# Preparation, spectral and thermal studies of pyrazinecarboxylic acids and their hydrazinium salts

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**Abstract.** Some new hydrazinium 2-pyrazinecarboxylate and 2,3-pyrazinedi-carboxylate salts of the formulae $N_2H_5pc$, $N_2H_5pc.H_2O$ (Hpc = 2-pyrazinecarboxylic acid), $N_2H_5Hpdc$, $(N_2H_5)_2pdc.H_2O$ and $N_2H_5(Hpdc).H_2pdc$ ($H_2pdc$ = 2,3-pyrazinedi-carboxylic acid) have been prepared by neutralization of aqueous hydrazine hydrate with the respective acids in appropriate molar ratios. The free acids and their hydrazinium salts have been characterized by analytical, IR spectroscopic and thermal studies. IR spectra of all the salts show N–N stretching frequencies of the $N_2H_5^+$ ion in the region 975–960 $cm^{-1}$. The thermoanalytical behaviour of the free acids and their salts has been investigated by simultaneous TG and DTA. While pyrazinecarboxylic acid shows single-step endothermic (229°C) complete decomposition, pyrazindi-carboxylic acid shows exothermic decarboxylation followed by identical endothermic decomposition as that of the former. Similarly, salts of the monocarboxylic acid show endothermic effects during pyrolysis, whereas salts of the dicarboxylic acid show endothermic followed by exothermic decomposition. The acids and their salts both undergo complete decomposition to gaseous products.
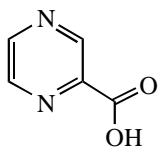
**Keywords.** Hydrazinium salts; pyrazinecarboxylic acids; IR spectra; thermal decomposition.

## 1. Introduction

Dibasic acids are known to form $N_2H_5HA$, $(N_2H_5)_2A$ and $N_2H_5HA.H_2A$ type salts ($H_2A$ = dibasic acid) with hydrazine. Though, a number of hydrazinium salts of the former two types with different dibasic acids have been reported,[1–6] there appears to be no report available in the literature on hydrazinium salts of the third type, viz., $N_2H_5HA.H_2A$, except with oxydiacetic acid.[4] However, such salts of oxalic acid with ammonium[7] and potassium,[7,8] and dipicolinic acid with sodium[9,10] have been studied in detail, including their crystal structures. The preparation of hydrazinium salts has become a subject of recent interest due to their wide use as additives in propellants, drugs to treat cancer and Hodgkin's disease, and explosives.[1] They have also been used as ligands for the preparation of metal hydrazinium/hydrazine complexes.[11–13] Some of these salts are also used as flame-retardants[14,15] and proton conductors.[16] Preparation and thermal behaviour of some salts from a few aliphatic[2,4] and aromatic[5] carboxylic acids have recently been

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reported from our laboratory. However, the thermal behaviour of pyrazine (hetero-aromatic) carboxylic acids and their hydrazinium salts has not been studied, except the low temperature (up to 500°C) decomposition of pyrazinedicarboxylic acid.[17] It is, therefore, considered interesting to prepare the hydrazinium salts of pyrazinecarboxylic acids and study their thermal properties. The results of these studies are presented in this paper. The structure of the 2-pyrazinecarboxylic and 2,3-pyrazinedicarboxylic acids is given below.
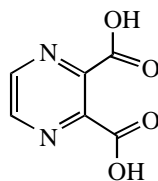


2-Pyrazinecarboxylic acid          2,3-Pyrazinedicarboxylic acid

## 2. Experimental

The hydrazinium salts were prepared by neutralization of the respective carboxylic acids and hydrazine hydrate (99–100%) in appropriate molar ratios. The acids were used as purchased (Merck) without further purification. All the other chemicals used were pure commercial grade and the solvents were distilled before use.

