

Preparation, characterization and thermal decomposition of sodium and potassium salts of dithiocarbamate

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Abstract

Pyrrolidinedithiocarbamate (Pyr), piperidinedithiocarbamate (Pip), morpholinedithiocarbamate (Mor), diethanolaminedithiocarbamate (DEDC) and hexamethylenedithiocarbamate (Hex) sodium and potassium salts, were synthesized, characterized by IR, elemental analysis, ¹H and ¹³C NMR and their thermal behaviors were investigated using thermogravimetry (TG) and differential scanning calorimetry (DSC). The decomposition of sodium salts occurred in different manner depending on the nature of the substituent, generating sodium polysulphides. The potassium salts decomposed via thiocyanate as predicted in the literature.

Keywords: Diethanolaminedithiocarbamate, DSC, hexamethylenedithiocarbamate, morpholinedithiocarbamate, piperidinedithiocarbamate, Pyrrolidinedithiocarbamate, TG, thermal decomposition.

1. Introduction

Dithiocarbamates (DTC) are the reaction products between primary or secondary amine and carbon disulphide in basic media. Depending on the nature of the amine used in the synthesis of these compounds, mono or dialkyldithiocarbamates are formed.

Dithiocarbamates have been studied extensively over last decades in a response to their growing applications in many new areas of chemistry, industry and medicine [1-3]. They have also been used in agriculture as insecticides, herbicides and fungicides. Additional uses are as biocides for industrial or other commercial applications, and in household products. Some are used as vector control in public health [4]. The thermochemistry of metal dithiocarbamate has been extensively reported and reviewed [5-10].

Despite their importance as reaction intermediates and precursors of metallic complexes the sodium and potassium salts of dithiocarbamates are rarely described in the literature in relation to their thermal properties [11-13]. In addition, it should be noted that the preparation of potassium salts is not so easy to perform since the yields are usually very low, this new synthesis strategies are important in order to improve the quantity of salts prepared in a reaction procedure [14, 15].

In this sense few is known about dialkyldithiocarbamates salts of the general formula M[S₂CNR]; M = Na⁺ or K⁺, and R = pyrrolidine (Pyr), piperidine (Pip), morpholine (Mor), hexamethylene (Hex), diethanolamine (DEDC) regarding their thermal behavior [16]. These salts are used to prepare the complexes with general formula ML₂ (M = Ag⁺, Co²⁺, Cu²⁺, Fe³⁺, Hg²⁺,

Mn²⁺, Ni²⁺ and Zn²⁺) whose thermal behavior were described earlier [17-22]. Considering their relevance and the few data described the present work deals with the thermal analysis (TG/DTG and DSC) study of Na[S₂CNR] and K[S₂CNR] in order to contribute the understanding their thermal decomposition pathway.

2. Experimental

2.1. Synthesis and characterization of DTC salts

The Na⁺ salts of the dithiocarbamates were prepared by slow addition of 0.1 mol of CS₂ to a cold mixture containing 0.1 mol of the amine (pyrrolidine, piperidine, morpholine, hexamethyleneimine or diethanolamine) and 0.1 mol of sodium 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 in a minimum volume of ethanol-water 1:1 (v/v) filtered in syntherized glass filters and dried in a vacuum oven at 50°C for 8 h [13, 21].

The K⁺ salts of the dithiocarbamates were prepared in similar way, by slow addition of 0.1 mol of CS₂ to a cold mixture containing 0.1 mol of the amine (pyrrolidine, piperidine, morpholine, hexamethyleneimine or diethanolamine) and 0.1 mol of potassium hydroxide dissolved in 30 mL of isopropyl alcohol-water 5:1 (v/v). During the reaction the mixture was kept in an ice bath. The reaction should be conducted in isopropyl alcohol/water 5:1 (v/v) as solvent in order to reach the best yield according to our investigation. The resulting solids were recrystallised from isopropyl alcohol filtered in syntherized glass filters and dried in a vacuum oven at 50°C for 8 h [13, 21].

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In all cases the reaction products were characterized by elemental analysis (C, N, H), infrared spectroscopy (FTIR) and ^1H and ^{13}C NMR spectrum.

