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THERMAL BEHAVIOR OF IMINODIACETIC ACID AND ITS DISODIUM SALT

F. GONZÁLEZ VÍLCHEZ, M.C. PUERTA VIZCAÍNO and M.F. GARGALLO ESTEBAN

Departamento de Química Inorgánica, Facultad de Ciencias, Cádiz (Spain)

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ABSTRACT

The thermal properties of iminodiacetic acid (IDA) and its disodium salt were investigated by DTA, TG and static heating. The gaseous evolved products were analysed by chromatography in order to follow the thermal process. The heating of the samples was stopped at characteristic decomposition steps and the residual substances were investigated by IR spectroscopy. The obtained data suggest the processes of decomposition for these compounds.

INTRODUCTION

Since 1965, a large number of papers has been published concerning the structure [1,2] and chelating properties of iminodiacetic acid (IDA) and several aspects of the complexes formed between this substance and the transition metals.

Nevertheless, a complete and systematic investigation of the thermal properties of IDA and its complexes has not yet been carried out. Khramov et al. [3] have studied the thermal decomposition of IDA and have inferred that this chelating agent loses one mole of water per mole at 250° C with the probable formation of cyclopeptides. The decomposition products suggested by these workers are not quite correct.

In the last few years, the synthesis of the coordination compounds formed between platinum group metals and IDA have been carried out by González Vílchez et al. [4, 5]. An important part of this investigation was concerned with the study of the thermal properties of the isolated substances using differential thermal analysis (DTA) and thermogravimetry (TG). By simultaneous combination of these techniques and gas chromatography (GC), it is possible to obtain very useful data in order to identify the gases released and the mechanisms involved in the thermal process. We present here the thermal and chromatographic behaviour of IDA and its disodium salt (IDA-Na_2). The solid intermediate products formed in the decomposition process have been identified by infrared spectroscopy.

EXPERIMENTAL

Reagents

The IDA was furnished by B.D.H. Chemicals Ltd., England. Its disodium salt was prepared according to Sawyer and Paulsen's method [6]. Both products were purified by recrystallization.

Equipment

The thermal decomposition (DTA, TG) was studied using Aminco 4-4442 A and Stanton Redcroft HT-M electrobalance instruments, respectively. The experiments were carried out under a helium atmosphere at normal pressure (flow rate 60 ml min^{-1}) employing a heating rate of 10°C min^{-1}. Chromel—alumel and Pt—Rh/Pt thermocouples were used to measure the temperature changes; α-Al_2O_3 was employed as the reference material in the DTA measurements.

The Hewlett-Packard 5700/A gas chromatograph employed was connected with the DTA instrument also using helium as carrying gas. The metallic columns were filled with solid Porapak Q (80—100 mesh).

The retention indexes for the GC column are shown in Table 1 and are given in the experimental conditions.

For static heating, two furnaces were employed, a Heraeus FT 420°C (below 300°C) and a Heron 74 10-PR/200 (below 1000°C). The heating was stopped at temperatures deduced from the thermogravimetric data, for the detection of possible stable intermediate compounds. The solid residual substances were investigated by IR spectroscopy and chemical analysis of the most interesting intermediate products was carried out.

TABLE 1

Relative retention indexes (with respect to water) of the Porapak Q column
Helium flow, 30 ml min^{-1}; column length, 2 m; column diameter 1/8 in.

Compound	Oven 100°C-Detector 150°C	Oven 140°C-Detector 200°C
Hydrogen	0.27	
Carbon monoxide	0.30	0.45
Methane	0.37	0.53
Carbon dioxide	0.49	0.63
Ethylene	0.69	0.80
Ethane	0.83	0.90
Ammonia	0.90	0.95
Water	1.00 (1.23 min)	1.00 (0.73 min)
Formaldehyde	1.75	1.71
Acetaldehyde	2.36	2.35

RESULTS AND DISCUSSION

Thermal and chromatographic behaviour of IDA

The temperatures of the endothermic and exothermic effects are shown in Table 2. It is observed that the exothermic effects are stronger and more numerous when DTA is carried out under an atmosphere of air because of the strong oxidation of the compounds. Nevertheless, the composition of the atmosphere has no influence on the most important endothermic effects.

