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THE THERMAL BEHAVIOUR OF ETHYLENEDIAMINETETRACETIC ACID AND ITS SODIUM SALTS

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ABSTRACT

The thermal properties of ethylenediaminetetracetic acid (EDTA) and its sodium salts were examined by differential thermal analysis, thermogravimetry and static heating. The gaseous evolved products were analysed by gas chromatography in order to follow the thermal process. The heating of the samples was interrupted at different characteristic decomposition steps and IR spectra of the residual substances were recorded. The obtained data allow us to suggest a decomposition process for the sodium salts of EDTA leading to the formation of Na_2CO_3 via the oxalate.

INTRODUCTION

Very interesting papers have been published on the thermal properties of ethylenediaminetetracetic acid (EDTA) and related compounds. Nevertheless, comparative conclusions concerning the thermal stability of these polydentate chelating agents were missing. The main interest of this research is derived from the procedures using sometimes higher temperatures than usual [1,2]. Furthermore, the possible anti-tumour properties of compounds derived from complexones [3] require a knowledge of the mechanism of decomposition for those polydentate compounds, which are able to act as very strong secondary ligands.

Important results are due to research by Wendlandt [4], Merciny [5], Ambro et al. [6] and Khramov et al. [7] on the thermal properties of several aminopolycarboxylic acids and some of their salts using mainly thermogravimetric (TG) and differential thermal analysis (DTA). Our present study uses the former techniques simultaneously with gas chromatography and IR spectroscopy, which have been very useful to predict probable structures for intermediate compounds [8,9].

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TABLE 1

Temperatures (°C) of thermal effects (DTA) for EDTA and its sodium salts

Compound	Endothermic effects		Exothermic effects	
	Static air atm.	Helium flow	Static air atm.	Helium flow
EDTA	260	265	373, 500	
Na-EDTA 1.3 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

EXPERIMENTAL

EDTA and its disodium salt were supplied by Riedel de Haen, AG, Germany, as analytical reagents. The rest of the sodium salts of EDTA were obtained according to the method of Sawyer and Paulsen [10] and every compound was carefully recrystallized. The number of H_2O molecules was deduced from the TG curves and confirmed by titration with Karl Fisher reagent.

The equipment and experimental conditions have been described in an earlier paper [9], the present paper being only a part of a wider comparative thermal study concerning different chelating agents.