2.2. Equipment

IR spectra (KBr pellets) were taken in a Bomem MB-102-FTIR spectrophotometer. The C, H and N contents were determined by elemental analysis using a Fisons EA 1108 CNHS-O instrument. The ^1H and ^{13}C NMR spectra were obtained in a Bruker ARX photometer, with 200 MHz frequency using D_2O as solvent.

The TG curves were recorded using a DuPont 2100 thermoanalyser coupled to a TGA 951 thermobalance under a 300 mL min^{-1} nitrogen gas flow, in a Pt crucible, at $5\text{ }^\circ\text{C min}^{-1}$ heating rate and the samples of about 7 mg for each compound at atmospheric pressure. Heating rate $5\text{--}20\text{ }^\circ\text{C min}^{-1}$ and gas flow $25\text{--}300\text{ mL min}^{-1}$ were optimized prior to the thermal investigation using about 7 mg of $\text{NaPyr}\cdot 2\text{H}_2\text{O}$ as a probe in a Pt crucibles. Temperature range from room temperature to $800\text{ }^\circ\text{C}$.

The DSC curves were recorded in a DuPont 2100 thermoanalyser coupled to a DSC 910 module under nitrogen purging (flow rate: 300 mL min^{-1}), in aluminum pans, at $5\text{ }^\circ\text{C min}^{-1}$ heating rate and 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 as recommended by the manufacturers. Temperature range from room temperature to $600\text{ }^\circ\text{C}$.

3. 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 Figure 1. The IR spectra show double bands in the $950\text{--}1050\text{ cm}^{-1}$ range attributed to $\nu(\text{C-S})$ for all the compounds confirming their saline character [23].

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

Compound	Found (calc.)/%			FTIR bands/ cm^{-1}	
	C	N	H	νCN	νCS
NaPyr.2H₂O	29.15 (29.26)	6.78 (6.82)	5.90 (5.89)	1461	942 998
KPyr	31.83 (32.40)	7.83 (7.56)	4.22 (4.35)	1461	947 1004
NaPip.2H₂O	33.10 (32.86)	6.45 (6.39)	6.48 (6.43)	1470	942 999
KPip.2H₂O	30.62 (30.61)	5.97 (5.95)	6.07 (5.99)	1468	968 1005
NaMor.2H₂O	27.65 (27.14)	6.46 (6.33)	5.64 (5.47)	1463	982 1025
KMor.H₂O	27.53 (27.38)	6.42 (6.39)	4.47 (4.59)	1450	975 1012
NaDEDC	28.56 (29.55)	6.61 (6.89)	4.93 (4.96)	1465	969 1042
KDEDC	27.77 (27.38)	6.49 (6.39)	4.60 (4.59)	1466	1019 1033
NaHex.2H₂O	56.78 (56.89)	10.30 (10.21)	9.43 (9.55)	1485	975 1010

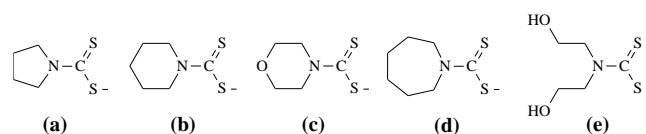


Figure 1. Formulas of dithiocarbamate derived from: (a) pyrrolidine (Pyr), (b) piperidine (Pip), (c) morpholine (Mor), (d) hexamethyleneimine (Hex) and (e) diethanolamine (DEDC).

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 $\nu(\text{C-N})$ bonds. However when a saline or monodentate behaviour is observed the $\nu(\text{C-N})$ 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 $1500\text{--}1400\text{ cm}^{-1}$ range [23].

The ^1H and ^{13}C NMR data are represented in Table 2. The chemical shift of the protons and carbon signals are not markedly different for K^+ and Na^+ salts since the compounds are dissociated in aqueous phase. Small shifts can be observed depending on the nature of the amminic substituent, mainly for the oxygenated Mor and DEDC.

