

## PREPARATION, CHARACTERIZATION AND THERMAL DECOMPOSITION OF AMMONIUM SALTS OF DITHIOCARBAMIC ACIDS

L. A. Ramos, É. T. G. Cavalheiro\* and G. O. Chierice

Departamento de Química e Física Molecular, Instituto de Química de São Carlos, USP, Av. do Trabalhador São-Carlense, 400 Centro, Caixa Postal 780, CEP: 13560-970 São Carlos, SP, Brazil

Pyrrolidinedithiocarbamate (Pyr), piperidinedithiocarbamate (Pip), morpholinedithiocarbamate (Mor) and diethanolaminedithiocarbamate (DEDC) ammonium salts; pyrrolidinedithiocarbamic acid-pyrrolidineammonium salt (HPyrPyr), piperidinedithiocarbamic acid-piperidineammonium salt (HPipPip), morpholinedithiocarbamic acid-morpholineammonium salt (HMorMor), hexamethylenedithiocarbamic acid-hexamethyleneammonium salt (HHexHex), diethanolaminedithiocarbamic acid-diethanolamineammonium salt (HDEAEDC) were synthesized, characterized by IR and elemental analysis and their thermal behaviours were investigated using thermogravimetry (TG) and differential scanning calorimetry (DSC).

**Keywords:** diethanolaminedithiocarbamic acid, DSC, hexamethylenedithiocarbamic acid, morpholinedithiocarbamic acid, piperidinedithiocarbamic acid, pyrrolidinedithiocarbamic acid, TG

### Introduction

Dithiocarbamates (DTC) are the reaction products between primary or secondary amine and carbon disulphide in basic media. These compounds have been widely used in analytical chemistry as complexing agents [1], fungicides [2], pesticides and insecticides in agriculture [3], and have a widespread application in the industry [4, 5]. The knowledge of their thermal properties is important since having such applications as mentioned above they submit to severe temperature changes [6].

They are also applied in medical fields, e.g. anti-alcoholic drug [7] and tuberculostatic agent [8]. More recently it is used as co-adjuvant agent in the treatment of AIDS disease [9].

Other examples of the importance and applications of the dithiocarbamates can be found in recent publications [10–13].

### Experimental

#### *Syntheses and characterization of DTC salts*

The  $\text{NH}_4^+$  salts of the dithiocarbamates were prepared by slow addition of 0.1 mol of  $\text{CS}_2$  to a cold mixture containing 0.1 mol of the amine (pyrrolidine, piperidine, morpholine, hexamethyleneimine or diethanolamine) and 0.1 mol of ammonium hydroxide dissolved in 30 mL of ethanol–water 1:1 (v/v). During the reaction the mixture was kept in an ice bath. The resulting solids

were recrystallised from ethanol–water 1:1 (v/v) and dried in a vacuum oven at 323 K (50°C) for 8 h [14, 15].

The  $\text{RNH}_2^+$  salts of the dithiocarbamates ( $R$ =pyrrolidine, piperidine, morpholine, hexamethyleneimine or diethanolamine), were prepared in similar way, by slow addition of 0.1 mol of  $\text{CS}_2$  to a cold solution containing 0.2 mol of the amine (pyrrolidine, piperidine, morpholine, hexamethyleneimine or diethanolamine) dissolved in 30 mL of ethanol–water 1:1 (v/v) medium. During the reaction the mixture was kept in an ice bath. The obtained solids were recrystallised from ethanol–water 1:1 (v/v) and dried in a vacuum oven at 323 K (50°C) for 8 h [14, 15].

In all cases the reaction products were characterized by elemental analysis (C, N, H) and infrared spectroscopy.

