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COMPARATIVE THERMAL STUDY OF SOME AMINOPOLYCARBOXYLIC CHELATING AGENTS

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ABSTRACT

The thermal properties of several aminopolycarboxylic acids and their sodium salts were studied comparatively by thermogravimetry, differential thermal analysis, and static heating. Gas chromatography was used to analyse the gases evolved during the thermal process. Residual substances at different temperatures were investigated by IR spectroscopy. The results indicated decarboxylation in one or two steps, depending on the structure of the compound. The thermal process for the sodium salts leads to sodium carbonate with oxalate as intermediate product.

INTRODUCTION

Previously published papers concerning the thermal behaviour of iminodiacetic acid [1], ethylenediaminetetracetic acid [2] and their sodium salts are only a small though the most meaningful, sample, of a more comprehensive comparative study carried out in our laboratories in recent years of the thermal and structural properties of chelating agents.

The literature earlier than 1980 was concerned mainly with analytical [3–6] or industrial processes [7,8] and some incorrect data were published in a paper related to ours [9], as proved by our experimental work [1].

We present here the comparative thermal study of several aminopolycarboxylic acids and some of their sodium salts, using static heating (SH), thermogravimetry (TG) and differential thermal analysis (DTA) in simultaneous combination with gas chromatography (GC). IR spectroscopy was used to analyse the residual substances at different decomposition stages.

The investigated compounds were iminodiacetic acid (IDA), nitrilotriacetic acid (NTA), 1,2-propylenediaminetetracetic acid (PDTA), ethylenediaminetetracetic acid (EDTA), hydroxyethylethylenediaminetriacetic

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acid (HEDTA), 1,2-diaminecyclohexanetetracetic acid (DCHTA), diethylenetriaminepentacetic acid (DTPA), ethyleneglycol bis(β-aminoethylether)-N,N'-tetracetic acid (EGTA) and some of their sodium salts.

EXPERIMENTAL

Reagents

Acid complexones were supplied by commercial firms as follows: IDA by B.D.H., Chemicals Ltd., England; EDTA and Na_2-EDTA by Riedel de Haen, AG, Germany; NTA, DTPA and EGTA by E. Merck, Darmstadt, Germany; PDTA and DCHTA by Fluka Chemische Fabrik, Switzerland; and HEDTA by Sigma Chemical Company, U.S.A.

The following sodium salts were obtained, according to Sawyer and Paulsen's method [10], under the necessary experimental conditions [11]: Na_2-IDA, Na-EDTA, Na_3-EDTA, Na_4-EDTA, Na_2-PDTA, Na_3-PDTA, Na_4-PDTA, Na_2-DCHTA, Na_3-DCHTA, and Na_4-DCHTA.

Equipment

Equipment and experimental conditions have been described previously [1].

RESULTS AND DISCUSSION

The static heating of these compounds was carried out at increasing temperatures, 50–250°C for the acids and 180–600°C for the sodium salts.

TABLE 1

Upper limit of stability for complexones by static heating.

IDA	180°C	Na_2-IDA	275°C
NTA	150°C	Na_2-PDTA	160°C
PDTA	150°C	Na_3-PDTA	170°C
		Na_4-PDTA	280°C
EDTA	200°C	Na-EDTA	200°C
HEDTA	120°C	Na_2-EDTA	220°C
		Na_3-EDTA	230°C
DTPA	120°C	Na_4-EDTA	280°C
DCHTA	120°C	Na_2-DCHTA	140°C
EGTA	120°C	Na_3-DCHTA	175°C
		Na_4-DCHTA	280°C

