Thermal Studies of L, D and β-Alanine

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Background

α-Amino acids are generally studied by spectroscopic techniques, to determine their structure and distinguish between L and D forms [1].Their study via thermal analysis is typically combined with other analytical techniques such as FT-IR, MS, HPLC, GC or NMR to identify the products of thermal decomposition [2,3].

It is intriguing to ascertain whether thermal analytical methods alone can provide useful information about amino acids, in terms of their physicochemical properties, and the ability of such techniques to distinguish between L and D forms.

Alanine was chosen for this study because it exists in both structural and stereoisomeric forms, making it an ideal candidate for comparative studies via thermal analysis.

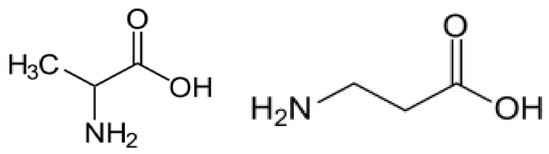

Figure 1: Structure of α-alanine (left) and β-alanine (right)

Methods

Four samples were used during this study: D-alanine, L-alanine, β-alanine and a 1:1 physical mixture (molar) of L/D-alanine. TGA experiments were performed using a TGA 2950 (TA Instruments). Samples were contained in aluminium sample pans held by platinum sample holders. Samples were subjected to various heating rates (2, 5 and 20°C/min) using a nitrogen flow rate of 50 mL/min.

DSC experiments were performed using a DSC Q2000 (TA Instruments). Samples were contained within aluminium sample pans capped with hermetically sealed aluminium lids. Samples were first equilibrated at 100°C for 5 min and then heated at a rate of 2°C/min to 400°C in nitrogen at a flow rate of 50 mL/min.

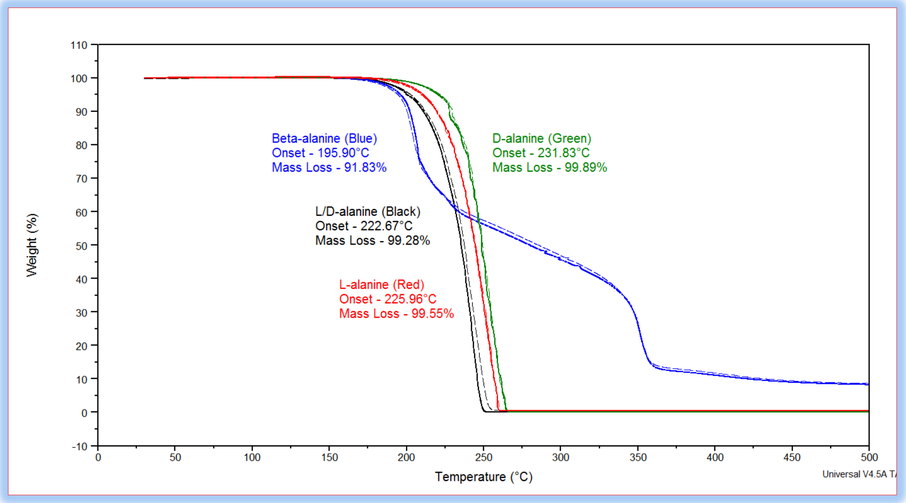

Figure 2: TG curves of D -, L-, β- and a physical mixture of L/D-alanine at 2°C/min. Onset is the calculated onset temperature of degradation. Mass loss is representative of the total percentage mass loss from 30-600°C.