### 2.1 *Preparation of $N_2H_5pc$ and $N_2H_5pc.H_2O$*

Anhydrous hydrazinium pyrazinecarboxylate and its monohydrate were prepared by mixing hydrazine hydrate and 2-pyrazinecarboxylic acid in 1 : 1 and 1 : 2 molar ratios (0·5 ml, 0·01 mol and 1·241 g, 0·01 mol; 0·5 ml, 0·01 mol and 2·482 g, 0·02 mol respectively) in 50 ml of distilled water. The resulting turbid solutions were heated over a waterbath for an hour, to obtain clear solutions, and were kept for crystallisation in a vacuum desiccator over calcium chloride. While the anhydrous salt separated out after a week as white crystalline powder, the monohydrated hydrazinium salt crystallized as light pink spongy crystals from the filtrate, after the removal of the excess acid deposited as white crystals in a couple of days. Both salts were washed with alcohol and dried in air.

### 2.2 *Preparation of $N_2H_5Hpdc$ and $(N_2H_5)_2pdc.H_2O$*

To prepare hydrazinium hydrogen-2,3-pyrazinedicarboxylate and dihydrazinium pyrazinedicarboxylate monohydrate, stoichiometric quantities of the acid (1·6811 g, 0·01 mol; 1·6811 g, 0·01 mol) and hydrazine hydrate (0·5 ml, 0·01 mol; 0·1 ml, 0·02 mol, respectively) were mixed in 50 ml of distilled water and heated over a waterbath to get clear solutions. The resulting solutions were allowed to crystallize at room temperature. Monohydrazinium salt separated out as white needle-shaped crystals after five days, whereas spongy yellow colour dihydrazinium salt crystallized out only after two weeks. These salts were filtered off and washed with absolute alcohol and dried in vacuum.

## 2.3  *Preparation of $N_2H_5(Hpdc).H_2pdc$*

The aforesaid procedure was repeated with a 2 : 1 molar ratio of the acid (1·6811 g, 0·01 mol) and hydrazine hydrate (0·25 ml, 0·005 mol) to prepare the title salt. The yellow coloured salt was isolated as square shaped crystals after a week and dried as above. All the salts are highly soluble in cold water, insoluble in alcohol and stable in air.

## 2.4  *Physico-chemical techniques*

The hydrazine content of these salts was determined volumetrically using a standard (0·025 M) $KIO_3$ solution under Andrews' condition.[18] Melting points were determined on mettler FP 5 instrument and are uncorrected. IR spectra were recorded as KBr pellets with a Perkin–Elmer FT-IR 1000 spectrophotometer in the 4000–400 cm$^{-1}$ range. Elemental analyses were performed on a Perkin–Elmer 240 B CHN analyser. Simultaneous TG-DTA measurements were carried out using universal V2.5H TA instruments. The experiments were carried out in air using platinum cups as sample holders with 5–10 mg of the samples at the heating rate of 10°C min$^{-1}$, up to 800°C.

## 3.  Results and discussion

The analytical data of the salts were consistent with the proposed formulae for each (table 1). It is worth mentioning here that $N_2H_5HA.H_2A$ type of salt is also obtained with pyrazinedicarboxylic acid, apart from the regular mono- and dihydrazinium salts. Further, the p$Ka$ values of 2,3-pyrazinedicarboxylic acid (p$Ka_1$ = 0·8 and p$Ka_2$ = 2·84)[19] indicate that the carboxyl groups have quite different acidities and hence forms both mono- and dihydrazinium salts, as reported in other cases.[2,4,5] It is also to be noted that in different experimental conditions 2-pyrazinecarboxylic acid forms anhydrous as well as hydrated monohydrazinium salts.

**Table 1.**  Analytical data.

| Compound | m.pt./d.pt (°C) | Found (calculated) % | | | | |
|---|---|---|---|---|---|---|
| | | Colour | Hydrazine | Carbon | Hydrogen | Nitrogen |
| Hpc | 229 (225d)* | White | – | 48·21 (48·35) | 3·19 (3·25) | 22·45 (22·56) |
| $N_2H_5pc$ | 150 | White | 20·27 (20·49) | 38·12 (38·44) | 4·98 (5·17) | 35·13 (35·87) |
| $N_2H_5pc.H_2O$ | 154 | Light pink | 19·02 (19·38) | 34·39 (34·46) | 5·62 (5·78) | 31·93 (32·17) |
| $H_2pdc$ | 185 (188d)* | White | – | 42·16 (42·83) | 2·17 (2·39) | 15·89 (16·66) |
| $N_2H_5Hpdc$ | 215 | White | 15·22 (15·99) | 34·87 (35·98) | 3·33 (4·03) | 26·58 (27·99) |
| $(N_2H_5)_2pdc.H_2O$ | 197 | Yellow | 25·02 (25·59) | 27·78 (28·79) | 5·42 (5·64) | 33·68 (33·59) |
| $N_2H_5(Hpdc).H_2pdc$ | 119 | Yellow | 8·62 (8·69) | 39·87 (39·12) | 2·97 (3·29) | 23·01 (22·81) |

