

## Short Communication

## THERMAL BEHAVIOUR OF IMINODIACETIC, OXYDIACETIC AND THIODIACETIC ACIDS

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The thermal decomposition of iminodiacetic, oxydiacetic, and thiodiacetic acids in helium atmosphere has been studied by means of thermogravimetry (TG), differential thermal analysis (DTA) and temperature-programmed pyrolysis directly coupled with mass spectrometry (TPPy-MS). Evolved gas analysis (EGA) profiles of iminodiacetic and oxydiacetic acids were obtained and compared with TG and DTA profiles.

The decomposition of iminodiacetic acid forms water, CO, CO<sub>2</sub>, CH<sub>3</sub>CN, HCN and some hydrocarbons. After water evolution a cyclic anhydride is formed, as well as for oxydiacetic acid. Thiodiacetic acid vaporizes without decomposition.

**Keywords:** decomposition mechanism, differential thermal analysis, simultaneous thermogravimetry, temperature-programmed pyrolysis-mass spectrometry (TPPy-MS), thermal decomposition

## Introduction

Aminopolycarboxylic acids are very important compounds in analytical chemistry, as they form stable complex species with several metal ions. This fact is due to the presence of several iminodiacetate groups in the ligands.

Chromium(III) complexes of diethylenetriaminopentaacetic acid (DTPA) have been investigated, both in aqueous solution and in the solid-state [1, 2]. The 1:1 chromium-DTPA complex is a stable species, having one iminodiacetate group free from coordination, thus being able to form dinuclear mixed complexes with several metal ions. The thermal analysis of the solid species has been performed to define decomposition steps starting from mass loss at different temperature.

In order to investigate more precisely the mechanism of the thermal decomposition, a study is performed starting from iminodiacetic acid, the main chelate group of the ligand. Furthermore, in this paper, also the ligands with oxygen and sulphur atoms, e.g. oxydiacetic and thiodiacetic acids have been considered.

Iminodiacetic, oxydiacetic, and thiodiacetic acids are of great interest in coordination chemistry, as they are potentially tridentate ligands, differing only in one donor atom, which is an aliphatic nitrogen, an ether oxygen and an ether sulphur, respectively.

Such ligands have been already extensively investigated in aqueous solution and in the solid-state to study several metal complexes. Thermal characterization of thiodiglycolate complexes of heavy lanthanide [3] and X-rays analysis of oxydiacetate complexes of nickel(II) and cobalt(II) [4] have been performed, as well as stability constants of the evidenced species have been calculated [5, 6].

In the case of the lead(II), besides normal and protonated complexes in solution [7], also solid species have been detected. A 1:1 molar ratio compounds were prepared with all the mentioned ligands as white, crystalline substances, and have been characterised by X-ray analysis and thermal measurements [8].

Thermal analysis was compared with MS analysis of the evolved products at different temperature. Also DSC was utilised to better explain the mechanism of decomposition.

## Experimental

## Apparatus

The thermal measurements were carried out using a TSG-2 thermal analyser and DSC scanning calorimeter, connected to a Data Station 3600 (PerkinElmer, Shelton, CT, USA) equipped with specific software packages for instrumental control and data process-

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ing. TG and DSC runs were made under nitrogen stream (flow rate about 50 mL min<sup>-1</sup>). The heating rate was 10°C min<sup>-1</sup> with samples of 1–3 mg.

The evolved gas analysis (EGA) system consists of a microfurnace pyrolyser (Pyrojector II, SGE, Austin, Texas) interfaced with a VG TS-250 mass spectrometer (MS) (Micromass, Manchester, UK) using a heated transfer line. The sample (2 mg) is introduced in the microfurnace and heated from 110 to 710°C at a rate of 10°C min<sup>-1</sup> under a flow of helium (18 mL min<sup>-1</sup>) at a pressure of 70.93 kPa. The capillary transfer line (5 m×0.32 mm deactivated fused silica tube) is heated at 250°C.

The whole gas evolved during the thermal decomposition was continuously transferred to the electron impact (EI) MS source operating at 70 eV electron energy and at a temperature of 180°C. The MS system, equipped with a NIST (National Institute of Standards and Technology) library data base to assign the mass spectra to the evolved unknown compounds, scanned 1–80 uma every second and acquired the total ion current (TIC).