### Equipment

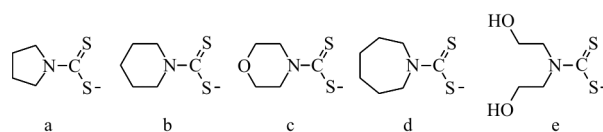
The compounds were characterized by IR spectroscopy (KBr pellets) in a Bomen MB-102-FTIR spectrophotometer. The C, H and N contents were determined by elemental analysis using a Fisons EA 1108 CNHS-O instrument. The TG curves were recorded using a DuPont 2100 thermoanalyser coupled to a TGA 951 thermobalance under a 320 mL  $\text{min}^{-1}$  nitrogen gas flow, in a Pt crucible, at 5 K  $\text{min}^{-1}$  heating rate and the sample mass was about 7 mg for each compound at atmospheric pressure. The DSC curves were recorded in a DuPont 2100 thermoanalyser coupled to a DSC 910 mod-

\* Author for correspondence: cavalheiro@iqsc.usp.br

ule under nitrogen purging (flow rate: 320 mL min<sup>-1</sup>), in hermetic aluminium pans, at 5 K min<sup>-1</sup> heating rate and the initial sample mass was about 5 mg for each compound at atmospheric pressure. The DSC cell was calibrated using metal In (>99.9%) as standard for temperature and energy changes.

## Results and discussion

The prepared compounds are listed in Table 1 and their given formulas are in a good agreement with the elemental analyses and IR data. The formulas of ligands are presented in Fig. 1. The IR spectra show double bands in the 950–1050 cm<sup>-1</sup> range for all the compounds confirming their saline character [16].



**Fig. 1** Formulas of dithiocarbamate derived from:  
a – pyrrolidine, b – piperidine, c – morpholine,  
d – hexamethyleneimine and e – diethanolamine

According to the literature, a single band in this region is due to the bidentate behaviour of the ligand that causes an equivalent stretching of both  $\nu(\text{C-S})$  bonds. However when a saline or monodentate behaviour is observed the  $\nu(\text{C-S})$  bonds are non-equivalent and they appear in the IR spectra as doublet bands. The characteristic  $\nu(\text{C-N})$  bond in the dithiocarbamates is represented by the strong absorption in the 1500–1400 cm<sup>-1</sup> range [16].

## Thermal results of the NH<sub>4</sub><sup>+</sup> salts

The thermal events, residues, mass losses and temperature ranges observed in each step of the recorded

TG/DTG and DSC curves for NH<sub>4</sub>Pyr, NH<sub>4</sub>Pip, NH<sub>4</sub>Mor and NH<sub>4</sub>DEDC are given in Fig. 2 and Table 2.

The shapes of TG/DTG curves suggest that the decomposition of the NH<sub>4</sub><sup>+</sup> salts took place in a multi-step overlapping processes, except in case of NH<sub>4</sub>Pip for which the DTG curve showed only one decomposition step. The observed temperature range is characteristic for each salt and the process did not result residue in the crucible.

However, the DSC curves exhibited different decomposition processes involving physical changes as described below. The samples were heated in a Vaseline bath in a test tube and the decomposition products were characterised on the basis of their physical appearances.

### NH<sub>4</sub>Pyr

The DSC curve showed several endothermic peaks. The first one was related to the loss of a NH<sub>3</sub> and occurred from the beginning of the heating generating pyrrolidinedithiocarbamic acid. The loss of NH<sub>3</sub> was confirmed by the characteristic smell of the evolved gas which was bubbled through a phenolphthalein solution while turned to red. The acid melts at 405 K (132°C), and its formation was confirmed by IR analysis of the liquid phase. Then the HPyr decomposed and H<sub>2</sub>S was liberated which was identified by its characteristic smell. Such observations are in agreement with the previously reported data [14].

### NH<sub>4</sub>Pip and NH<sub>4</sub>Mor

Both melting was followed by evaporation. The volatilization of the salt is evidenced by the crystals condensed on the walls of the tube and was confirmed by IR spectra.

**Table 1** Results of the characterization of the dithiocarbamate salts: FTIR bands, and their analytical data

Compound	Found (calc.)/%						FTIR bands/cm <sup>-1</sup>		
	C		N		H		$\nu_{\text{CN}}$	$\nu_{\text{CS}}$	
NH <sub>4</sub> Pyr	38.39	(36.56)	16.66	(17.05)	7.39	(7.36)	1416	991	1004
HPyrPyr	49.63	(49.50)	13.76	(12.83)	8.25	(8.31)	1465	939	997
NH <sub>4</sub> Pip	41.50	(40.42)	15.60	(15.71)	7.95	(7.91)	1464	971	1002
HPipPip	52.43	(53.61)	11.94	(11.37)	8.59	(9.00)	1460	972	1001
NH <sub>4</sub> Mor	33.29	(33.31)	15.68	(15.54)	6.79	(6.71)	1453	995	1023
HMorMor	43.57	(43.17)	12.05	(11.19)	7.25	(7.25)	1452	986	1023
NH <sub>4</sub> DEDC	30.72	(30.29)	13.65	(14.13)	6.99	(7.12)	1467	972	1024
HDEAEDC	37.62	(37.74)	10.04	(9.78)	7.86	(7.74)	1464	978	1044
HHexHex	56.78	(56.89)	10.30	(10.21)	9.43	(9.55)	1476	975	1012