*Reported value; d: decomposition

**Table 2.**   IR spectral data ($cm^{-1}$).

| Compound | $n_{(OH)}$ of acid/water[a] | $n_{(NH)}$ | $n_{(C=O)}$ of acid | $n_{asy(OCO)}$ | $n_{sy(OCO)}$ | $n_{(N-N)}$ |
|---|---|---|---|---|---|---|
| Hpc | 3115(*s*) | 3064 2800 | 1716 | – | 1394 | – |
| $N_2H_5pc$ | – | 3282 3049 | – | 1623 | 1380 | 966 |
| $N_2H_5pc.H_2O$ | 3419(*b*) | 3243 3031 | – | 1622 | 1379 | 972 |
| $H_2pdc$ | 3266(*s*) | 3065 2846 | 1720 | – | 1360 | – |
| $N_2H_5Hpdc$ | 3334(*s*) | 3194 3071 2915 | 1732 | 1611 | 1433 | 972 |
| $(N_2H_5)_2pdc.H_2O$ | 3433(b) | 3283 3066 | – | 1615 | 1346 | 967 |
| $N_2H_5(Hpdc).H_2pdc$ | 3323(s) | 3203 | 1721 | 1633 | 1436 | 962 |

[a]*b*: broad; *s*: sharp

## 3.1   *Infrared spectra*

Important infrared absorption bands of the acids and their salts along with their band assignments are listed in table 2. The IR spectra of the hydrazinium pyrazinecarboxylate monohydrate and dihydrazinium pyrazinedicarboxylate monohydrate show a broad band at 3419 and 3433 $cm^{-1}$, respectively, due to O–H stretching of the water molecule. The N–N stretching frequency of the free $N_2H_5^+$ ion is known to occur in 990–960 $cm^{-1}$ region.[1] The observed N–N stretching frequencies in the region 975–960 $cm^{-1}$ clearly reveal the presence of $N_2H_5^+$ ion in these salts. The bands in the region 1640–1610 and 1450–1375 $cm^{-1}$, for these salts, are assigned for asymmetric and symmetric stretching frequencies of the carboxylate ions, respectively. The free carboxyl groups of the acids and salts show the free carbonyl asymmetric stretching frequencies in the region 1735–1715 $cm^{-1}$.

## 3.2   *Thermal studies*

In order to understand the mode of decomposition during pyrolysis, the simultaneous TG-DTA measurement of free acids and their hydrazinium salts was carried out and the results are provided in table 3.

3.2a   *2-Pyrazinecorboxylic acid, Hpc:*   DTA of the 2-pyrazinecarboxylic acid shows a sharp endotherm at 229°C due to melting with complete decomposition of the acid into gaseous products. Corresponding to this, the TG shows a distinct single step decomposition between 150 and 235°C with almost 100% weight loss. This decomposition temperature of the free acid is in good agreement with the literature value.[20]

3.2b   *Hydrazinium pyrazinecarboxylate, $N_2H_5pc$ and its monohydrate, $N_2H_5pc.H_2O$:*   Simultaneous TG and DTA curves show that the title salt is thermally stable up to 145°C and then it undergoes melting with decomposition. The sharp endotherm observed at

150°C, without weight loss, is assigned to the melting temperature. The melt further decomposes into gaseous products, in single step, between 155 and 320°C leaving a very small amount of tar (black residue) in the cup. The corresponding decomposition is observed as endothermic peaks at 207 and 315°C in DTA. The final endotherm at 561°C is attributed to the decomposition of small amounts of tar[5,12] in the cup as shown by the very low percentage of degradation in the TG curve.