Table 2. ^{13}C -NMR and ^1H -NMR data for dithiocarbamate salts

Compound	^{13}C -(D_2O) ppm			^1H -(D_2O) ppm			
	δ_1	δ_2	δ_3	δ_1	δ_2	δ_3	δ_4
NaPyr	193.37	45.83	16.52	---	3.75	1.96	---
KPyr	194.02	45.73	16.40	---	3.73	1.96	---
NaPip	196.02	43.89	16.52	14.66	4.21	1.56	1.53
KPip	196.02	43.85	16.66	14.82	4.19	1.56	1.53
NaMor	200.19	42.38	57.16	---	4.32	3.75	---
KMor	200.13	42.12	56.87	---	4.36	3.74	---
NaDEDC	202.08	50.01	47.63	---	4.25	3.87	---
KDEDC	201.82	49.98	47.57	---	4.28	3.94	---
NaHex	197.64	46.33	17.64	17.23	4.13	1.73	1.53

3.1. Definitions of thermal analysis conditions

During a preliminary study the NaPyr showed a dehydration process followed by the decomposition and formation of an unstable residue, which agrees with earlier findings [24]. After the residue formation, an oxidation can be observed, which was not expected in nitrogen. So an investigation to optimize the gas flow that could prevent this oxidative process was performed. The results are presented in Figure 2.a, in which it is possible to observe that a stable residue was obtained only at 300 mL min^{-1} ; even in pure N_2 (99.999%). This was attributed to a non-effective sealing of the furnace. However the relatively high gas flow was possible since the horizontal furnace configuration admits the gas in 90° in relation to the balance arm axis, preventing turbulence. This is confirmed by the stable TG/DTG profiles.

It was also found that the heating rate influenced the TG curves. Best results were obtained when heating the sample at $5\text{ }^\circ\text{C min}^{-1}$, according to the data in Figure 2.b.

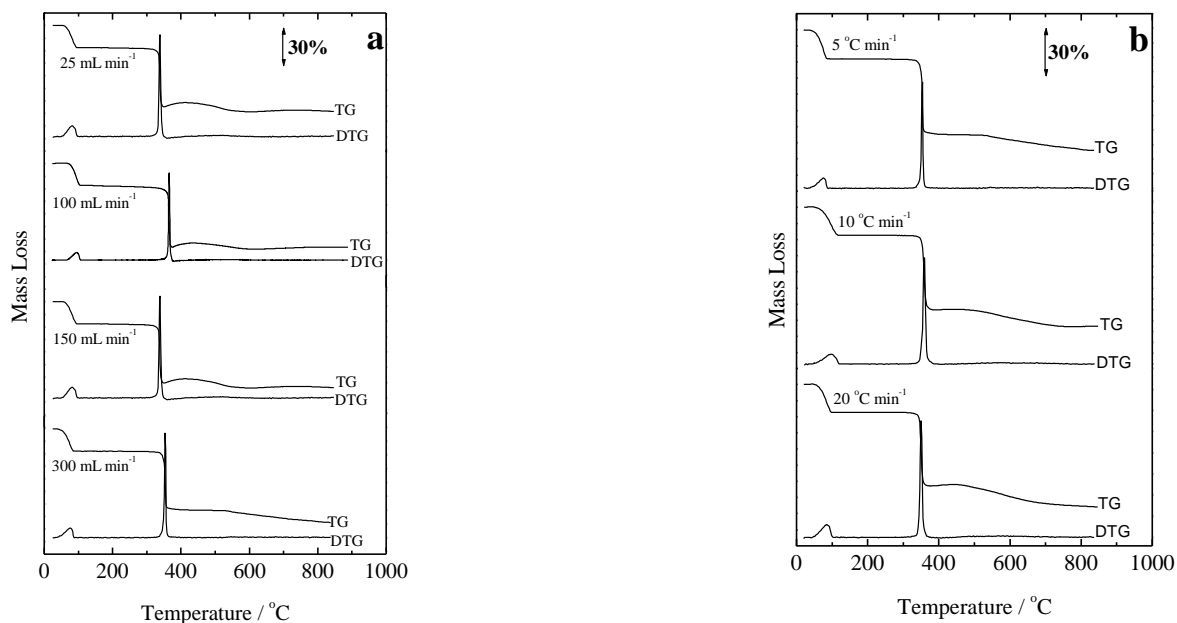


Figure 2. (a) TG/DTG curves of the sodium pyrrolidinedithiocarbamate salt in *nitrogen* atmosphere (sample mass ca. 7 mg, $5^{\circ}\text{C min}^{-1}$, Pt crucible, N_2 flow 25, 100, 150 and 300 mL min^{-1}). (b) TG/DTG curves of the sodium pyrrolidinedithiocarbamate salt in *nitrogen* atmosphere (sample mass ca. 7 mg, 5° , 10° and $20^{\circ}\text{C min}^{-1}$, Pt crucible, N_2 flow 300 mL min^{-1}).