The DTA curve of IDA (in helium flux) first shows a strong minimum at 230°C (Fig. 1) due to the elimination of one water molecule per mole of compound [3] (weight loss in TG = 16%). Immediately above 250°C, an endothermic split peak of medium intensity is probably due to the decarboxylation process.

The TG curve shows a weight loss of a little more than 1 mole CO_2 at 300°C (theor. 46.6%; exptl. 55%). A new decomposition step in the TG curve from 375 to 500°C leads to a carbonized residue (wt. loss 90.3%).

The evolution of gases released in the decomposition against temperature is shown in Fig. 1. A high release of CO_2 and H_2O is observed with a maximum at 300°C. At this temperature, the cracking of the substance begins. This cracking is evident, on the one hand, in the traces of formaldehyde detected between 300 and 400°C and, on the other hand, in the formation of methane, ethane and ethylene from the free radicals.

According to a published paper [3] on the decomposition of IDA, a weight loss is attributed to the liberation of ammonia, but this gas has not been detected in the very different experimental conditions reported here. The nitrogen is probably lost as amines which condense on the cold parts of the instrument.

By static heating at 240°C (Table 3), the IDA shows a weight loss of 16%, (one mole of water per mole of substance). A melting process was not observed. The crystals became a grey colour but showed the same form which they had before heating. There is an inital process of carbonization and sublimation. This effect is larger at 300°C where the sample shows a weight loss of 78%.

TABLE 2

Temperatures (°C) of the principal endothermic and exothermic effects (DTA) of IDA and IDA-Na_2

Compound	Endothermic effects		Exothermic effects	
	Static air atmosphere	Helium flow	Static air atm.	Helium flow
IDA	230, 250	230, 275, 295, 310	310, 450	252
IDA-$Na_2 \cdot 1.4\ H_2O$	73, 118, 135, 170, 360	73, 118, 137, 156, 310, 395	310, 415	365

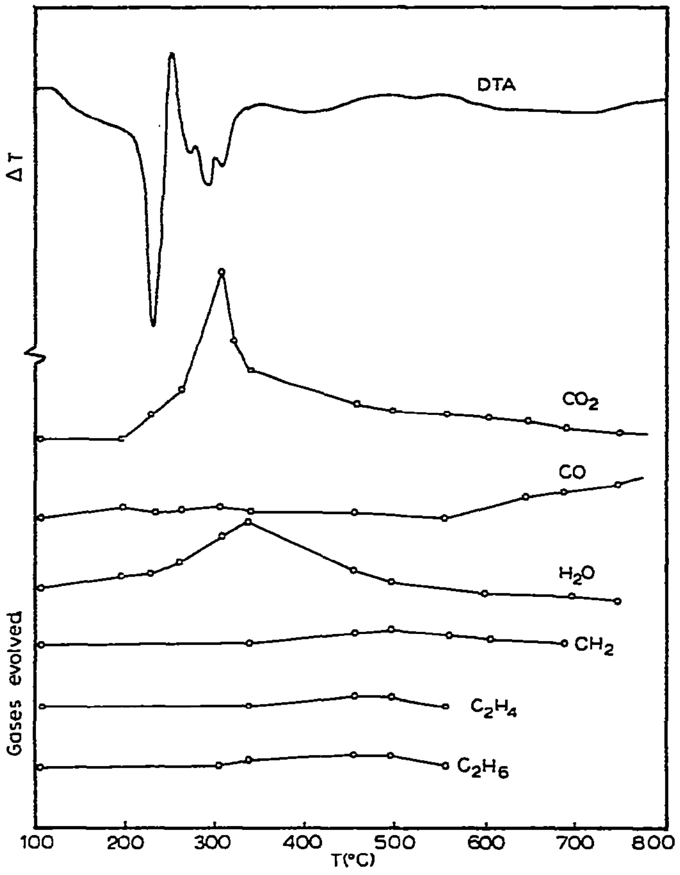


Fig. 1. Thermal and chromatographic behaviour of IDA.