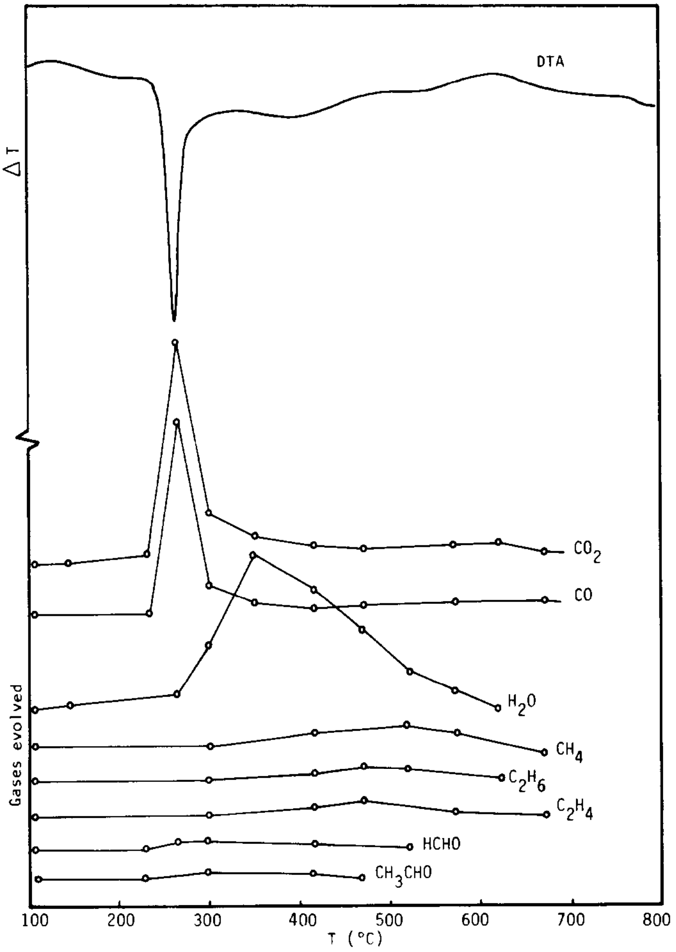

Fig. 1. DTA and gas chromatography of EDTA.

RESULTS AND DISCUSSION

The temperatures of the most important thermal effects (DTA) observed for these substances are shown in Table 1. It is observed that the most important endothermic effects are not affected by the composition of the atmosphere, but the exothermic effects are stronger in an atmosphere of air because of the vigorous oxidation process of the compounds.

Thermal behaviour of EDTA

The DTA curve of EDTA (Fig. 1) shows a single strong endothermic effect at 260°C, where the compound melts and its cracking begins. The TG plot shows a 60% weight loss at this temperature, equivalent to four –COOH groups. The GC analysis detects CO_2, H_2O, formaldehyde and acetaldehyde. The pyrolysis proceeds until 600°C with a total weight loss of over 90%. Traces of hydrocarbons are detected: methane, ethane, ethylene and even propylene, produced from free radicals. Nitrogen is lost as amines, not detected by chromatography because, as was observed, they condense on the cold parts of the instrument. The released water shows the same effect and is detected a little later than expected.

The long static heating of EDTA shows its stability up to 200°C, which is in agreement with former data [4,11]. The IR spectrum at this temperature is identical to the original (Fig. 2). The weight loss of the sample at 240°C is

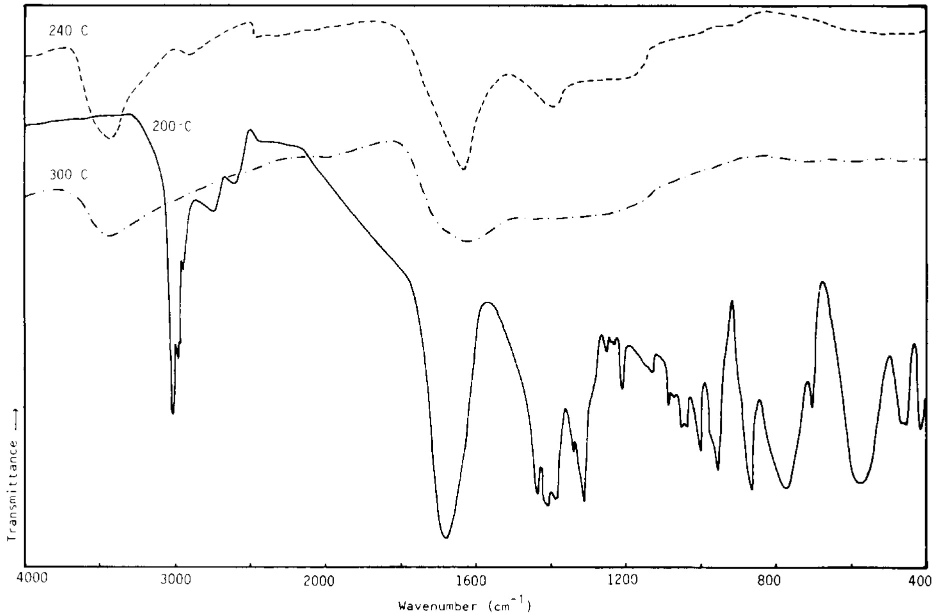

Fig. 2. Spectra of EDTA at different temperatures.

59%. There is a very high release of gases and it becomes dark brown and hygroscopic. The spectrum at this temperature shows almost entirely broad absorbances due to the different vibrations of water. At 300°C, the weight loss is 74%. The spectrum shows very bad resolution.