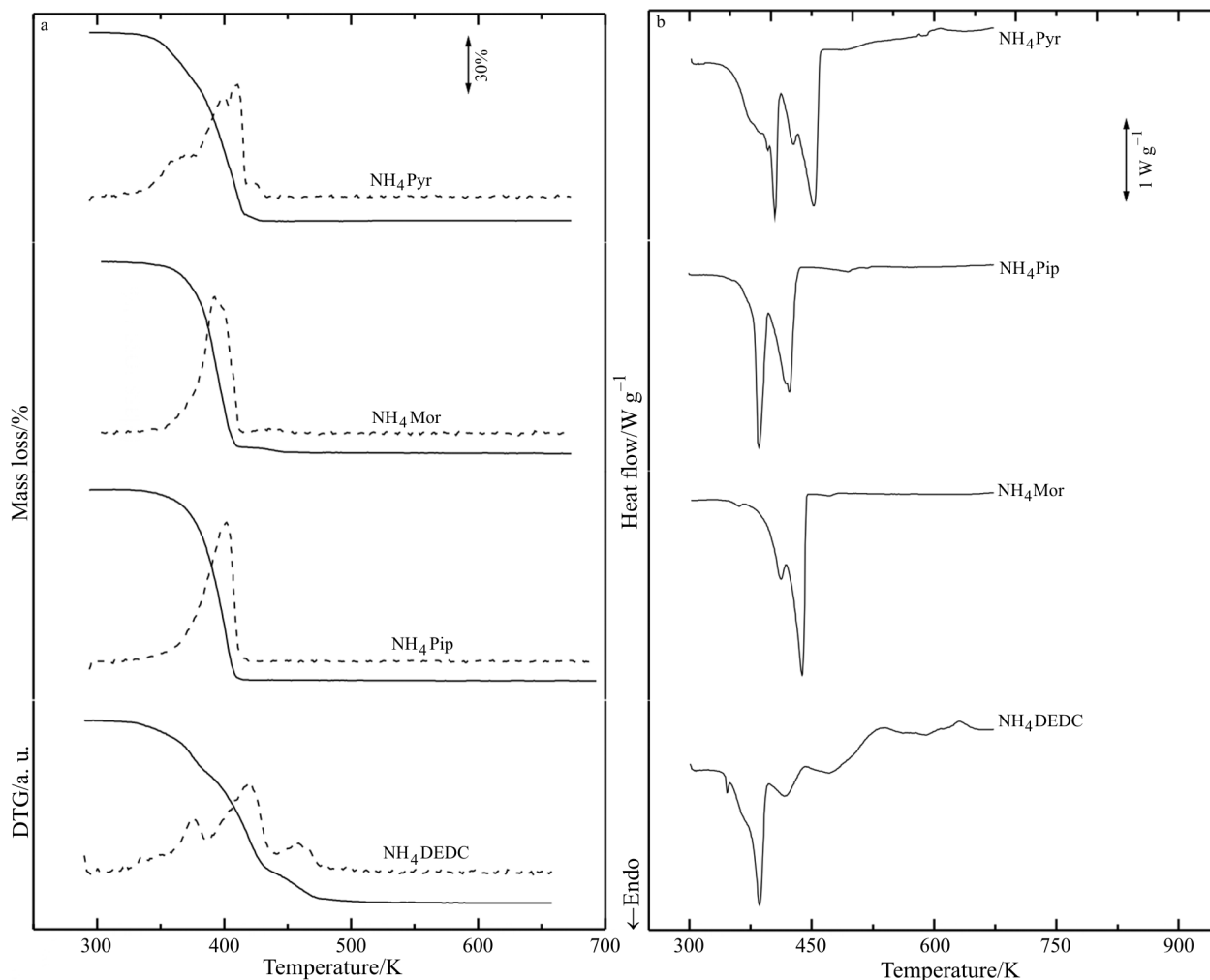


Fig. 2 a ——— TG and --- DTG curves of the dithiocarbamate salts; b – DSC curves of the salts

#### *NH<sub>4</sub>DEDC*

The DSC curve presented an endothermic peak at 386 K (113°C) attributed to the melting of the salt. The liquid compound decomposed by endothermic processes.