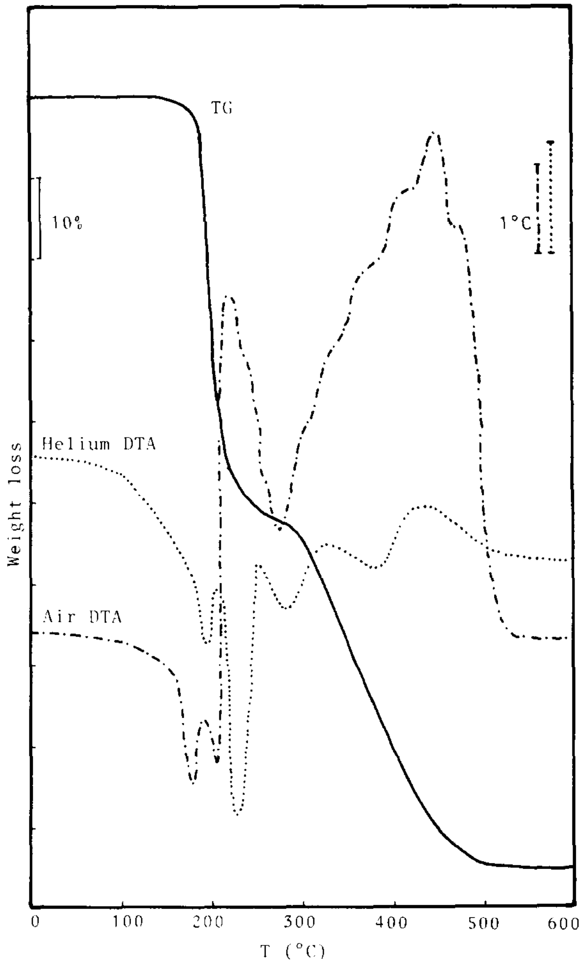

Fig. 1. Thermal behaviour (TG, DTA) of DCHTA.

The results obtained by this technique were compared with those from TG and GC in order to follow the different stages of the thermal process.

The experimental conditions of the static heating and TG were very different in the heating method, weight of sample, container, etc. Nevertheless, the same stability range was observed for the compounds studied by both techniques. There was only a little progressive difference between the temperatures relative to the same stage of decomposition, but the process was qualitatively similar.

The upper limit of stability by static heating of these compounds, confirmed by their IR spectra, is shown in Table 1. The stability temperatures for the sodium salts were recorded overlooking:

DTA was carried out mainly with respect to two factors: the atmosphere surrounding the sample and the heating rate. Though the two factors are

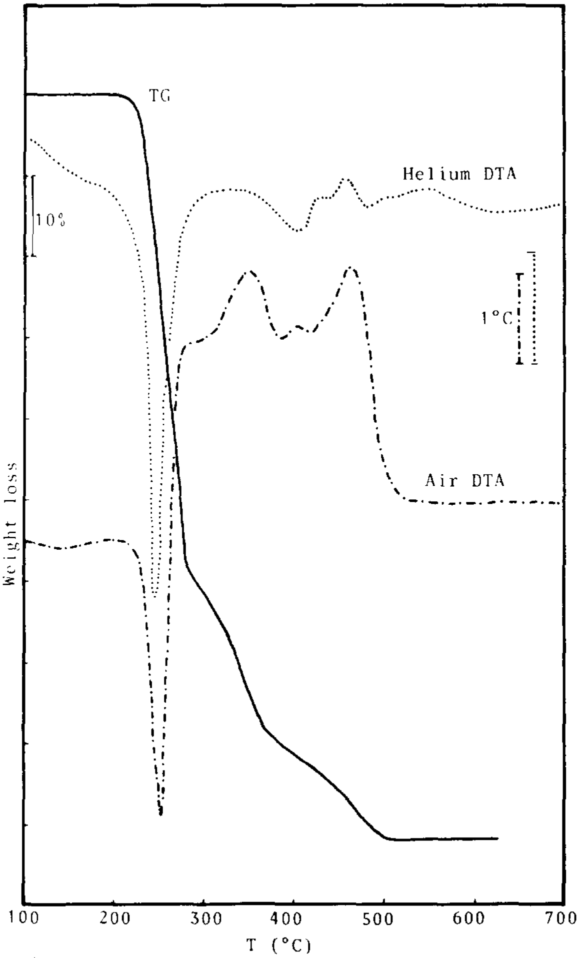

Fig. 2. Thermal behaviour (TG, DTA) of NTA.

important, the results obtained with different but close heating rates (6–10°C min^{-1}) were almost identical. For this reason, we considered the DTA results in different atmospheres (air/helium).

