Structural Dependence of the Thermal Stability of Citrates

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Introduction

Citric acid and its derivatives are commonly found in the atmosphere, especially in aerosol (tiny particles suspended in the air). Citric acid commonly exist in aerosol phase as citrate salts. Detailed properties of these salts, however, are currently missing from the literature. This research project investigated the thermal decomposition profiles and mechanisms of a group of ammonia citrates to determine their thermal properties. Such information will contribute to our knowledge on citrates and their transformation in the atmosphere.

Citric acid belongs to a specific class of carboxylic acids: polyacids; they are acid molecules with more than one carboxyl group on them. Citric acid is classified as a poly acid because it has three carboxyl groups. As a result, there are three possible products that can be formed when the citric acid reacts with ammonia depending on the ratio. When three molecules of an ammonia react with one molecule of citric acid, the resulting citrate is considered fully neutralized and called ammonium citrate tribasic. Ammonium citrate dibasic is produced from two ammonia and one citric acid and ammonium dihydrogen citrate is from one ammonia and one citric acid; and these compounds are partially neutralized.

Approach

There were three compounds investigated, ammonium citrate tribasic (99% pure), ammonium citrate dibasic (99% pure), and ammonium dihydrogen citrate (95%pure). The chemicals were purchased from Fischer Scientific and other chemical companies. There was no further purification process. The thermal gravimetric analysis (TGA) was collected using a Q-series 600 instrument. The sample sized ranged from 7.5 mg to 9.0 mg, using an empty sample pan as a reference. Each sample was placed in the instrument and heated using the parameters for a fast run. The parameters for a fast run include: initial temperature of 25°C and a ramp of 20°C/minute; nitrogen flow of 100mL/min. Each scan was repeated to ensure reproducibility of the collected data.

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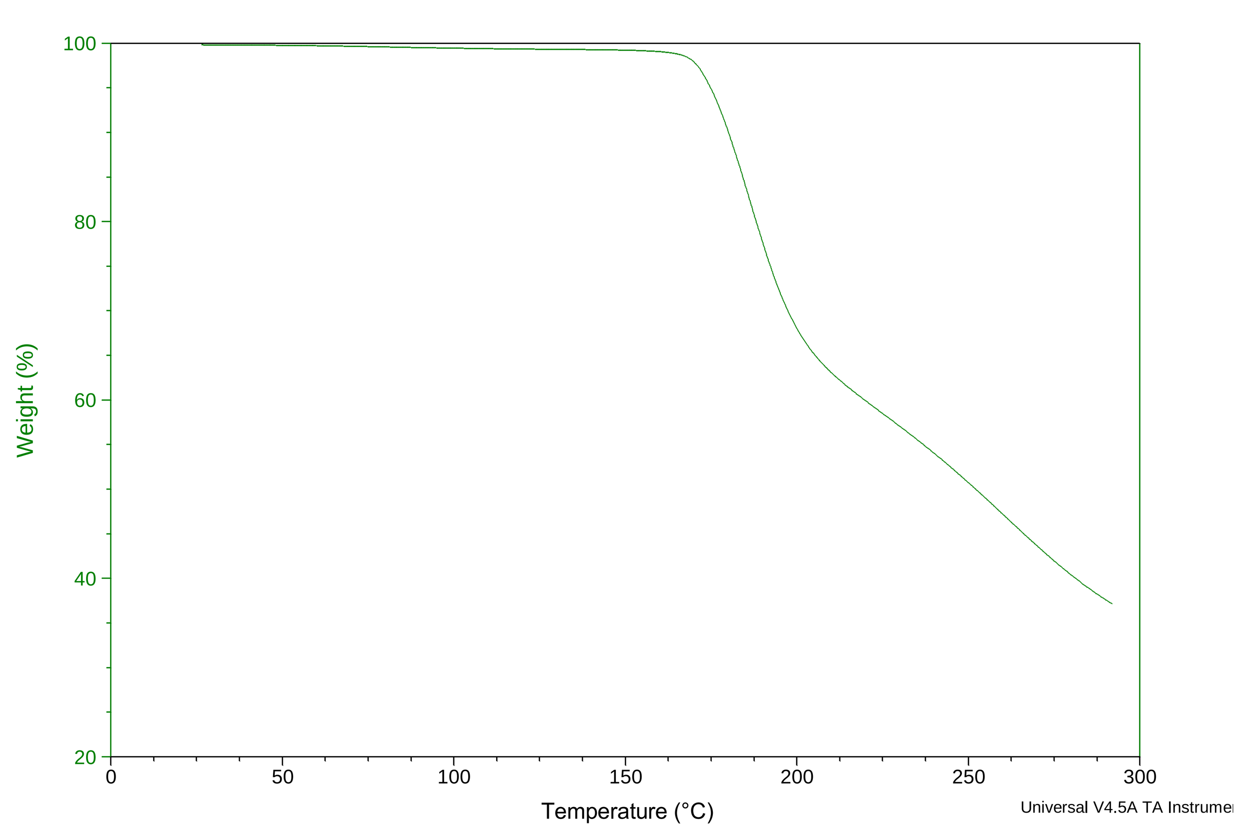