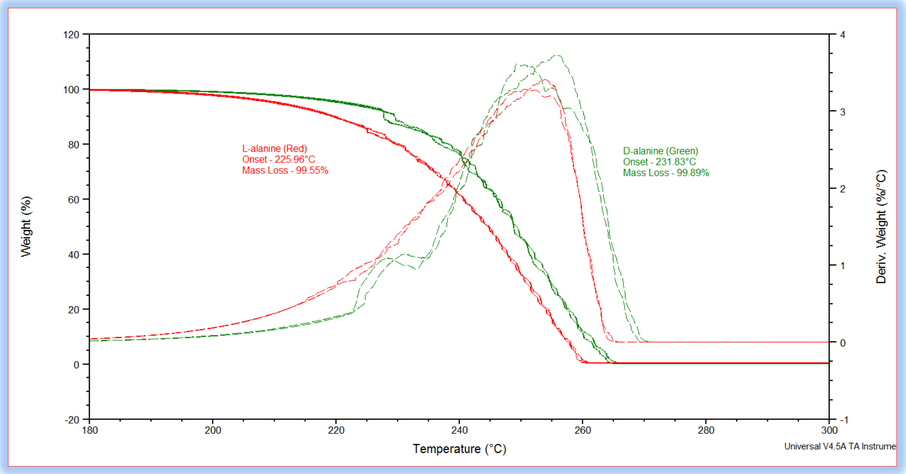

Figure 3: TG (solid line) and dTG (broken line) curves of D-, L-alanine at 2°C/min. Onset is the calculated onset temperature of degradation. Mass loss is representative of the total percentage mass loss from 30-600°C.

DSC Results and Discussion

DSC studies were undertaken on L-, D- and β-alanine at heating rates of 2 and 20°C/min. All results obtained via DSC were irreproducible. Hermetically sealed and standard pans were used with neither yielding reproducible data. Hermetic pans gave sharp intense peaks, but with a wide range of onset temperatures for a particular event. Peaks obtained using standard pans were much broader, less intense, and once again, irreproducible. Parameters such as sample size and grinding of the samples, to yield a homogeneous sample, were varied with little effect on reproducibility. These findings highlight a scenario whereby DSC is not particularly useful in characterising the solid state properties of a sample.

TGA Results and Discussion

TGA experiments were undertaken on all samples at heating rates of 2, 5 and 20°C/min. Results from heating rates of 5 and 20°C/min were irreproducible, indicating a kinetically dependent event. Figure 2 shows the TG curves for D/L/β/LD-alanine at 2°C/min. D- and L-alanine show close to 100% weight loss over the temperature range of 30-300°C, with no signs of moisture. The sharp and almost complete mass loss are distinctive of sublimation; this was confirmed by HSM. β-alanine shows a distinct two stage mass loss (derived from dTG, not shown) with an onset of 196°C; a first mass loss of 46.04% and a second mass loss of 45.79%, equating to a total mass loss of 91.83%. These results show the ability of TGA to distinguish structural isomers.

Figure 3 shows the TG/dTG curves of L/D-alanine at 2°C/min. There is a subtle but distinct reproducible difference in the TG and dTG curves for L and D-alanine. L-alanine and D-alanine exhibit onset temperatures of mass loss at 225.96°C and 231.83°C, respectively, showing the L-isomer to be more susceptible to temperature change than the D-isomer. Examination of the dTG curve highlights a small shoulder for D-alanine, a distinguishable feature not seen for L-alanine. These results indicate there is a difference in thermal stability between stereoisomers of L and D-alanine, presumably, as a result of a variation in molecular packing of the two enantiomers. These findings also indicate that TGA has the potential to distinguish not only structural isomers, but also stereoisomers.

TGA experiments of the 1:1 physical mixture (molar) of D- and L-alanine (Fig. 1) show a single stage mass loss of 99.28%, with no shoulder in the dTG, and an onset temperature of 222.67°C, lower than either the D or L forms; indicating a solid state interaction between the two forms during mixing and grinding.

Conclusions

TGA and DSC experiments were undertaken on three structural/stereo isomers of alanine. TGA results were able to partially characterise the solid state properties of the samples as well as distinguish between structural isomeric (α and β), and stereoisomeric (L and D) forms. DSC studies were conducted with little success in characterising the samples. Reproducible data was not obtained and therefore no results from DSC could be confidently used to characterise alanine. This study has highlighted a scenario where the sometimes overlooked technique of TGA, can yield much more information when characterising a sample, than DSC.

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