**Table 3.** Thermal decomposition data.

| Compound | DTA peak temp (°C) | Thermogravimetry (TG) | | | Decomposition phenomena/product |
|---|---|---|---|---|---|
| | | Temp. range (°C) | Mass loss (%) | | |
| | | | Found | Calcd. | |
| Hpc | 229(+) | 150–235 | 99·00 | 100·00 | Melting with complete decomposition |
| $N_2H_5pc$ | 150(+) | – | – | – | Melting |
| | 207(+) | | | | |
| | 315(+) | 155–320 | 97·00 | – | Black residue |
| | 561(+) | 320–565 | 100·00 | 100·00 | Complete decomposition |
| $N_2H_5pc.H_2O$ | 114(+) | 38–140 | 10·00 | 10·33 | Dehydration |
| | 154(+) | – | – | – | Melting |
| | 177(+)*sh* | | | | |
| | 216(+) | | | | |
| | 323(+) | 140–480 | 100·00 | 100·00 | Complete decomposition |
| $H_2pdc$ | 185(+) | – | – | – | Melting |
| | 191(–) | 180–195 | 28·00 | 26·76 | Decarboxylation and formation of 2-pyrazinecarboxylic acid |
| | 225(+) | 195–230 | 99·00 | 100·00 | Complete decomposition |
| $N_2H_5Hpdc$ | 215(+) | – | – | – | Melting |
| | 221(+) | 198–225 | 59·00 | 59·96 | Pyrazine |
| | 441(–) | | | | |
| | 637(–)*sh* | | | | |
| | 671(–) | 225–680 | 99·00 | 100·00 | Complete decomposition |
| $(N_2H_5)_2pdc.H_2O$ | 197(+) | 160–200 | 7·00 | 7·19 | Melting with dehydration |
| | 206(–) | | | | |
| | 219(+) | 200–240 | 66·00 | 68·76 | Pyrazine |
| | 446(–) | | | | |
| | 678(–) | 240–690 | 99·00 | 100·00 | Complete decomposition |
| $N_2H_5(Hpdc).H_2pdc$ | 119(+) | 105–125 | 4·80 | 4·88 | Melting with elimination of water & formation of acid anhydride adduct |
| | 172(+) | | | | |
| | 183(+)*sh* | | | | |
| | 199(+) | 125–230 | 67·00 | 66·30 | 2-pyrazinecarboxylic acid |
| | 437(–) | | | | |
| | 650(–) | 230–655 | 99·00 | 100·00 | Complete decomposition |

(+): endotherm; (–): exotherm; *sh*: shoulder

The hydrated salt shows very similar modes of decomposition to that of the anhydrous salt with the exception of the first endotherm at 114°C due to dehydration. This loss of water is supported by the mass loss in TG (found: 10%; calcd: 10·33%).

3.2c	*2,3-Pyrazinedicarboxylic acid, $H_2pdc$:* DTA of pyrazinedicarboxylic acid shows a sharp endotherm at 185°C, without any weight loss in TG, assigned to its melting temperature which is in agreement with the reported value.[17] The TG shows two-stage mass loss in accordance with DTA indicating a sharp exotherm followed by an endotherm. The exotherm at 191°C is attributed to the decarboxylation of the melt to form 2-pyrazinecarboxylic acid, which further decomposes completely, identical to that of the free acid (table 3) showing an endotherm at 225°C.[20]

3.2d	*Hydrazinium hydrogenpyrazinedicarboxylate, $N_2H_5Hpdc$:* TG and DTA curves for the title salt show that it is thermally stable up to 210°C. The endothermic signal of the DTA at 215°C, characterises the melting for which no mass loss is observed in the TG as expected. The melt undergoes endothermic decomposition at 221°C and is assigned to the formation of the probable pyrazine intermediate, which further undergoes slow and steady continuous exothermic decompositions to gaseous products. From the successive exothermic (441 and 671°C) effects it follows that the pyrazine, after its pyrolytic synthesis, gradually sublimes from the crucible and evaporates at this relatively high temperature (b.p. of pyrazine, 115ºC). Such decomposition intermediates have been reported in the related pyridinedicarboxylic acid system.[22] The observed weight losses for the above steps compare favorably with theoretical values (table 3).

