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Thermal decomposition of acetylsalicylic acid (aspirin)

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Abstract

The thermal decomposition of aspirin in air and dry air flux was investigated. Thermogravimetry–derivative thermogravimetry (TG–DTG), differential scanning calorimetry (DSC), nuclear magnetic resonance (NMR), infrared absorption spectra and thin layer chromatography have been used to study the thermal decomposition of this compound. The results permit the identification of some compounds revealed in the first step of the TG–DTA curves, and also suggest the thermal decomposition mechanism.

Keywords: Acetylsalicylic acid; Differential scanning calorimetry; Infrared absorption spectra; Nuclear magnetic resonance; Thermal decomposition; Thermogravimetry

1. Introduction

Several investigations have been carried out on the application of thermal analysis to investigate aspirin and aspirin in the presence of tablet excipients. The identification of non-prescription internal analgesics have been investigated by means of TG and DTA [1]. Studies of acetylsalicylic acid [2], mixtures of acetylsalicylic acid and *p*-chloroaniline [3], and aspirin [4, 5] have also been investigated.

In the present work, aspirin was studied using TG–DTA, DSC, ^{13}C NMR, IR absorption spectra and thin layer chromatography to elucidate the thermal decomposition mechanism.

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2. Experimental

Acetylsalicylic acid (aspirin) was obtained from Biogalenica Quimica e Farmaceutica Ltda.

The TG–DTG and DSC curves were obtained using a Mettler TA 4000 thermoanalyser system with an air and dry air flux of 150 ml min^{-1}, a heating rate of 10°C min^{-1} and with the sample weighing about 8 mg. An alumina crucible was used for the TG–DTG curves and an aluminium crucible with a perforated cover was used for the DSC curve.

^{13}C nucleation magnetic resonance spectra was recorded on a Brucker A.C.-200, multinuclear spectrometer in $CDCl_3$ solution with tetramethylsilane as the internal standard infrared spectra were recorded on a Nicolet Impact-400, with a resolution of 4 cm^{-1}, by using the liquid film technique in $HCCl_3$.

Thin layer chromatography analysis was carried out using the systems silica 60G–chloroform: acetic acid (80:1) and iodine for visualization.

3. Results and discussion

The TG–DTG curves of aspirin, Fig. 1, show mass losses in two consecutive steps, between 120 and 400°C. The first step up to 260°C, occurs with the loss of 42.8% followed by the loss of 57.2% in the second step. No difference was observed in the curves obtained in air or dry air flux, and they show a great similarity with the TG–DTG curves in nitrogen atmosphere [1, 4, 5], except for the mass losses that occur in each step.

The first mass loss of the TG–DTG curves is due to the elimination of acetic acid (characteristic odour) and evaporation of acetylsalicylic and salicylic acids. The evaporation of these acids were identified by chromatography (Fig. 2) with the condensed solid product being gathered during the first step of the thermal decomposition (including another unidentified product).

When heated again, the residue of the thermal decomposition up to 260°C gave a liquid which contained acetic acid (characteristic odour).

For the analysis of the residue, a sample of aspirin (1g) was heated up to 260°C in an oven in the same conditions as the TG–DTG curves, with the elimination of about 43% of the sample. The residue had an acetic acid odour and was washed with distilled water until the acetic acid was eliminated; it was then dried at ambient temperature. Tests with ferric hydroxamate [6] on the residue and washed residue indicated the presence of an ester in both residues without any evidence of formation of an anhydride.

The IR spectra of the washed residue showed the absence of absorption bands in the region of 1800 cm^{-1}, indicating the absence of any anhydride in this residue, which presents a normal mode of relative vibration of the C=O stretching in this region [7]. A strong band of absorption at 1749 cm^{-1} is assigned to the stretching of the (C=O) group characteristic for the ester function.

In the higher frequency region of the IR spectrum (2861–2933 cm^{-1}), bands were observed due to the symmetric and asymmetric stretchings of CH_3 group. Other stretching bands were observed at 1380 and 2966 cm^{-1} and were ascribed to the