### Reagents

Iminodiacetic acid (BDH), oxydiacetic acid (Fluka), and thiodiacetic acid (Fluka) were used without further purification. The alkalimeter equivalent of the dried products was considered satisfactory. Melting points were in agreement with literature data.

## Results and discussion

### Iminodiacetic acid

The TG, DSC and TIC curves for thermal decomposition of iminodiacetic acid is reported in Fig. 1. The TG curve shows two different mass loss steps, at 217–252 and at 280–338°C, as also evidenced by TIC curve (maxima at 239 and 320°C). The DSC plot shows a double endothermic peak with maxima at the 239°C (the sharp peak corresponding to melting point of iminodiacetic acid) and 244°C. The mass spectra of the evolved gases at 239°C peak-top temperature is shown in Fig. 2 (upper).

The evolution of water is indicated by simultaneous detection of peaks at  $m/z$  18 (H<sub>2</sub>O<sup>+</sup>), 17 (OH<sup>+</sup>) and 19 (H<sub>3</sub>O<sup>+</sup>). The intensity ratio of (OH<sup>+</sup>)/(H<sub>2</sub>O<sup>+</sup>) is about 30% (NIST database reports 21.2%). Therefore, the main iminodiacetic acid thermal degradation is approximately coincident with its melting and the decomposition mechanism could be the following:

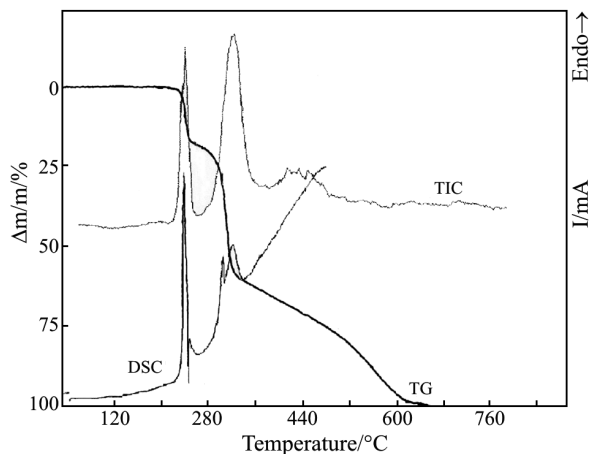
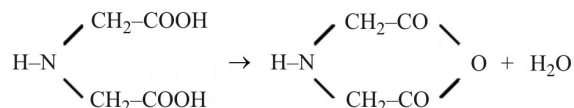


Fig. 1 TG, DSC and TIC curves for thermal decomposition of iminodiacetic acid

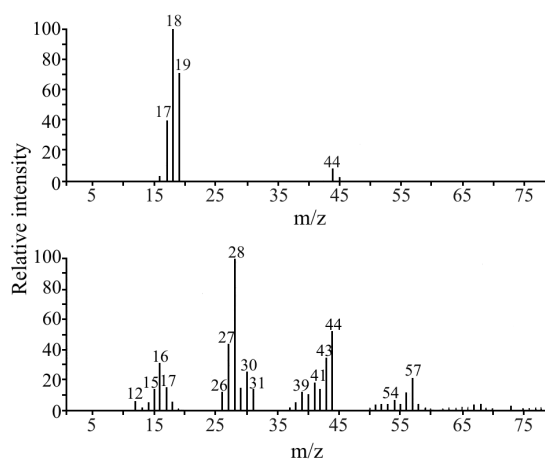


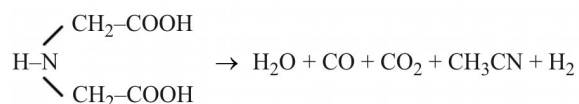
Fig. 2 Mass spectra of decomposition products of iminodiacetic acid: upper  $T=239^\circ\text{C}$ , lower  $T=320^\circ\text{C}$

In fact, the TG curve shows a first mass loss of more than 1 mole of water per mole of the acid (theor. 13.53%, exper. 17.4%). Furthermore, a peak of low intensity at  $m/z=44$  indicates also a little evolution of carbon dioxide (CO<sub>2</sub><sup>+</sup>). This fact indicates a simultaneous partial decarboxylation process.