3.2. Thermal results of the Na^+ salts

The thermal events, residues, mass losses and temperature ranges observed in each step of the recorded TG/DTG and DSC curves for NaPyr, NaPip, NaMor, NaHex and NaDEDC are given in Figure 3 and Table 3.

NaPyr

The NaPyr salt showed dehydration followed by a two steps decomposition, with sodium polysulphide and a carbonaceous residue as decomposition products under nitrogen atmosphere. It was the most stable compound in the series studied the onset temperature for decomposition is 350°C .

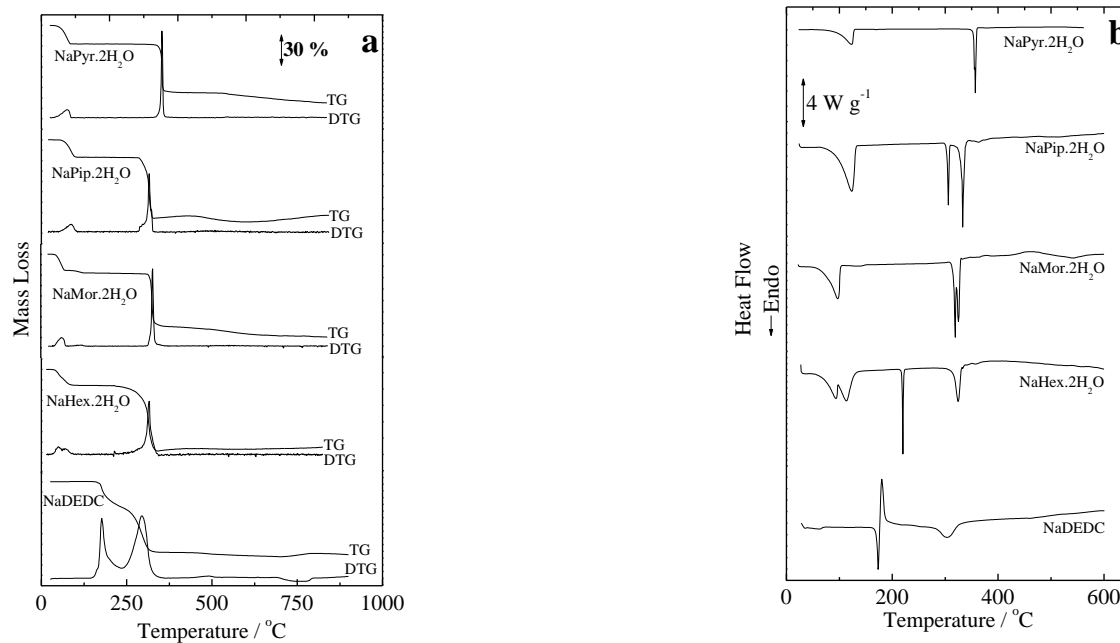


Figure 3. (a) TG/DTG curves of the salts dithiocarbamates in *nitrogen* atmosphere (sample mass ca. 7 mg, $5^{\circ}\text{C min}^{-1}$, Pt crucible, N_2 flow 300 mL min^{-1}). (b) DSC curves of the salts in *nitrogen* atmosphere (sample mass ca. 5 mg, $5^{\circ}\text{C min}^{-1}$, covered Al crucible, N_2 flow 300 mL min^{-1}).