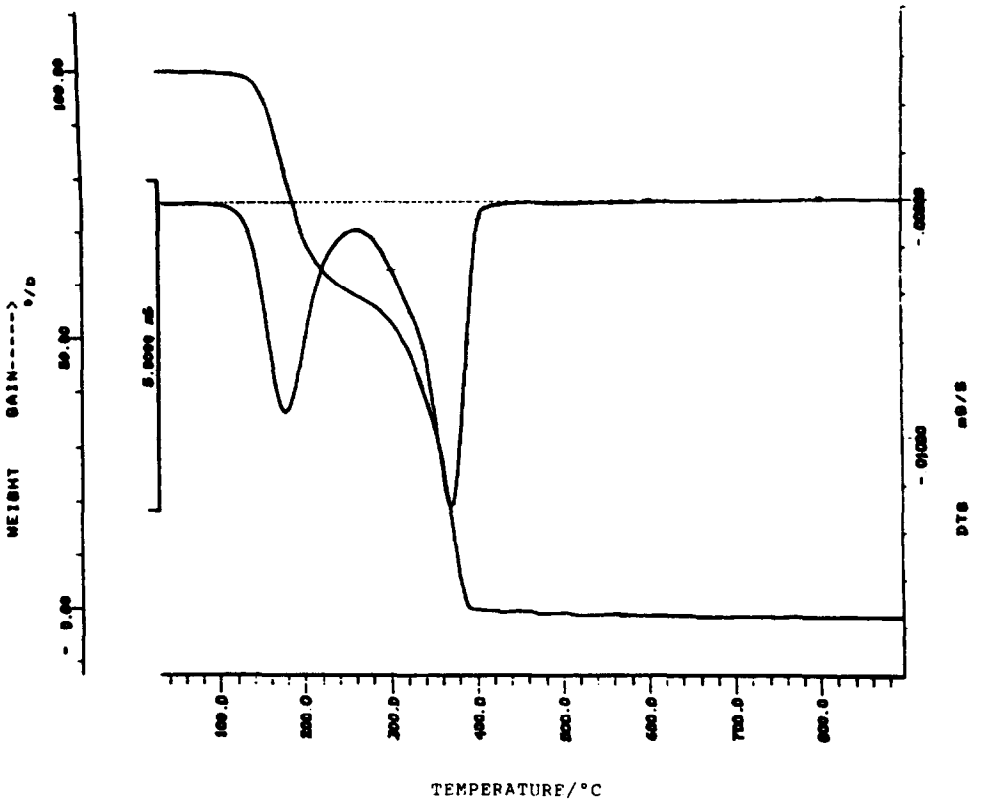

Fig. 1. TG–DTG curves of acetylsalicylic acid (8.131 mg); heating rate, 10 C min^{-1}; air flux, 150 ml min^{-1}.

angular deformation $\delta(CH_3)$ of the acetate group and (C═H) stretching relative to the normal mode of vibration of breathing of the aromatic ring.

These data allowed us to propose the formation of 2,2′-bis(acetate) diphenyl ester during the first step of the TG–DTG curves.

In the ^{13}C NMR spectrum of this residue, the carbonyl signal concerning the acetate group occurs at 169 ppm, while in aspirin the same signal occurs at 162 ppm. The shift of the signal of this carbon atom to lower field can be explained by the loss of a strongly electronegative group, such as the (CO_2H). This spectrum also showed a signal at 21 ppm ascribed to the (OCH_3) group.

The chemical shifts of the aromatic carbon atoms for the 2,2′-bis(acetate) diphenyl ester were calculated [8] and the following values for δ(ppm) were obtained: 122.9, 126.9, 128.5, 129.0, 135.5, and 150.5, in agreement with the spectrum data observed: 122.1, 126.3, 130.6, 130.9, 136.0, and 151.1.

Thus, this result permits us to suggest that the hydrolysis of aspirin is due to the reaction

The second step of the TG–DTG curves is due to the elimination of the residual acetic and salicylic acids, and the thermal decomposition of the 2,2′-bis(acetate) diphenyl ester.

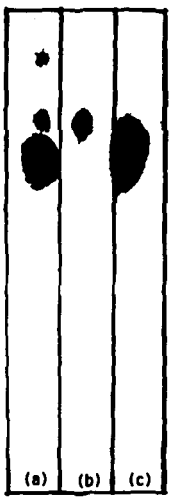

Fig. 2. Thin layer chromatography: (a) sample (b) acetylsalicylic acid and (c) salicylic acid.

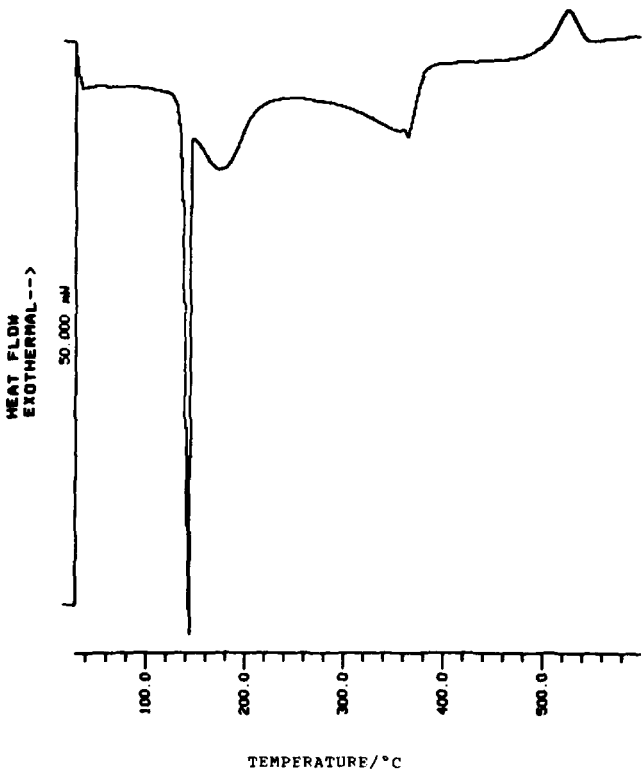

Fig. 3. DSC curves of the acetylsalicylic acid (8.022 mg); heating rate, 10°c min^{-1}; air flux, 150 ml min^{-1}.

The DSC curve, Fig. 3, show endothermic and exothermic peaks, and a close similarity with the DTA [1, 5] and DSC curves [4] up to 400°C. The first endothermic peak at 140°C followed by a second endothermic peak at 180°C are due to the fusion, followed by the elimination of acetic acid accompanied by evaporation of acetylsalicylic and salicyclic acids, corresponding the first mass loss of the TG–DTG curves. The endothermic peak at 370°C is ascribed to the mass loss observed in the second step of the TG–DTG curves.

The exothermic peak at 520°C is probably due to the oxidation reaction of a product formed during the final thermal decomposition as a result of the perforated cover used for the DSC curve.

4. Concluding remarks

The results obtained in this study, allowed us to verify that the stoichiometric analysis of the TG–DTG curves is impossible, as already observed in Ref. [5]. These data also permitted us to obtain information which has not yet been reported in the literature.

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