At higher temperatures the DSC curve shows a second double endothermic peak at 302 (a sharp peak) and 320°C. The sharp peak is probably related to the boiling point of iminodiacetic anhydride. In fact, calculated boiling point (299.0±33.0°C) available from Chemical Abstract Service of American Chemical Society data base is in keeping with DSC data.

The mass spectrum observed at 320°C of TIC curve is shown in Fig. 2 (lower): the formation of CO<sub>2</sub> is evident ( $m/z$  44), together with H<sub>2</sub>O and CO ( $m/z$  28, CO<sup>+</sup>). At higher temperature (>400°C), a broad peak is shown in the TIC plot as result of cracking of the substance (Fig. 2). The formation of CH<sub>3</sub>CN is evidenced

by a peak at  $m/z=41$ . Therefore, the overall proposed decomposition mechanism is the following:



Further decomposition leads to the formation of HCN, formaldehyde ( $m/z$  30) and  $\text{C}_1\text{-C}_4$  hydrocarbons, showing typical  $M-n^+$  ( $n=1,2,\dots$ ) peaks.

#### Oxydiacetic acid

Figure 3 shows the TG, DSC and TIC curves for thermal decomposition of oxydiacetic acid. The sharp endothermic peak at  $140^\circ\text{C}$  of DSC curve corresponds to the melting point of the oxydiacetic acid ( $140\text{--}144^\circ\text{C}$ , Fluka catalogue). The TG curve shows a considerable mass loss between  $160\text{--}250^\circ\text{C}$ , that in DSC curve appears as two endothermic processes partially overlapped, at  $214$  and  $234^\circ\text{C}$ . The TG and DSC curves are in good correspondence with the TIC curve which shows two unresolved peaks at  $218$  and  $238^\circ\text{C}$ .

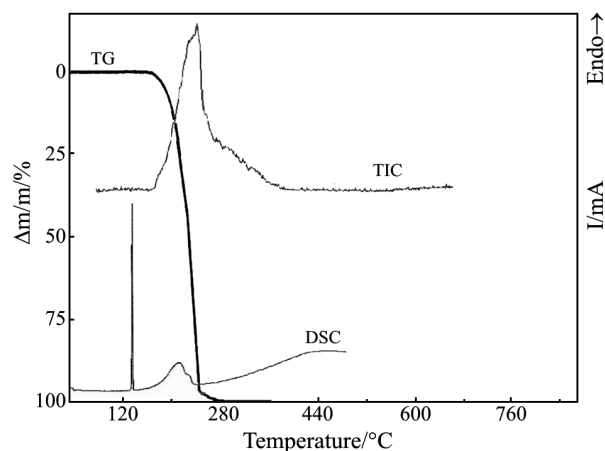


Fig. 3 TG, DSC and TIC curves for thermal decomposition of oxydiacetic acid

The mass spectra of evolved gas acquired between  $210$  and  $250^\circ\text{C}$  are recognized to be similar to each other because the intensity ratios of fragments are approximately constant. The average mass spectrum shown in Fig. 4 (upper) suggests the simultaneous evolution of different compounds. Besides the production of water explained by the presence of peaks at  $m/z$  18 ( $\text{H}_2\text{O}^+$ ), 17 ( $\text{OH}^+$ ) and 19 ( $\text{H}_3\text{O}^+$ ), the spectrum shows the peaks at  $m/z$  29 ( $\text{COH}^+$ ), 42 ( $\text{CH}_2\text{CO}^+$ ) and 44 ( $\text{CO}_2^+$ ) that are consistent with the formation of the oxydiacetic anhydride. This hypothesis is supported by the observation of the oxydiacetic anhydride mass spectrum available in the NIST database and reported in Fig. 4 (lower).