Though the experimental conditions for static heating and TG are not the same, the range of thermal stability for this and related substances is similar in both techniques.

Thermal behaviour of sodium salts of EDTA

Data concerning the thermal analysis of these compounds are shown in Table 1. The temperatures (°C) of maximum release of CO_2 and CO are

	EDTA	Na-EDTA	Na_2-EDTA	Na_3-EDTA	Na_4-EDTA
CO_2	260	240–375	250–400	270–420	420
CO	260	240	240	270–420	

The endothermic effects in the TDA curves below 200°C (Fig. 3 and 4) are due to the loss of water, making possible the formation of condensed products. Water is detected by GC with some delay, as reported above.

The decarboxylation of acid groups corresponds to the endothermic effects recorded between 200 and 300°C. These effects decrease from Na-EDTA to Na_3-EDTA and are missing in Na_4-EDTA. CO_2, CO and H_2O are detected by GC at this temperature (Figs. 3 and 4).

The thermal effects between 300 and 500°C, very strong in air, are due to the second decarboxylation process, associated with cracking, releasing CO_2, CO (a lesser amount), NH_3 and traces of hydrocarbons. The amount of NH_3 detected is not stoichiometric, but increases with increasing number of sodium atoms in the molecule. Nevertheless, most of nitrogen is released as amines.

The amounts of CO_2 from the first and second decarboxylation are proportional to the number of –COOH and $-COO^-$ groups, respectively. Na_4-EDTA shows only the second decarboxylation process.

The TG of sodium salts shows much clearer steps than the similar one from EDTA.

Na-EDTA 1.3 H_2O is stable up to 140°C. From this temperature to 200°C, the weight loss corresponds to the molecules of water. At 280°C, three acid groups are lost (exptl. wt. loss 45.4%; theoret., 45.8%). At 450°C, 0.5 mole Na_2CO_3 is left (exptl. wt. loss 81.4%; theoret., 84.4%).

Na_2-EDTA 1.7 H_2O shows data in its thermal decomposition as described in previous papers [4,6]. Its dehydration begins at 120°C and proceeds to 200°C. At 240–285°C, a second weight loss corresponds to 2 CO_2 (exptl. wt.

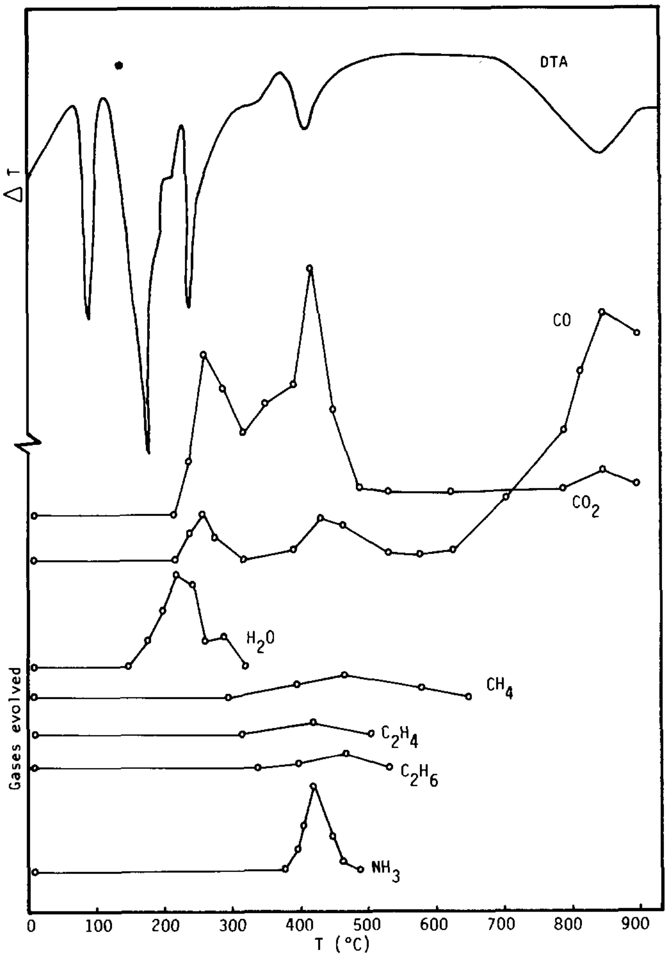

Fig. 3. DTA and gas chromatography of Na_3-EDTA.