The IR spectrum of IDA heated to 180°C is the same as that of the original sample, indicating that this acid is stable at this temperature. At 240°C, the sample has lost a molecule of water per mole of substance and the spectrum shows many very important differences with respect to the IDA spectrum before heating (Fig. 2). The strong hydrogen bonds have not been detected and the shape and frequency of some bands have changed. A broad absorption band between 3500 and 2500 cm^{-1} is attributed to C—H (CH_2) stretching vibration. Two strong overlapping absorptions at 1765 and 1740 cm^{-1} are due probably to the C=O stretching vibration of free carboxylic groups. A very strong band at 1630 cm^{-1} is characteristic of cyclic tertiary amides with six membered rings [7]. It is also suggested [8] that one of the bands at 1700—1800 cm^{-1} is due to lactam rings with a smaller number of members.

The band registered at 1495 cm^{-1}, similar to that of the *N*-methylacetamide at 1490 cm^{-1}, could probably be due to the C—N stretching vibration with a strong double bond character. Nevertheless, this band is probably due to a complex vibration with participation of the atoms contiguous to the C—N group [9,10].

The bands registered at 1400, 1350 and 950 cm^{-1} are the same as those

TABLE 3

Analysis of the intermediate substances in the thermal decomposition of IDA

Compound	% Loss	Loss/mole	Rest/mole	%C	%H	%N	%O	Estimated formula
IDA	16	18	115	41.22	4.34	12.17	42.27	$C_4H_5NO_3$
	54.78	72.3	60.7	46.65	4.00	23.07	26.28	$C_{2.3}H_{3.4}NO$
	56.6	75.26	57.74	50.56	3.45	19.99	26.0	$C_2H_3N_{0.82}O_{0.94}$

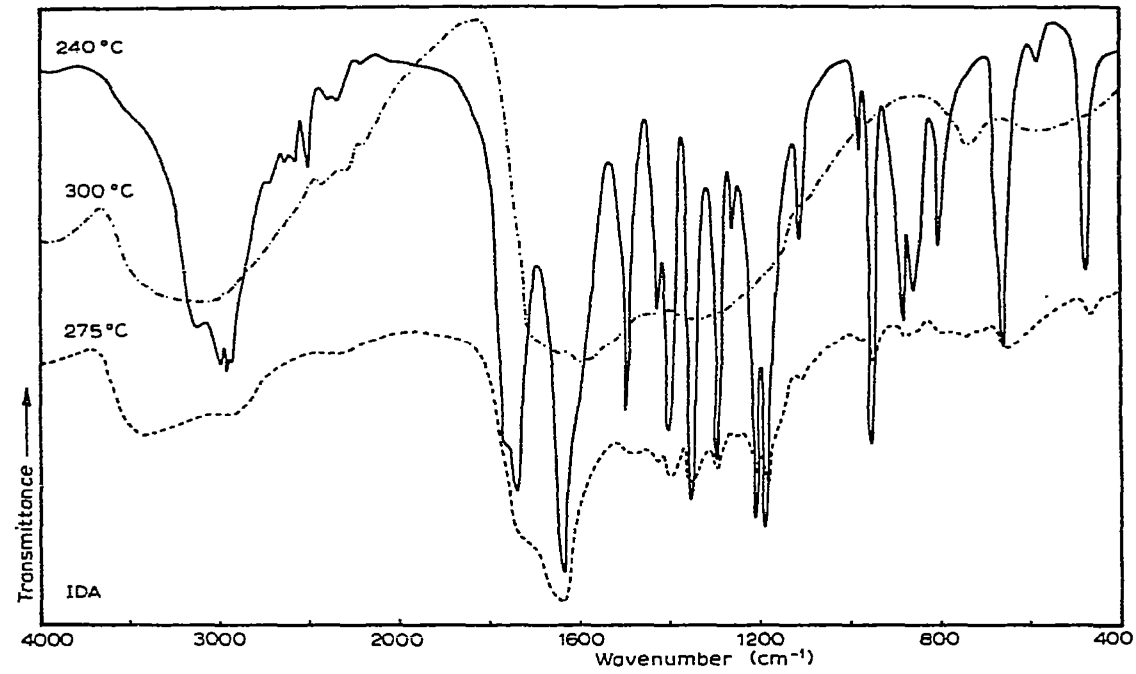
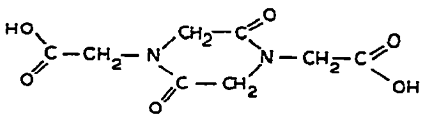


Fig. 2. Spectra of IDA at different temperatures.

for IDA, but that at 1290 cm^{-1} is stronger and sharper, similar to the vibrations of O—C—N and N—H bonds in secondary amines [11—14]. The band at 1110 cm^{-1} is characteristic of the C—N bond and the strong peak at 660 cm^{-1} can be assigned to the deformation vibration of the N—H bond [7].