The most important endothermic effects (below 300°C) were not affected by the presence or absence of oxygen, but exothermic effects (300–500°C) were very important in the DTA curves recorded in air, showing only alternatively exo- and endothermic effects of minor intensity when recorded under helium flow (Figs. 1 and 2)

THERMAL BEHAVIOUR OF THE ACID COMPLEXONES

The temperatures of the thermic effects for these compounds are shown in Table 2.

TABLE 2

Temperatures (°C) of thermal effects (DTA) for acid complexones

Compound	Endothermic effects		Exothermic effects	
	Static air atm.	Helium flow	Static air atm.	Helium flow
IDA	230, 250	230, 275, 295, 310	310, 450	252
NTA	254, 380, 415	245, 405	350, 400, 462	455
EDTA	260	265	373, 500	
PDTA	250	250, 400	360, 475	
HEDTA	165, 220	165 220, 240	285, 370, 520	
DTPA	215, 305, 430	225, 375	275, 370, 470	
DCHTA	180, 205, 275	195, 230, 280, 385	220, 450	435
EGTA	248, 365, 400	252	263, 370, 452	

Acid complexones exhibit a similar thermal behaviour, the most outstanding common facts being as follows.

A dehydration process with strong endothermic effects is shown by IDA (230°C, 16% weight loss) and HEDTA (165°C, 6% wt. loss), cyclopeptides being formed for IDA [1,9] and a lactama for HEDTA [12].

Most of acid complexones show the strongest endothermic effects in DTA

TABLE 3

Temperatures showing a maximum release of CO_2 and CO (°C)

Compound	CO_2	CO
IDA	310	
NTA	245, 405	245
PDTA	250, 400	250
EDTA	265	265
HEDTA	240	240
DTPA	225, 375	225
DCHTA	230	230
EGTA	252	
Na_2-IDA	395	
Na_2-PDTA	245, 365	245
Na_3-PDTA	325, 407	407
Na_4-PDTA	426	426
Na-EDTA	230, 340	230
Na_2-EDTA	250, 360	250
Na_3-EDTA	238, 405	238, 405
Na_4-EDTA	422	422
Na_2-DCHTA	252, 420	252, 420
Na_3-DCHTA	258, 426	258, 426
Na_4-DCHTA	460	460

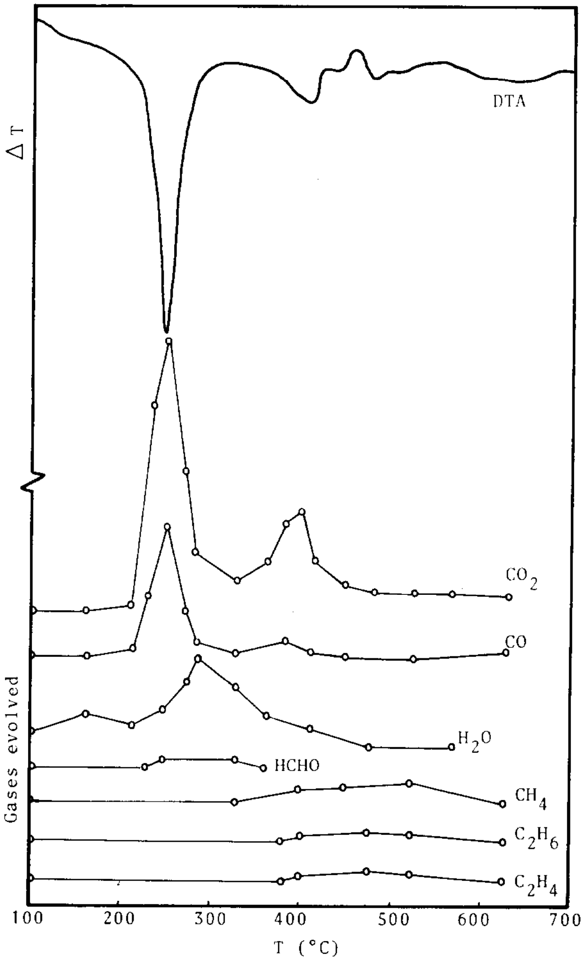

Fig. 3. Thermal and chromatographic behaviour of NTA.

from 200 to 300°C, TG curves recording a fast weight loss due to decarboxylation in a single though wide step, as proved by GC [1,2].