loss 33.2%; theoret., 32.4%). The third weight loss leads to 480°C, where only Na_2CO_3 is left (exptl. wt. loss 71.7%; theoret. 71.6%).

Na_3-EDTA 3.5 H_2O loses water in two steps: the first, below 100°C, corresponds to 1.5 H_2O, and the second, up to 195°C, represents the loss of the two remaining moles. One mole of CO_2 is lost between 230 and 300°C (exptl. wt. loss 25.5%; theoret. 25.5%). The decomposition proceeds with formation of 1.5 mole of Na_2CO_3 at 500°C. (expt. wt. loss 62.82%; theoret. 62.25%).

Na_4-EDTA 3 H_2O loses the water below 160°C and its decomposition begins at 320°C. At 500°C, 2 mole Na_2CO_3 are left (explt. wt. loss 47.93%; theoret. 49.1%).

IR spectra of these salts after heating are unchanged below 200°C. Above 200°C, mono- and disodium salts have very similar spectra, in the same way

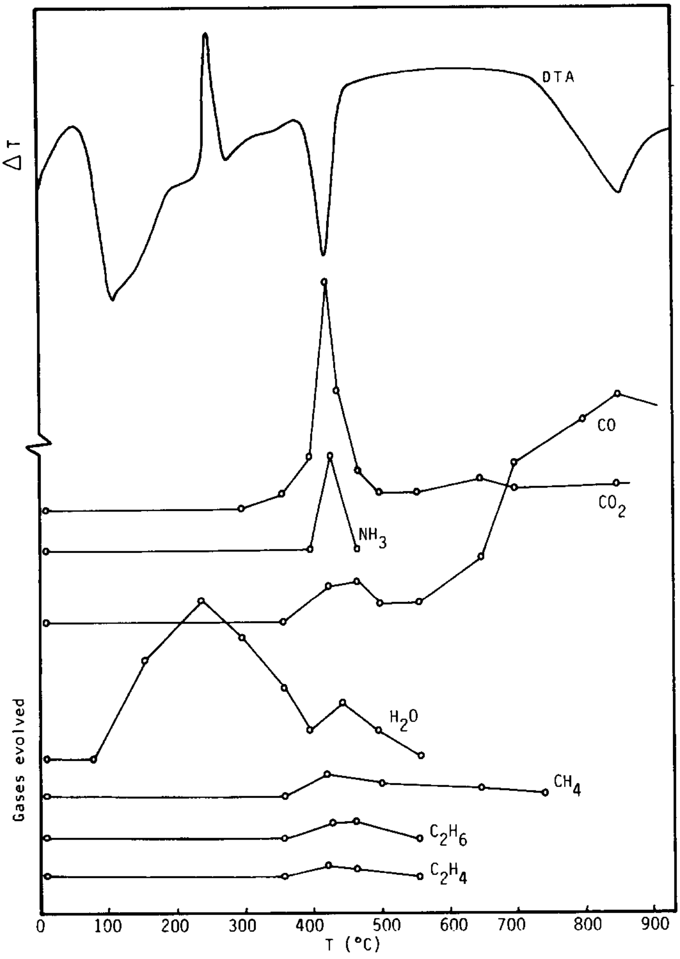

Fig. 4. DTA and gas chromatography of Na_4-EDTA.

that tri- and tetrasodium salts do. Water adsorbed by the samples gives a strong absorption at 3400 cm^{-1} due to the OH stretching vibration

The Na_2-EDTA IR spectrum at 240°C (Fig. 5) shows that the bands at the vibration frequencies of methylenic groups have almost disappeared. The difference between the assymetric and symmetric stretching vibrations of the C=O bond in the carboxylic groups is rather less than that in the original salt, which indicates an important increase in the ionic character of the bonds of the $-COO^-$ groups. The spectrum of the sample heated at 300°C shows the same effect more pronounced. The observed values of these differences at increasing temperatures are as follows: 200°C, 230 cm^{-1}; 240°C, 190 cm^{-1}; and 300°C, 160 cm^{-1}.