The probable structure for IDA at 240°C, deduced from this data is

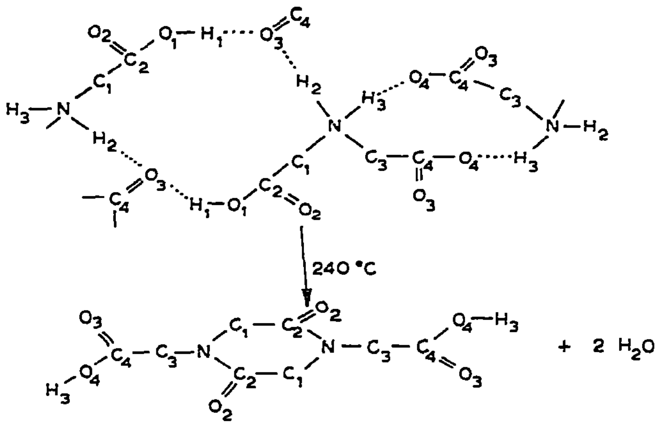


This formula contains the suggested functional groups forming cyclopeptides of different rings in such a way that some acid groups and N—H bonds remain free.

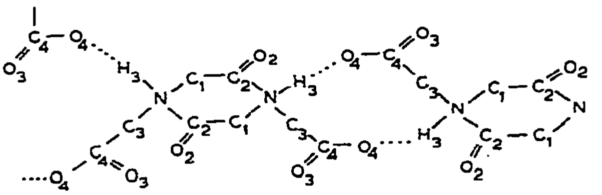
The spectra of IDA heated at 275 and 300°C are also shown in Fig. 2. The absorption bands disappear progressively: in fact, only two wide absorptions remain in the latter, i.e. 3500—3000 cm^{-1} (N—H, CH_2) and 1800—1600 cm^{-1} (C=O).

Mechanism of the thermal decomposition of IDA

From the crystalline structure of IDA [2] and the thermal and spectroscopic data, it can be deduced that the first effect produced by the increasing temperature is the breaking of the strong hydrogen bonds and the loss of two moles of water per two bonded molecules. The following decomposition process can be suggested.

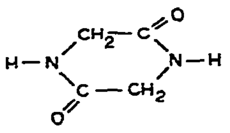


The bonded molecules could be represented in the form



This structure could explain the double IR absorption registered at 1700—1800 cm^{-1} as due to different C=O groups. It can also explain the NH^+ absorption at about 3100 cm^{-1}, weaker than the NH^+ band in the acid. The IR spectrum also shows weak O ··· H ··· N bonds.

The decomposition step corresponding to a weight loss of 55% (C_2H_3NO) leads to the loss of acetic groups, and the structural formula with only the lactam rings could be



Thermal decomposition of IDA-Na_2 · 1.4 H_2O

The DTA curves of IDA-Na_2 show some endothermic effects below 200° C (Fig. 3) due to the loss of the water of crystallization. The thermic effects between 300 and 500° C correspond to cracking of the molecule. There is a release of CO_2, H_2, NH_3 and traces of hydrocarbons. The TG data show the loss of 1.4 mole of water (13.18%) between 60 and 200° C. The anhydrous salt is stable up to 290° C, at which temperature decomposition begins and continues up to 450° C. The weight loss points to the formation of Na_2CO_3 as the final product (exptl. wt. loss 46.8%; theor. 47.57%).