Table 3. TG (mass losses, residues and temperature range) and DSC data corresponding to the decomposition of the sodium salts under nitrogen

Process	$T_{\text{range}}/^{\circ}\text{C}$	Mass loss or residue/%		DSC peak temperature ^a / $^{\circ}\text{C}$
		TG	calc.	
NaPyr.2H ₂ O → NaPyr + 2H ₂ O	39-110	17,73	17,56	123 endo
NaPyr _(s) → NaPyr _(l)	340-365	---	---	356 endo
NaPyr _(l) → decomposition	300-400	46,34	---	359 endo
NaPip.2H ₂ O → NaPip + 2H ₂ O	10-100	16,55	16,43	123 endo
NaPip _(s) → NaPip _(l)	280-350	---	---	306 endo
NaPip _(l) → decomposition	265-340	60,75	---	333 endo
NaMor.2,25H ₂ O → NaMor.0,25H ₂ O + 2H ₂ O	30-75	15,44	15,96	97 endo
NaMor.0,25H ₂ O → NaMor + 0,25H ₂ O	80-140	2,53	2,00	97 endo
NaMor _(s) → NaMor _(l)	300-350	---	---	319 endo
NaMor _(l) → decomposition	290-375	50,42	---	325 endo
NaHex.2H ₂ O → NaHex + 2H ₂ O	25-100	15,14	15,44	96 and 119 endo
NaHex _(s) → NaHex _(s)	210-240	---	---	220 endo
NaHex _(sl) → NaHex _(l) + decomposition	190-350	62,13	---	318 endo
NaDEDC → NaMor + H ₂ O	129-180	9,00	8,87	173 endo e 180 exo
NaMor → decomposition	230-375	60,47	---	304 endo

^aexo - exothermic process, endo - endothermic process.

The presence of the polysulphide is in agreement with an observation in earlier works [7], and was characterized by X-ray diffraction.

The DSC curves for NaPyr salt presented two endothermic peaks attributed to a loss of water and decomposition under nitrogen atmosphere, respectively, without evidences of melting.

NaPip

This salt showed a very similar behavior to NaPyr. The decomposition occurred in two steps under nitrogen atmosphere after dehydration relative to the loss of 2H₂O. The two steps related to decomposition and formation of sodium polysulphide as residues were observed under nitrogen atmosphere and the residue was confirmed by X-ray diffraction. This piperidine derivative was the second most stable compound in the series studied, with a decomposition onset temperature of 306 °C.

The DSC curve for the NaPip salt showed three endothermic peaks under nitrogen atmosphere. The first at 123 °C was related to water loss, the second a sharp peak at 306°C, attributed to a melting process. The last one at 333°C, attributed to the decomposition.

NaMor

The decomposition of the NaMor salt occurred in two steps under nitrogen atmosphere, after the first mass loss to the releasing 2H₂O. The other steps are related to decomposition and formation of sodium polysulphide as a residue under nitrogen atmosphere. This residue was confirmed by X-ray diffraction. This morpholine derivative decomposed with an onset temperature of 322 °C.

The DSC curves for the NaMor salt showed three endothermic peaks under nitrogen atmosphere. The first at

97 °C was related to water loss, the second a sharp peak at 319°C, was attributed to a melting process. The last one at 325°C, was attributed to the decomposition.

NaHex

The decomposition of the NaHex occurred in two steps under nitrogen atmosphere. The first step showed relative to the loss of 2H₂O. The second step was related to decomposition resulting in of sodium polysulphide as a residue under nitrogen atmosphere. This residue was confirmed by X-ray diffraction. This hexamethyleneimine presented an onset temperature of decomposition at 304 °C.

The DSC curves for the NaHex salt showed four endothermic peaks under nitrogen atmosphere. The first showed two peaks at 96 and 119 °C was related to water loss that occurred in two steps in agreement with the DTG curve (Fig. 3.a), the second a sharp peak at 220°C, was attributed to a melting process. The last one at 318°C, was attributed to the decomposition.

NaDEDC

The decomposition of the anhydrous NaDEDC occurred in two steps under nitrogen atmosphere. The first related to the dehydration of the diethanolamine in order to produce morpholine [18]. The second step is related to decomposition to produce morpholine and formation of sodium polysulphide as a residue under nitrogen atmosphere. The residue was confirmed by X-ray diffraction. This diethanolamine derivative was the less stable in the series studied the onset temperature for decomposition is 170 °C.

