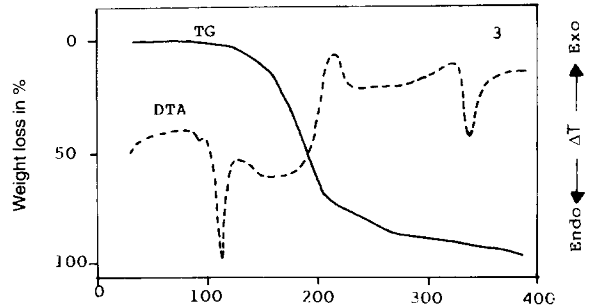


Fig. 2. TG of: (a) hydrazinium hydrogenmalonate; (b) hydrazinium hydrogensuccinate; (c) dihydrazinium succinate; (d) hydrazinium hydrogenglutarate; (e) hydrazinium hydrogenadipate.



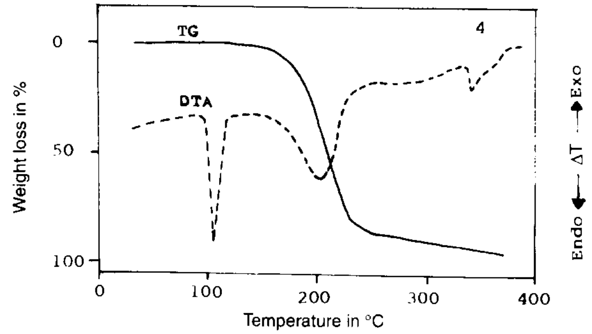
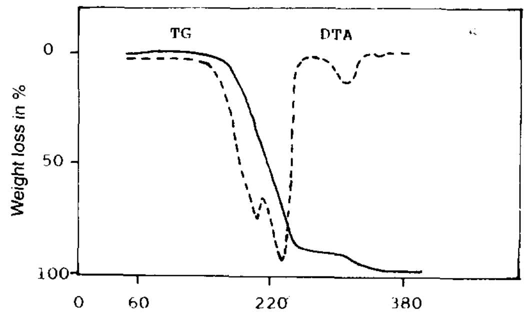


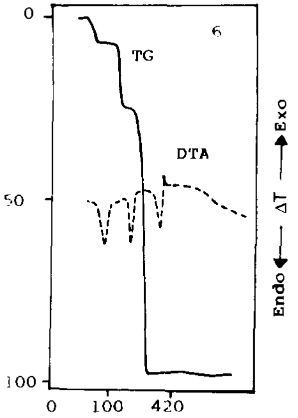
Fig. 3. Simultaneous TG–DTA of hydrazinium benzoate.

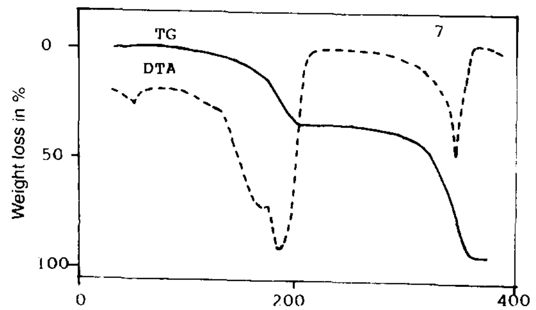
Fig. 4. Simultaneous TG–DTA of hydrazinium salicylate.

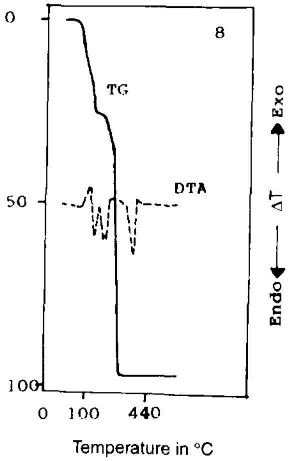
the salt. The endotherm at 205°C for salicylate is due to 95% decomposition. For *p*-hydroxybenzoate the endotherm at 210 and 235°C as a doublet corresponds to 95% decomposition of the salt.