NTA, PDTA and DTPA show a single endothermic effect close to 250°C. The observed weight loss (45–60%) is equivalent to (n–1) CO_2, the TG curves showing at this point a clear inflexion (Fig. 2). Lighter endothermic effects (300–500°C), overlapping with the strong exothermic ones in the DTA curves recorded in air, (Fig. 2) correspond to the loss of the last carboxylic group in the TG curve. Cracking and pyrolysis occur over the same range of temperatures, the process showing a very high energetic character when carried out in air (Fig. 2).

The chromatographic analysis of the evolved gases confirm the data obtained by DTA and TG.

A maximum release of CO_2 and CO is observed at the temperatures of the

TABLE 4

Temperatures (°C) of thermal effects (DTA) for sodium complexones

Compound	Endothermic effects		Exothermic effects	
	Static air atm.	Helium flow	Static air atm.	Helium flow
Na_2-IDA 1.4 H_2O	73, 118, 135, 170, 360	73, 118, 137, 156, 310, 395	310, 415	365
Na-EDTA 1.27 H_2O	165, 217, 237, 361	147, 230, 340	306, 391	307, 414
Na_2-EDTA 1.7 H_2O	158, 240, 315, 365	165, 250, 360	300, 346, 387	338, 385
Na_3-EDTA 3.5 H_2O	90, 176, 240, 385	86, 172, 238, 405	348, 410	360
Na_4-EDTA 3.0 H_2O	100, 420, 439	110, 422	250, 373, 448	250
Na_2-PDTA 3.0 H_2O	125, 170, 365	115, 145, 170, 182, 230, 245, 365, 405	318, 375	
Na_3-PDTA 3.2 H_2O	130, 225, 310	192, 230, 270, 325, 407, 435	288, 355, 415	415
Na_4-PDTA 4.7 H_2O	114, 400	122, 408, 426	270, 331, 420	280, 417
Na_2-DCHTA 4.0 H_2O	110, 212	90, 187, 252, 360, 420	305, 350	
Na_3-DCHTA 4.0 H_2O	100, 225, 430	97, 167, 225, 258, 426	385, 440	
Na_4-DCHTA 4.8 H_2O	120, 341, 360	112, 135, 460, 530	320, 420	318

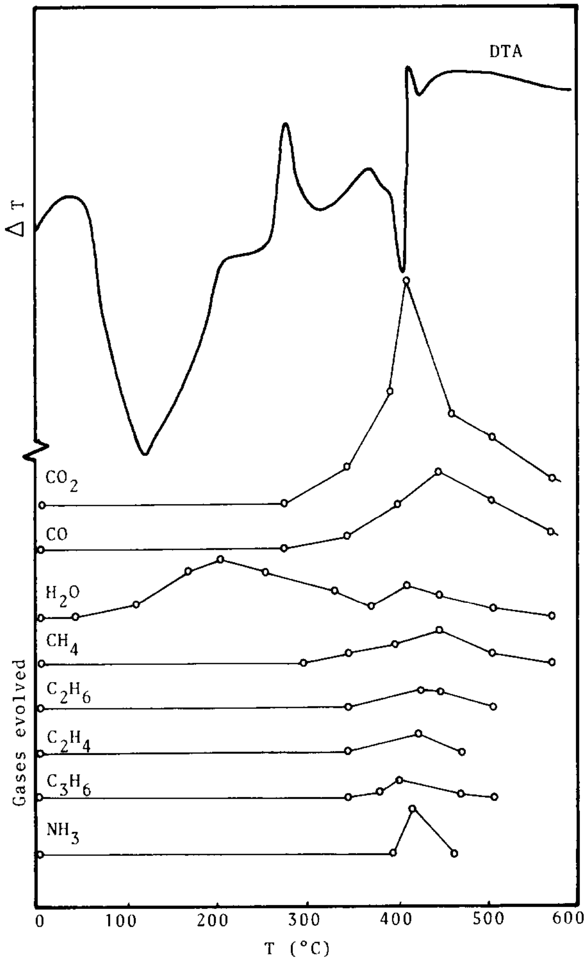

Fig. 4. Thermal and chromatographic behaviour of Na_4-PDTA.

recorded endothermic effects (Table 3) and there is evidence of one or two stages of decarboxylation for these compounds. (Fig. 3).