The DSC curves for the NaDEDC salt showed three peaks under nitrogen atmosphere. The onset temperature for melting is 168 °C which is followed by an exothermic event at 172 °C related to the conversion of diethanolamine to

morpholine. The last endothermic peak at 304 °C, was attributed to the decomposition.

3.2. Thermal results of the K⁺ salts

The thermal events, residues, mass losses and temperature ranges observed in each step of the recorded TG/DTG and DSC curves for KPyr, KPip, KMor and NaDEDC are given in Figure 4 and Table 4.

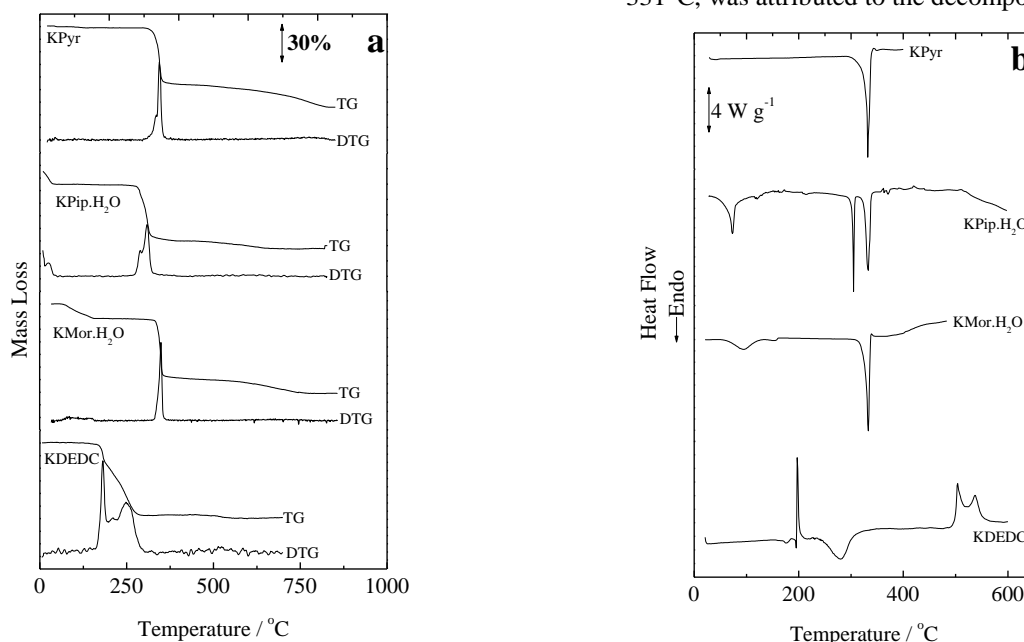


Figure 4. (a) TG/DTG curves of the salts dithiocarbamates in *nitrogen* atmosphere (sample mass ca. 7 mg, 5° C min⁻¹, Pt crucible, N₂ flow 300 mL min⁻¹). (b) DSC curves of the salts in *nitrogen* atmosphere (sample mass ca. 5 mg, 5° C min⁻¹, covered Al crucible, N₂ flow 300 mL min⁻¹).

KPyr

The TG curve presented a single mass loss step between 240 and 390 °C, with loss of mass of 54.25% (52.43% calculated for KSCN), the onset temperature for decomposition is 329 °C. According to Sengupta and Kumar [8], the organic portion of the ligand is decomposed, resulting in the formation of the respective metal thiocyanates at the end of the first step of decomposition, as evidenced by IR analysis of the residue. The metal sulphides on heating at higher temperature lose sulphur and form non-stoichiometric metal sulphides. The KPyr salts presented decomposition in a step generating KSCN as residue, characterized by IR, around 400 °C. The respective thiocyanates undergo decomposition at higher temperatures and the respective metal sulphides are obtained. The thiocyanate presents axial deformations of the triple bond in the area 2280 to 2000 cm⁻¹.

The DSC curves presented an endothermic peak at 332 °C attributed to the melting of the salt.