After almost complete decomposition (about 95%) as seen in the TG curves, the DTA traces of these salts show endotherms at 340, 340 and 325°C, respectively. It is possible that there was a small amount of tar in the cup and the decomposition may be due to that tar [20] as shown by slight decomposition in the TG curves.









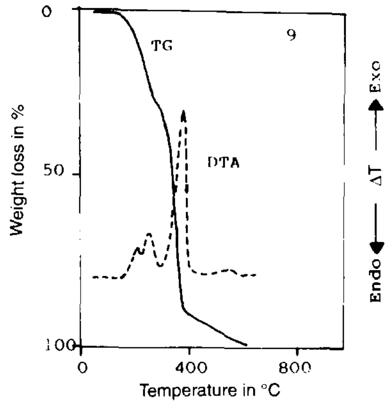


Fig. 5. Simultaneous TG–DTA of hydrazinium *p*-hydroxybenzoate.

Fig. 6. Simultaneous TG–DTA of hydrazinium hydrogenphthalate monohydrate.

Fig. 7. Simultaneous TG–DTA of dihydrazinium phthalate.

Fig. 8. Simultaneous TG–DTA of dihydrazinium isophthalate.

Fig. 9. Simultaneous TG–DTA of dihydrazinium terephthalate.

5.5. *Dihydrazinium succinate and phthalate*

The DSC and TG traces of succinate and simultaneous TG–DTA of phthalate salts are shown in Figs. 1(c), 2(c) and 7, respectively. They undergo decomposition after melting. Both salts show a two-step decomposition in the TG curves. These results are in accordance with the DSC and DTA traces. For succinate, the DSC shows an endotherm at 118°C which is assigned to its melting temperature. The endotherm at 170°C is assigned to the loss of two N_2H_4 molecules to form the acid as the intermediate. The endotherm at 285°C is assigned to decomposition of the intermediate to gaseous products.

For phthalate, the DTA trace shows an endotherm at 52°C corresponding to its fusion temperature. The endotherm at 170 and 190°C as a doublet is due to the loss of two N_2H_4 molecules to give phthalic acid which undergoes further endothermic decomposition at 340°C to gaseous products.

5.6. *Dihydrazinium isophthalate and terephthalate*

The simultaneous DTA and TG traces of these salts are given in Figs. 8 and 9 respectively. Both undergo decomposition without melting and show a three-step decomposition in TG. These results are in accordance with the DTA traces. For isophthalate the exotherm at 120°C is assigned to decomposition of the salt with the loss of one N_2H_4 molecule. The second endotherm at 150 and 195°C as a doublet is assigned to loss of a second N_2H_4 molecule to give the acid as the intermediate. This decomposes endothermically at 340°C to gaseous products. For terephthalate the exotherms at 169, 220 and 350°C, respectively, are assigned to the decomposition of the salt with the loss of the first and second N_2H_4 molecules and complete decomposition of the acid intermediate to gaseous products.

6. Conclusion

Malonic, glutaric and adipic acids do not form dihydrazinium salts, whereas isophthalic and terephthalic acids form only dihydrazinium salts. The hydrazinium and dihydrazinium salts of aliphatic acids reported here undergo endothermic decomposition, in contrast to the exothermic decomposition of the corresponding salts of oxalic acid [16]. While hydrazinium benzoate and dihydrazinium isophthalate undergo both exothermic and endothermic decompositions, the dihydrazinium terephthalate undergoes only exothermic decomposition and other salts undergo only endothermic decomposition.

Hydrazinium hydrogensuccinate, hydrogenadipate, benzoate and salicylate, and dihydrazinium succinate and phthalate undergo melting followed by decomposition, whereas the other salts decompose directly. Only hydrazinium salts of aromatic monocarboxylic acids undergo slight decomposition of the tar in the final stage after about 95% decomposition initially. All the salts reported here decompose completely to give gaseous products.

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