3.2e	*Dihydrazinium pyrazinedicarboxylate monohydrate, $(N_2H_5)_2pdc.H_2O$:*	TG of the dihydrazinium salt shows three stages of mass loss between the temperature range 160 and 690°C. The first stage, which occurs in the range 160–200ºC, is due to loss of water molecules. The corresponding sharp endothermic peak at 197°C in DTA is attributed to melting with dehydration. This loss of water is supported by the weight loss in TG (found: 7·00%; calcd: 7·19%). In the second stage, the anhydrous salt undergoes exothermic (206°C) and then endothermic (219°C) decomposition to give pyrazine as the probable intermediate, which further undergoes successive exothermic decompositions at 446 and 678°C to gaseous products as seen in the monohydrazinium salt. The exotherm observed at 206°C (table 3) is similar to that observed for free dicarboxylic acid due to decarboxylation.

3.2f	*Hydrazinium hydrogenpyrazinedicarboxylate pyrazinedicarboxylic acid, $N_2H_5$ $(Hpdc).H_2pdc$:* Simultaneous TG-DTA curves reveal that the elimination of water (119°C) takes place with the melting of the salt in an endothermic reaction. This type of cleavage of a water molecule has been reported earlier in the aromatic dicarboxylic acids[23] and the consequent adduct formation is supported by the TG weight loss (found: 4·8%; calcd: 4·88%). The anhydride adduct then decomposes endothermically at 172°C with shoulders around 183° and 199°C, possibly by further decarboxylation, to give pyrazinecarboxylic acid as an intermediate. The observed weight loss (67%) for this step agrees well with the theoretical value (66·30%). The formation of this acid intermediate is observed as an endotherm, instead of an exotherm (as observed in the decomposition of $H_2pdc$), and may be due to the combustion/secondary reaction in air of the primary product formed during pyrolysis. The acid intermediate decomposes gradually by further

decarboxylation and ring rupturing, leading to gaseous products as seen in the other cases.

Our effort to isolate the intermediates was unsuccessful due to their continuous degradation. Hence, we have tried to assign the possible intermediates as observed from the TG mass losses which are consistent with the calculated mass losses. Further, since the TG curves of all the salts show continuous decomposition, the loss of the hydrazine moiety has not been observed as a distinct step. However, from the DTA it is clear that these moieties undergo endothermic decomposition as reported in the related hydrazinium phthalate salts.[5] Thermograms of the monohydrazinium salts of 2-pyrazinecarboxylic and 2,3-pyrazinedicarboxylic acids are shown in figures 1 and 2 respectively, as representative examples.

## 4. Conclusions

It is interesting to observe that pyrazinedicarboxylic acid differs from simple aliphatic and aromatic dicarboxylic acids[2,5] in terms of its salt-forming ability. It forms three types of hydrazinium salts in three different molar ratios.

