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Using thermal and spectroscopic data to investigate the thermal behavior of epinephrine

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ABSTRACT

Epinephrine is a neurotransmitter of the catecholamine class that acts in the mammalian central nervous system. The TG-DTA curves of epinephrine showed that the anhydrous compound starts decomposition at 165 °C, under the conditions used in this work. The reflectance FTIR spectra and X-ray powder diffraction patterns of epinephrine before and after heating up to 210 °C, as well as the TG-FTIR spectra of sample heated between 30 and 600 °C, were obtained and reveled that after heating, structural changes occurred in the sample. At temperatures higher than 205 °C the thermal decomposition took place with elimination of methylamine in agreement with the first mass loss observed in the TG curve in both air and N_2 atmospheres (TG = 17.0%, calcd. = 17.0%). The melting was observed at 205 °C (DTA) or 203 °C (DSC) but this process occurred overlapped with decomposition characteristic of an incongruent melting process.

1. Introduction

Epinephrine (EP, adrenaline, Fig. 1) is a neurotransmitter of the catecholamine class that acts in the mammalian central nervous system [1]. Cathecolamines control the nervous system in a series of biological reactions and chemical processes [2].

Many diseases are related to changes of EP concentration in living systems. It also serves as a chemical mediator for converting the nerve pulse to different organs. Many phenomena are related to the EP concentration in blood as well as in urine. The normal amount of epinephrine in a healthy person serum stays at nmol L^{-1} level. Due to its importance in living systems and common use in emergency medicine [3], epinephrine has attracted much attention of the scientists working on life science and medicine fields [4].

There are many methods applied in the determination of EP in aqueous solutions, such as high performance liquid chromatography (HPLC) [5,6], capillary electrophoresis [7,8], flow injection [9,10], chemiluminescence [11,12], fluorimetry [13] and spectrophotometry [14,15]. As an electroactive molecule, it has also been determined via electrochemical techniques and some reports showed the electrochemical response of EP at different kind of electrodes, such as electrochemically pretreated glassy carbon electrode [16], carbon fiber microelectrode [17], polymer film modified glassy carbon electrode [18,19] and self-assembled monolayer modified electrode [20,21], among others.

Previous works reported the EP melting at 211–212 °C or 215 °C (when rapidly heated), but in this case accomplished by decomposition [22]. Lee and Burton [23] described studies concerning the thermal stability of several EP-derivative formulations since these compounds use to be both light and thermally unstable. These authors submitted epinephrine maleate, fumarate, hydrochloride and bitatrate salts to heating at 95 °C during 20 days and concluded that the stability is related to the melting of the salt. Any previous report employing thermoanalytical techniques in the evaluation of the thermal behavior of epinephrine was found in the literature.

Thus this work aims to contribute with a better understanding of the physical chemical properties of EP. Thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) were used to evaluate the thermal behavior of EP in solid state. Volatile decomposition products were characterized by TG-FTIR coupled analysis while the solid residues were investigated using FTIR and mass spectrometry.

2. Experimental

Epinephrine (Sigma, minimum 98.0% purity) was submitted to thermal analysis as received. Simultaneous thermogravimetry and differential thermal analysis (TG-DTA) were performed in a

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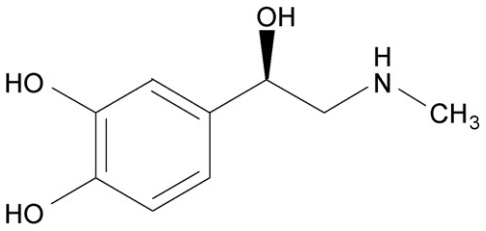

Fig. 1. Structure of epinephrine.

SDT Q600 apparatus from TA Instruments. All the TG-DTA curves were obtained under air and N_2 dynamic atmospheres (gas flow of 100 mL min^{-1}) and at a heating rate of 10 °C min^{-1}. The sample masses were about 8 mg. Alumina crucibles were used in the TG-DTA experiments. The simultaneous TG-DTA modulus was calibrated with aluminum (99.99+ %) for temperature.

DSC curves were recorded using a DSC Q10 modulus (TA instruments) under an air flow of 100 mL min^{-1} and at a heating rate of 10 °C min^{-1}. The sample masses were about 3 mg and covered aluminum crucibles with a pin hole (ϕ = 0.7 mm) in the center of the lid were employed during the analysis. DSC modulus was calibrated using indium metal (99.99+ %) for temperature and enthalpy.

Epinephrine samples were heated up to 205 °C in the thermobalance and the residue collected after cooling. This residue was submitted to mass spectrometry analysis in a Brüker ULTROTOF-Q with electron spray ionization. Samples were dissolved in methanol and introduced in an infusion pump at a 100 μL h^{-1} flow. The capillary was heated at 150 °C with a nebulizing gas flow of 4 L min^{-1} and 4 kV.