KPip

The decomposition occurred in three steps under nitrogen atmosphere. The first relative to the loss of 2H₂O, the second is related to decomposition and formation of

potassium thiocyanate as a residue under nitrogen atmosphere. Next KSCN decomposes to potassium polysulphide the residue was confirmed by IR. This piperidine derivative started to decompose at 292 °C onset temperature.

The DSC curves for the NaPip salt showed three endothermic peaks under nitrogen atmosphere. The first at 73 °C was related to water loss, the second a sharp peak at 305 °C, was attributed to a melting process. The last one at 331 °C, was attributed to the decomposition.

KMor

The decomposition of the KMor salt occurred in three steps under nitrogen atmosphere. The first relative to the loss of H₂O. The second step is related to decomposition and formation of potassium thiocyanate as a residue under nitrogen atmosphere followed by formation of polysulphide. All these residue were confirmed by IR. This morpholine derivative started decomposition is 340 °C.

The DSC curves for the NaMor salt showed two endothermic peaks under nitrogen atmosphere. The first at 86 °C was related to water loss, the second a sharp peak at 232 °C, was attributed to a melting process. The liquid compound decomposed by endothermic processes.

KDEDc

This salt showed a very similar behavior to NaDEDC. The decomposition of the KDEDc occurred in two steps under nitrogen atmosphere. The first related to the dehydration of the diethanolamine in order to produce morpholine [18]. The second step is related to decomposition to produce morpholine and formation of potassium thiocyanate as a residue under nitrogen atmosphere. All these residue were confirmed by IR.

Table 4. TG (mass losses, residues and temperature range) and DSC data corresponding to the composition of the potassium salts under nitrogen

Process	$T_{\text{range}}/^{\circ}\text{C}$	Mass loss or residue/%		DSC peak temperature ^a / $^{\circ}\text{C}$
		TG	calc.	
KPyr → KSCN	240-390	54,25*	57,70*	332
KSCN → decomposition	390-780	35,62*	30,00*	---
KPip.1H ₂ O → KPip + 1H ₂ O	10-70	14,79	15,30	74 endo
KPip _(s) → KPip _(l)	256-293	11,86	---	305 endo
KPip _(l) → KSCN	225-409	41,49*	41,28*	331 endo
KSCN → decomposition	410-700	33,78*	---	---
KMor.1,4H ₂ O → KMor + 1,4H ₂ O	66-166	11,30	11,65	86 endo
KMor → KSCN	323-370	42,05*	42,55	232
KSCN → decomposition	400-763	29,33*	24,13*	---
KDEDC → KMor + H ₂ O	129-180	8,64	8,21	195 endo and 198 exo
KMor → KSCN	220-320	42,60*	44,30*	280
KSCN → decomposition	320-700	40,90	---	503 and 528 endo

*residue

^aexo - exothermic process, endo - endothermic process.

This diethanolamine derivative was the less stable in the series studied the onset temperature for decomposition is 177 °C.

The DSC curves for the KDEDC salt showed five peaks under nitrogen atmosphere. The onset temperature for melting is 194 °C followed by conversion of diethanolamine to morpholine with an exothermic peak at 195°C. In the sequence the endothermic peaks at 208 °C, and two exothermic peaks at 503 e 528 °C were attributed to the decomposition.

4. Conclusions

The decomposition of sodium salts occurred in different manner depending on the nature of the substituent, generating sodium polysulphites. The potassium salts decomposed via thiocyanate as predicted in the literature.

The DTC sodium salts were thermally more stable compared with the DTC potassium salts in the same DTC. The mechanism of thermal decomposition of the sodium salts do not follow the mechanism proposed by Sharma via sodium thiocyanate. What has been observed is that the decomposition mechanism leads to a residual sodium sulfide in an inert atmosphere.

Potassium salts, in turn, follows the mechanism proposed by Sharma via potassium thiocyanate intermediate, in an inert atmosphere. The order of stability for anhydrous salts was: NaPyr (350 °C) < KMor (340 °C) < KPyr (329 °C) < NaMor (322 °C) < NaPip (306 °C) < NaHex (304 °C) < KPip (292 °C) < KDEDC (177 °C) < NaDEDC (170 °C).

Acknowledgements

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