Traces of formaldehyde and acetaldehyde are released between 200 and 300°C, indicating an incipient breaking of N–CH_2–COOH bonds.

Traces of light hydrocarbons are detected joining the cracking of the molecules (300–500°C). Sometimes, they are obtained by reaction between free radicals: ethane, ethylene (IDA, NTA), propylene (PDTA, HEDTA).

In no case was ammonia detected during the thermal process of acid complexones. Nitrogen is lost as amines, not detected by GC under the operating conditions.

The high temperatures of the second step of decarboxylation should be noted, similar to the ones recorded for salts and complexes [13] (see Table 3). This fact can be explained by the strong basic character of the nitrogen atom holding the last proton, this basic character being increased by the close methyl group (PDTA) and the next acetate groups (NTA, DTPA) and making possible a chelation effect for the proton in the original molecule.

The thermal behaviour of the NTA can be related to its crystal structure [14]. The hydrogen atom bonded to the central nitrogen is very close to the oxygen atoms of the two adjacent acetate groups in the same molecule. The H · · · O distances are short and correspond to an almost symmetric intramolecular bond, which explains the low values for the third dissociation constant of this acid and the thermal stability of its third carboxylic group. The lattice in the crystal structure of NTA consists of two interconnected helices. The method of this connection and the strength of the hydrogen bonds could be the reason for the retention of the third carboxylic group in the molecule.

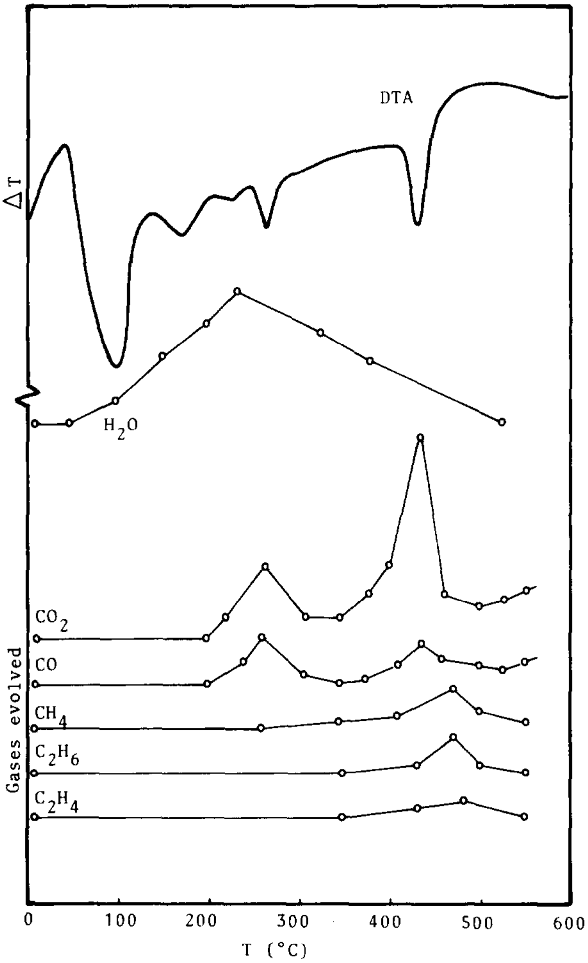

Fig. 5. Thermal and chromatographic behaviour of Na_3-DCHTA.

THERMAL BEHAVIOUR OF THE SODIUM COMPLEXONES [15]

The temperatures of the thermal effects for these compounds are shown in Table 4. The endothermic effects below 200°C (except Na_2DCHTA, which undergoes decomposition at 175°C) are due to their dehydration process, in one or two steps, as confirmed by their TG curves, and the detection of only H_2O at this temperature by GC, though with some delay, due to its condensation on the cold parts of the instrument.

The completely neutralised salts (Fig. 4) begin their thermal decomposition at about 300°C. The TG curves show a single step, while DTA suggests several steps of different energetic character. Gases released all at once (CO_2, CO, NH_3 and hydrocarbons) prove that decarboxylation and cracking are simultaneous. At 500°C, stoichiometric residues of Na_2CO_3 are left.