X-ray diffraction powder patterns were obtained using a D-5000 X-ray diffractometer (Siemens), with Cu Kα radiation (λ = 1.544 Å) and a setting of 40 kV and 20 mA. A 2θ range from 5° to 70° was used.

Coupled TG-IR analysis was performed in a Nicolet iS10 spectrophotometer (Thermo Scientific) coupled to the gas exhaust of a TGA/SDTA 851 Mettler Toledo.

Reflectance FTIR spectra of epinephrine and its decomposition product obtained at 205 °C were recorded in a Nicolet iS10 spectrophotometer (Thermo Scientific).

3. Results and discussion

The TG-DTA curves of epinephrine are shown in Figs. 2 and 3. These curves show that, under the experimental conditions used in this work, the anhydrous compound is stable up to 165 °C and above this temperature the thermal decomposition occurs in three (N_2) or four (air) consecutive and/or overlapping steps between 165 and 450 °C (N_2) or 165 and 600 °C (air) and thermal events corresponding to these losses.

In both atmospheres, the first step occurs between 165 and 209 °C with loss of 17%, corresponding to a sharp endothermic peak at 205 °C. For the N_2 atmosphere the last two overlapping steps observed between 220 and 450 °C with loss of 47%, the thermal decomposition occur with the formation of carbonaceous residue. Any thermal event corresponding to these losses is observed in the DTA curve, probably due to the heat involved in these steps is insuf-

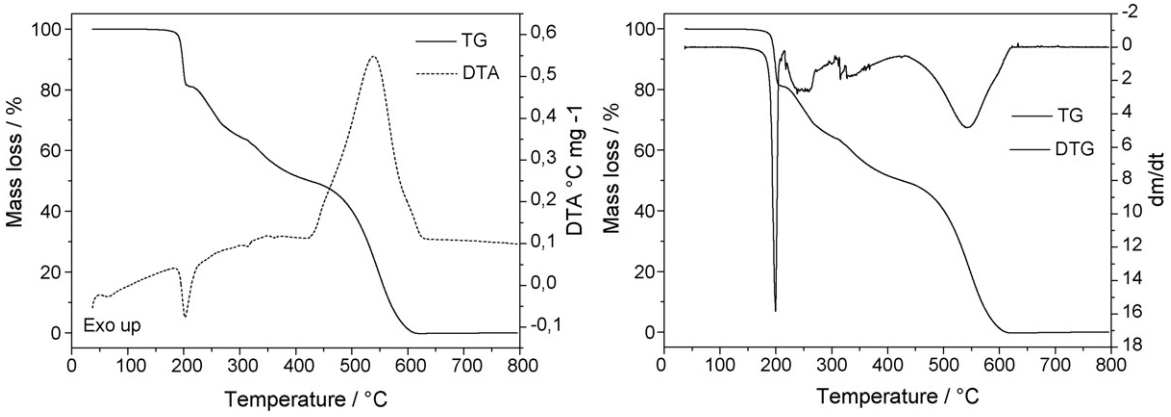

Fig. 2. TG-DTA and TG/DTG curves of epinephrine (m_i = 7.641 mg), under air atmosphere.

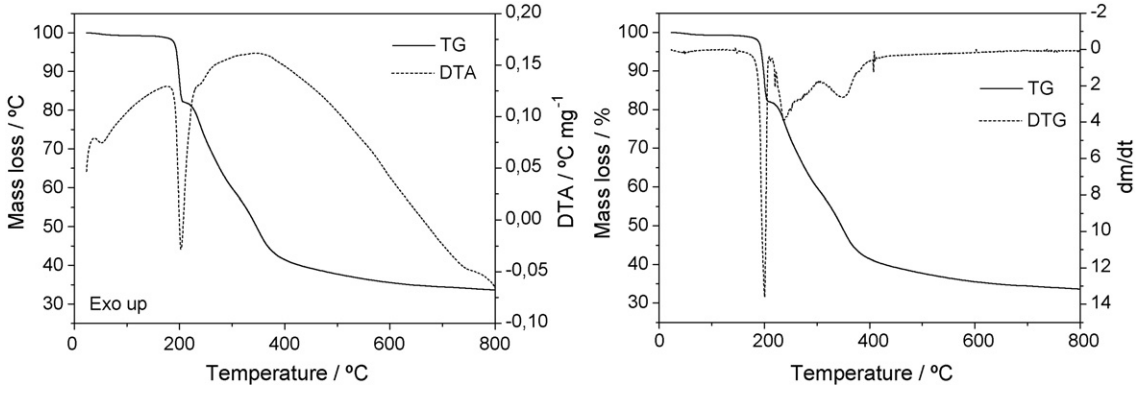

Fig. 3. TG-DTA and TG/DTG curves of epinephrine (m_i = 8.768 mg), under N_2 atmosphere.