The IR spectrum of IDA-Na_2 heated at 240° C (Fig. 4) is analogous to that of the original sample. The corresponding spectrum of the sample heated at

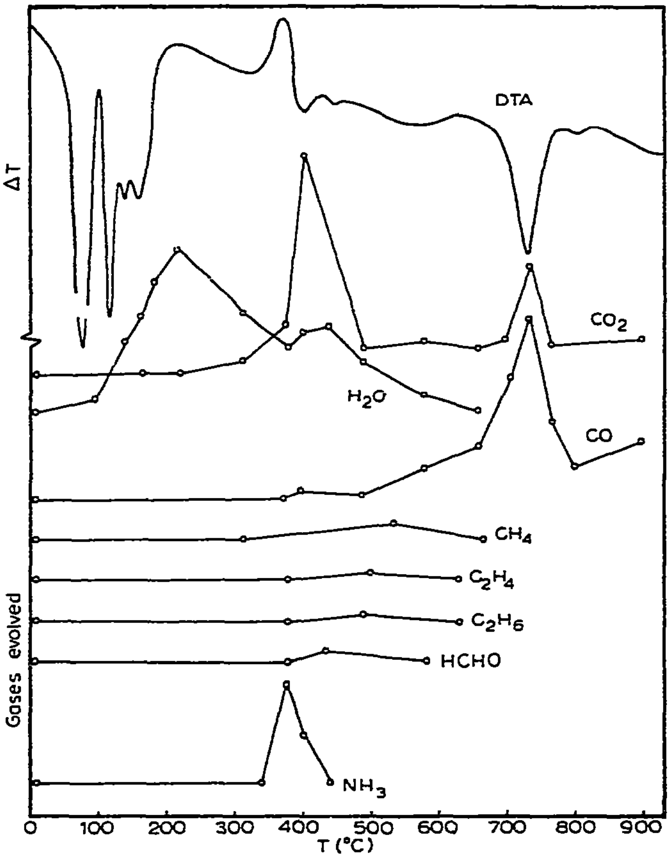


Fig. 3. Thermal and chromatographic behaviour of IDA-Na_2.

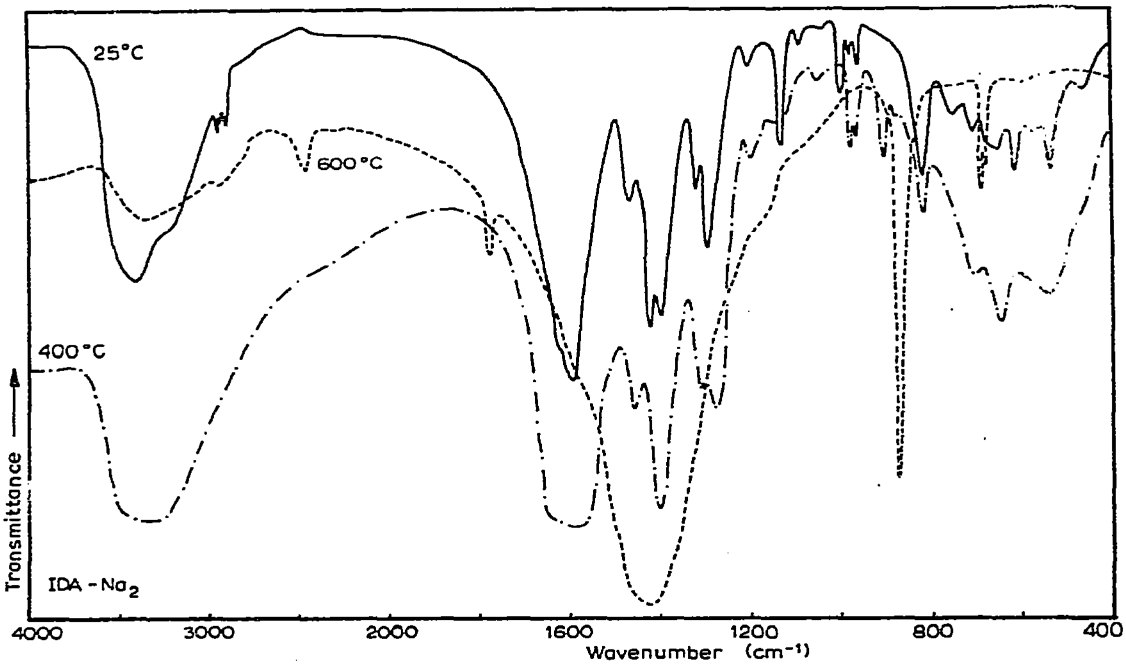


Fig. 4. Spectra of IDA-Na_2 at different temperatures.

400° C shows a mixture of sodium oxalate and carbonate, but not so clearly as the salts of EDTA [15]. At 600° C, the spectrum shows Na_2CO_3 as the only product.

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