All the prepared salts undergo melting with decomposition. While hydrazinium salts of pyrazinecarboxylic acid show only endothermic decomposition, the salts of pyrazinedicarboxylic acid undergo both endothermic and exothermic decompositions, perhaps because one of the carboxylic groups is susceptible to decomposition due to the intramolecular hydrogen bond between the nitrogen atom and the carboxylic group in the ortho position. The reaction mechanism therefore is assumed to be as below in 2,3-pyridinedicarboxylic acid.[23]
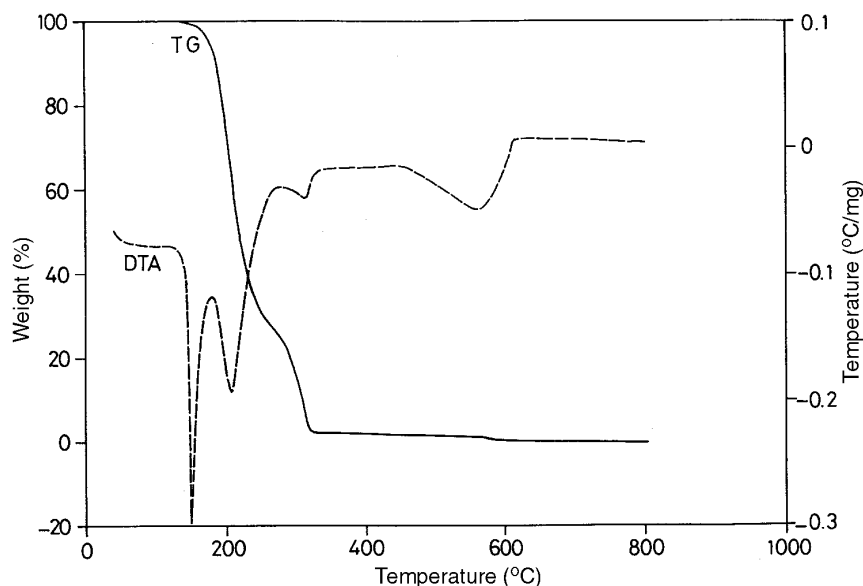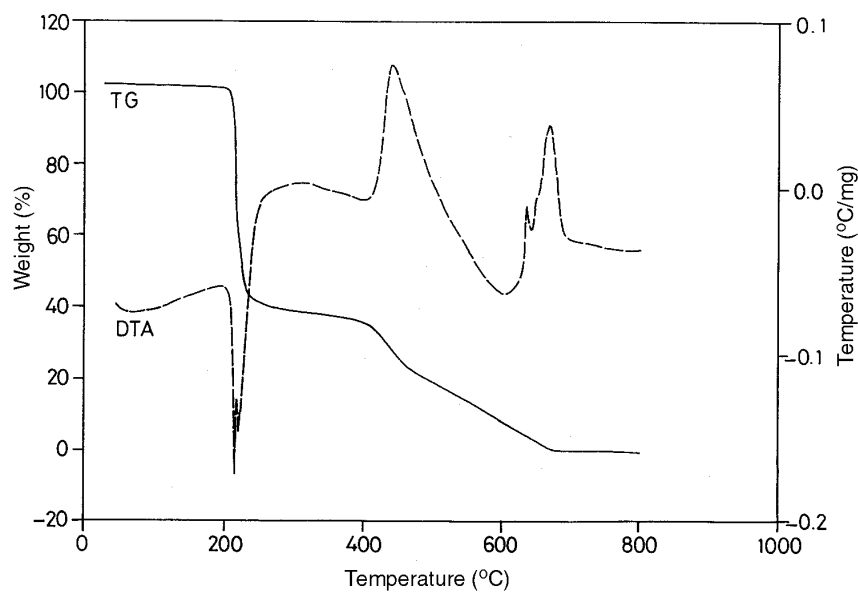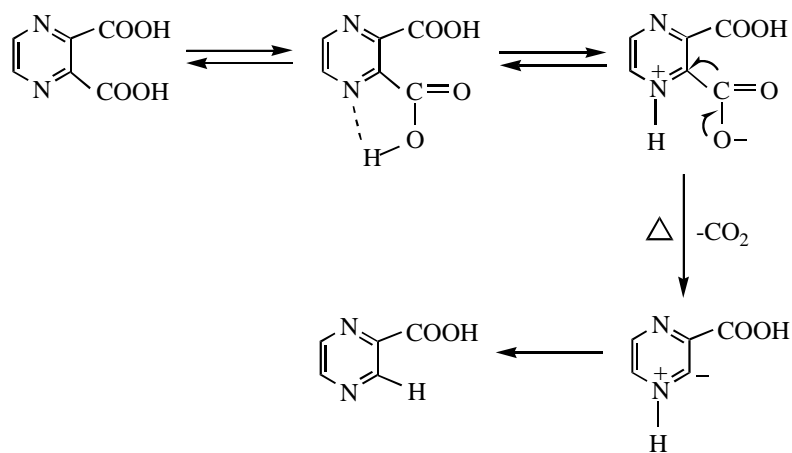


**Figure 1.** Simultaneous TG-DTA of $N_2H_5pc$.

**Figure 2.**  Simultaneous TG-DTA of $N_2H_5Hpdc$.



Also, salts of the former acid decompose at comparatively lower temperatures (around 330–480ºC) whereas salts of the latter undergo pyrolytic decomposition at higher temperatures (around 650°C), which may be ascribed to the additional hydrogen bonding network.

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