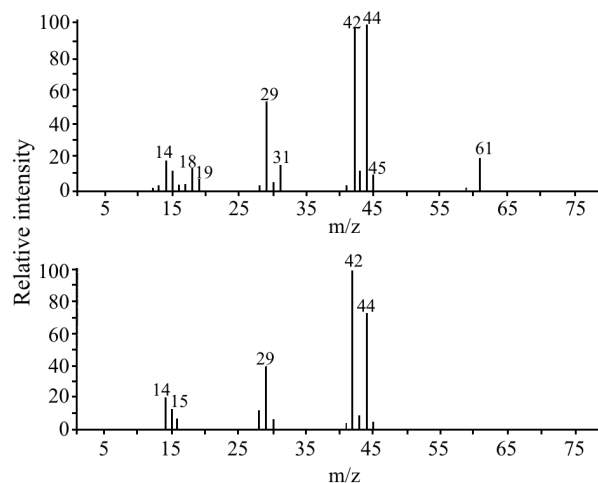
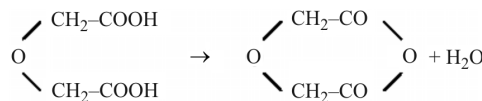


Fig. 4 Mass spectra of decomposition products of oxydiacetic acid. (Upper) mass spectrum of total evolved gas between  $210\text{--}250^\circ\text{C}$ . (Lower) reference mass spectrum (NIST data base) of oxydiacetic anhydride

So, we can suppose the formation of a heterocyclic ring by a dehydration process:



The oxydiacetic anhydride, therefore undergoes a complete evaporation (boiling point  $240\text{--}241^\circ\text{C}$  [9]) without any decomposition.

#### Thiodiacetic acid

Thiodiacetic acid shows, in the TG curve, a single mass loss near  $200^\circ\text{C}$ , starting at  $135^\circ\text{C}$ , corresponding to an endothermic process evidenced in the DSC plot (Fig. 5), due to a sublimation process without any decomposition. Only a 5% of the residue decomposes at  $250^\circ\text{C}$  forming mainly  $\text{CO}_2$ .

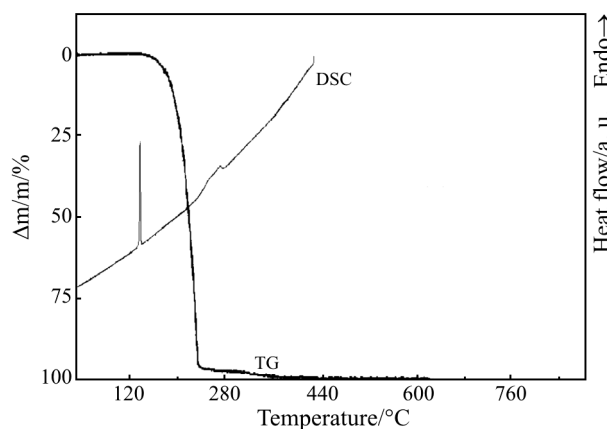


Fig. 5 TG and DSC curves for thermal decomposition of thiodiacetic acid

## Conclusions

Iminodiacetic acid decomposes in two steps, at 239 and 320°C. In the first step mainly one water molecule per mole of acid is evolved. In the second step since different products are evolved simultaneously, it was difficult to elucidate the decomposition mechanism by simple TG-DTA. The analysis of evolved gases using MS was able to determine the intermediate products in the course of the decomposition.

A likely stable six-member cyclic structure is hypothesized in the first step with successive decomposition forming also CH<sub>3</sub>CN. Besides, HCN and formaldehyde are detected, together with several hydrocarbons.

Gonzalez Vilchez *et al.* [10] have investigated the thermal behaviour of iminodiacetic acid by DTA, TG and static heating. The analysis of the evolved gases was made by gas chromatography and IR measurements. Some identified gases are the same detected by us, but the supposed decomposition mechanism is quite different.

The oxydiacetic acid decomposes with simple fragmentation in the 200–250°C temperature range forming the corresponding anhydride with loss of water. At this temperature, the six-member cyclic structure undergoes complete evaporation without any degradation producing a broad double peak in the DSC curve.

Yasodhai and Govindarajan [11], in a study about preparation and characterization of oxydiacetate complexes show similar results but different interpretation of thermal degradation of oxydiacetic acid. They suggest the probable loss of ethylene as principal step but no evidence of this compound is explained.

Finally, thiodiacetic acid vaporizes without decomposition.

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