#### Thermal results of the $\text{RNH}_2^+$ salts

All transitions, temperature ranges, mass losses and DSC analyses were carried out under nitrogen purging and the results are presented in Table 2. The TG/DTG and DSC curves are presented in Fig. 3.

The TG curves presented a single mass loss step between specific temperatures for each compound, while the DTG curve of HHexHex indicated a multi-step process.

The DSC curves of both HPyrPyr and HHexHex indicated melting followed by volatilization of the HPyrPyr and HHexHex. It was also confirmed by the

IR spectrum analysis of the condensed material inside the test tube. The HPipPip and HMorMor curves presented a single endothermic peak related to the sublimation of the compounds. This sublimation process was confirmed by IR spectra of the sublimate condensed in the test tube.

The DSC curve of HDEAEDC presented a complex decomposition mechanism. The onset temperature for melting is 296 K (23°C) with a peak at 304 K (31°C). In the sequence several endothermic decomposition peaks can be observed between 413 K (140°C) and 573 K (300°C). The endothermic peak observed at 423 K (150°C) should be related to the dehydration of the diethanolamine in order to produce morpholine, since the peaks at 473 K (200°C) are coincident with the decomposition of the HMorMor.

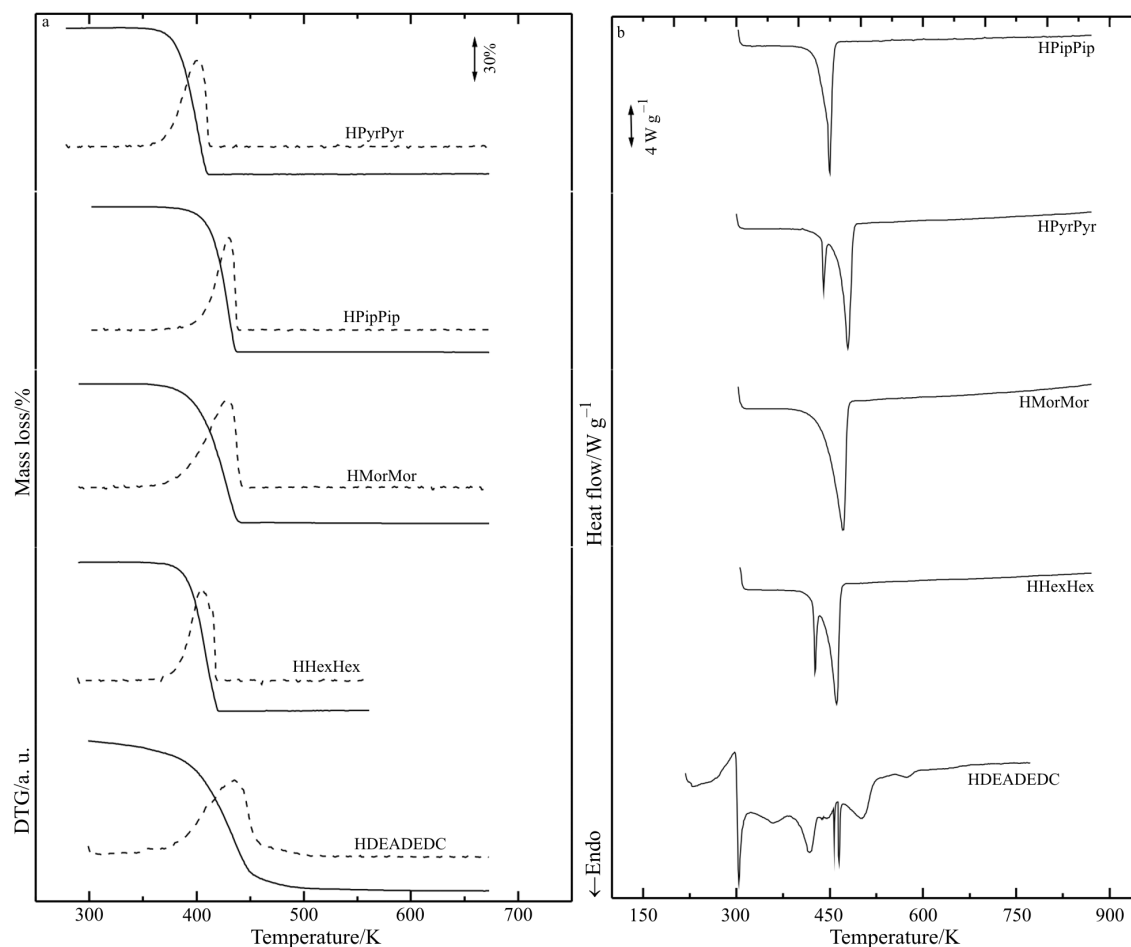


Fig. 3 a — TG and --- DTG curves of the dithiocarbamate salts; b – DSC curves of the salts

Table 2 TG (mass losses, residues and temperature range) and DSC data corresponding to the composition of the dithiocarbamate under nitrogen

Process	$T_{\text{range}}/\text{K}$	Mass loss or residue/%		DSC peak temperature <sup>a</sup> /K
		TG	calc.	
$\text{NH}_4\text{Pyr} \rightarrow \text{HPyr} + \text{NH}_3$	293–359	11.11	10.37	–