At 300°C, sodium oxalate and carbonate are present in the sample (characteristic bands for oxalate: 1635, 1330, 775, 510 cm^{-1}; for carbonate:

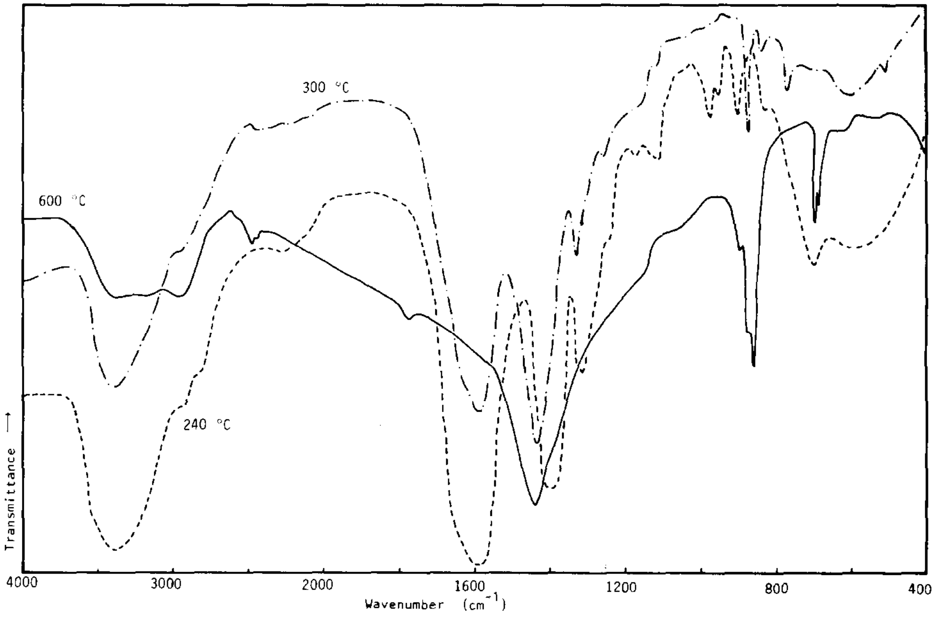

Fig. 5. Spectra of Na_2-EDTA at different temperatures.

1435, 875, 700 cm^{-1}). At 500°C, only sodium carbonate is present in the sample, as shown by its IR spectrum.

The spectra of Na_3-EDTA and 275°C and Na_4-EDTA at 300°C show the beginning of the formation of sodium oxalate and carbonate. At 400°C, the spectra are those of mixed oxalate and carbonate. At 500°C, the spectrum records only the presence of Na_2CO_3 in both samples.

It is not possible to set up any mechanism of decomposition for EDTA, because of its early and highly energetic cracking, but the following conclusions can be drawn for the sodium salts of EDTA.

(a) The dehydration process of the compounds proceeds at temperatures below 200°C.

(b) The decarboxylation processes depend on the number of –COOH and –COONa groups. Thus, there is a first process between 200 and 300°C, stronger with a greater number of carboxylic groups, and a second one between 350 and 450°C, stronger with the greater number of carboxylate groups.

(c) The cracking process of the molecules studied occurs in the same temperature range as the second decarboxylation and is shown by release of hydrocarbons, detected by GC.

(d) After the second decarboxylation process, the most thermostable parts of the molecule, the carboxylate groups, rearrange producing sodium oxalate as the precursor to sodium carbonate at 500°C.

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