The acid salts (Fig. 5), after their dehydration, undergo decarboxylation, showing thermic effects at about 250°C and weight loss equivalent to the CO_2 from the acid groups in the molecule. CO_2, CO, acetaldehyde, and formaldehyde are released in a process similar to the one undergone by the free acids between 200 and 300°C. The second decarboxylation process takes place above 300°C, associated with cracking, in a similar way to the neutral salts. CO_2, CO, NH_3 and hydrocarbons are released and detected by chromatography. The stoichiometric amount of Na_2CO_3 is left at about 500°C.

The amounts of CO_2 relative to the first and second decarboxylation steps are in agreement with the number of COOH and COO^- groups.

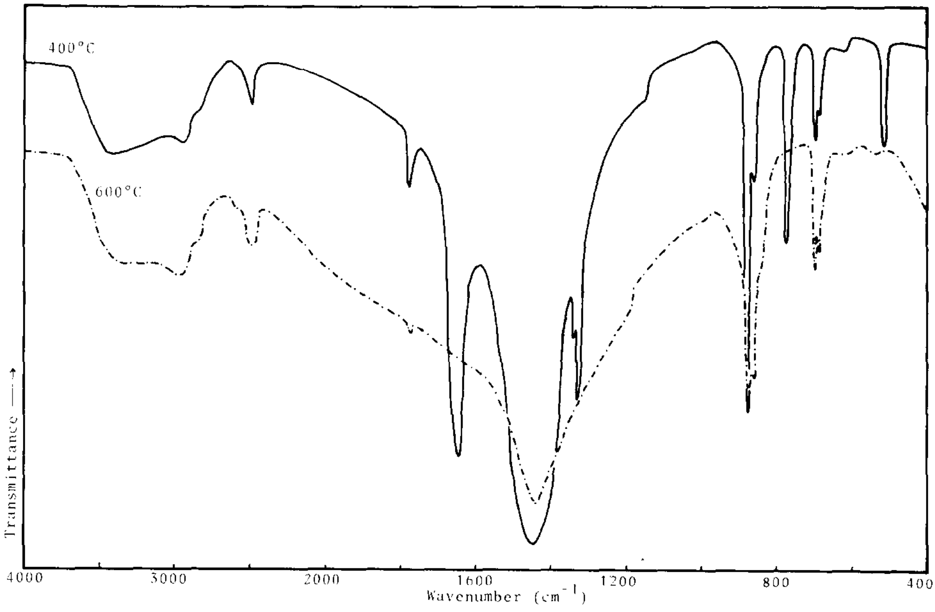

Fig. 6. IR spectra of Na_3-EDTA at 400 and 600°C.

Most of the nitrogen is released as amines. Nevertheless, the amount of NH_3 detected as traces, increases with the increasing number of sodium atoms in the molecule.

The IR spectra of the sodium salts heated at different temperatures made possible the identification of sodium oxalate as intermediate product and Na_2CO_3 as the final product of their thermal process (Fig. 6). Characteristic bands for carbonate are 1435, 875 (split), and 700 (split) cm^{-1} and for oxalate 1635, 1330 (split), 775, 510 cm^{-1}.

CONCLUSIONS

The following general conclusions can be reported from the study.

(a) The investigated acid complexones are stable up to 120°C. Furthermore, NTA, PDTA are stable below 150°C, IDA below 180°C, and EDTA below 200°C. Sodium complexones show increasing thermal stability with increasing number of sodium atoms in the molecule.

(b) It is not possible to establish any mechanism for the thermal decomposition of acid complexones, except for IDA [1], due to the cracking of the molecule.

(c) The decarboxylation processes depend fundamentally on the number of carboxylic and carboxylate groups. There is a first process (200–300°C) stronger with a greater number of –COOH groups, and a second (350–450°C) stronger with a greater number of –COONa groups. Thus, most of acid complexones only show the first decarboxylation step and the completely neutralised salts only show the second. The two decarboxylation stages shown by NTA, PDTA and DTPA suggest a chelation effect occurring in these compounds due to the strong basic character of the nitrogen atom holding the last proton.

(d) The thermal process of the sodium complexones leads to sodium oxalate as intermediate product and Na_2CO_3 as final product. Both are easily identified by IR spectroscopy.

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