$\text{HPyr}_{(s)} \rightarrow \text{HPyr}_{(l)}$	363–413	–	–	369, 405 endo
$\text{HPyr}_{(l)} \rightarrow \text{decomposition with liberation of H}_2\text{S}$	413–473	100	–	428, 453 endo
$\text{NH}_4\text{Pip}_{(s)} \rightarrow \text{NH}_4\text{Pip}_{(l)}$	323–398	–	–	385 endo
$\text{NH}_4\text{Pip}_{(l)} \rightarrow \text{NH}_4\text{Pip}_{(g)}$	398–473	100	–	424 endo
$\text{NH}_4\text{Mor}_{(s)} \rightarrow \text{NH}_4\text{Mor}_{(l)}$	367–418	–	–	411 endo
$\text{NH}_4\text{Mor}_{(l)} \rightarrow \text{NH}_4\text{Mor}_{(g)}$	418–460	100	–	439 endo
$\text{NH}_4\text{DED C}_{(s)} \rightarrow \text{NH}_4\text{DED C}_{(l)}$	289–399	–	–	346, 386 endo
$\text{NH}_4\text{DED C}_{(l)} \rightarrow \text{decomposition}$	399–493	100	–	419, 476 endo
$\text{HPyrPyr}_{(s)} \rightarrow \text{HPyrPyr}_{(l)}$	343–493	–	–	440 endo
$\text{HPyrPyr}_{(l)} \rightarrow \text{HPyrPyr}_{(g)}$	343–493	100	–	480 endo
$\text{HPipPip}_{(s)} \rightarrow \text{HPipPip}_{(g)}$	363–453	100	–	444 endo
$\text{HMorMor}_{(s)} \rightarrow \text{HMorMor}_{(g)}$	353–493	100	–	472 endo
$\text{HHexHex}_{(s)} \rightarrow \text{HHexHex}_{(l)}$	353–463	–	–	426 endo
$\text{HHexHex}_{(l)} \rightarrow \text{HHexHex}_{(g)}$	353–463	100	–	461 endo
$\text{HDEAED C}_{(s)} \rightarrow \text{HDEAED C}_{(l)}$	223–323	–	–	303, 368 endo
$\text{HDEAED C} \rightarrow \text{decomposition}$	323–873	100	100	416, 457, 465, 503, 574 endo

<sup>a</sup>exo – exotherm process, endo – endotherm process.

## Conclusions

Most of the salts presented the volatilization process instead of decomposition even in relatively low temperatures, as evidenced the TG/DTG, DSC curves and the test tube experiments. The decomposition process was observed only for NH<sub>4</sub>Pyr and for HDEADED. C.

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