Figure 1- TGA of Ammonium Dihydrogen Citrate.

Results

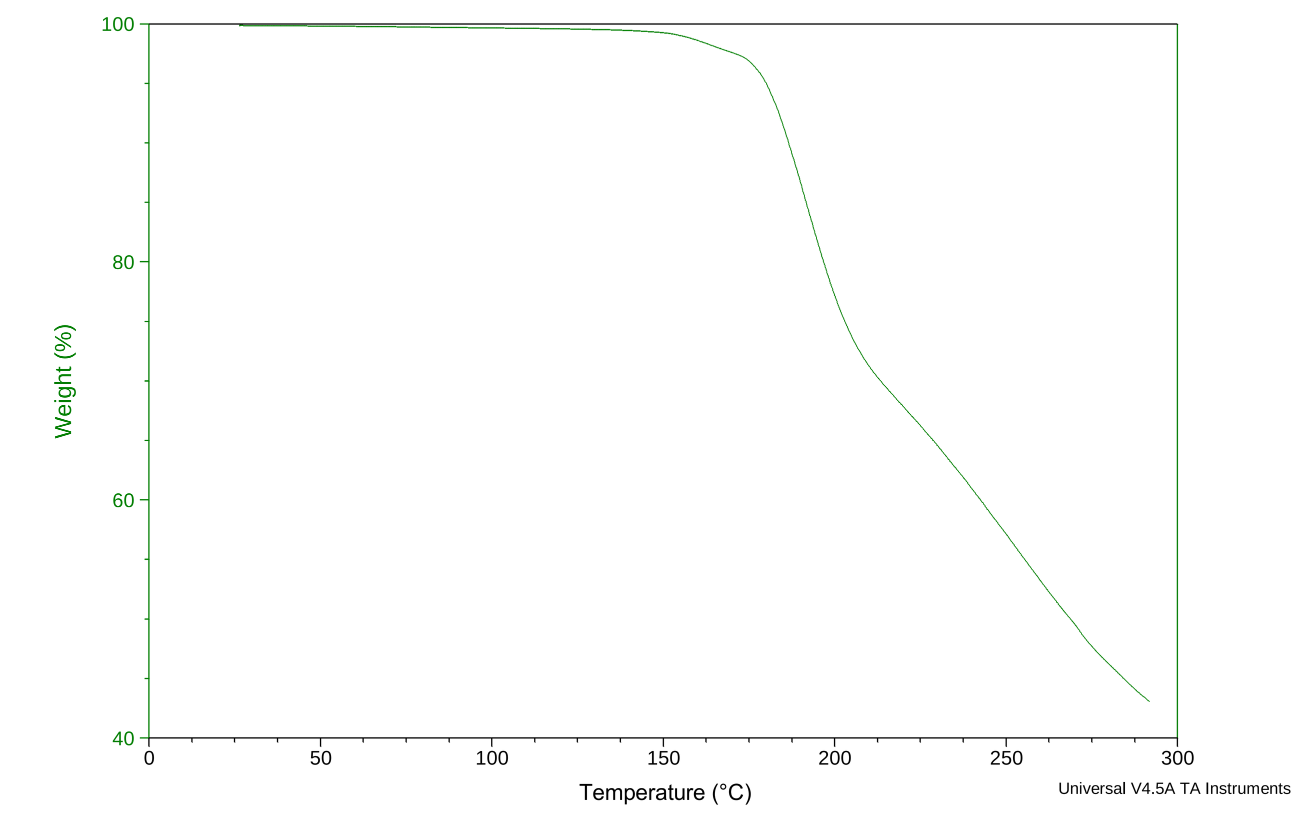

Figure 2- TGA of Ammonium Citrate Dibasic.

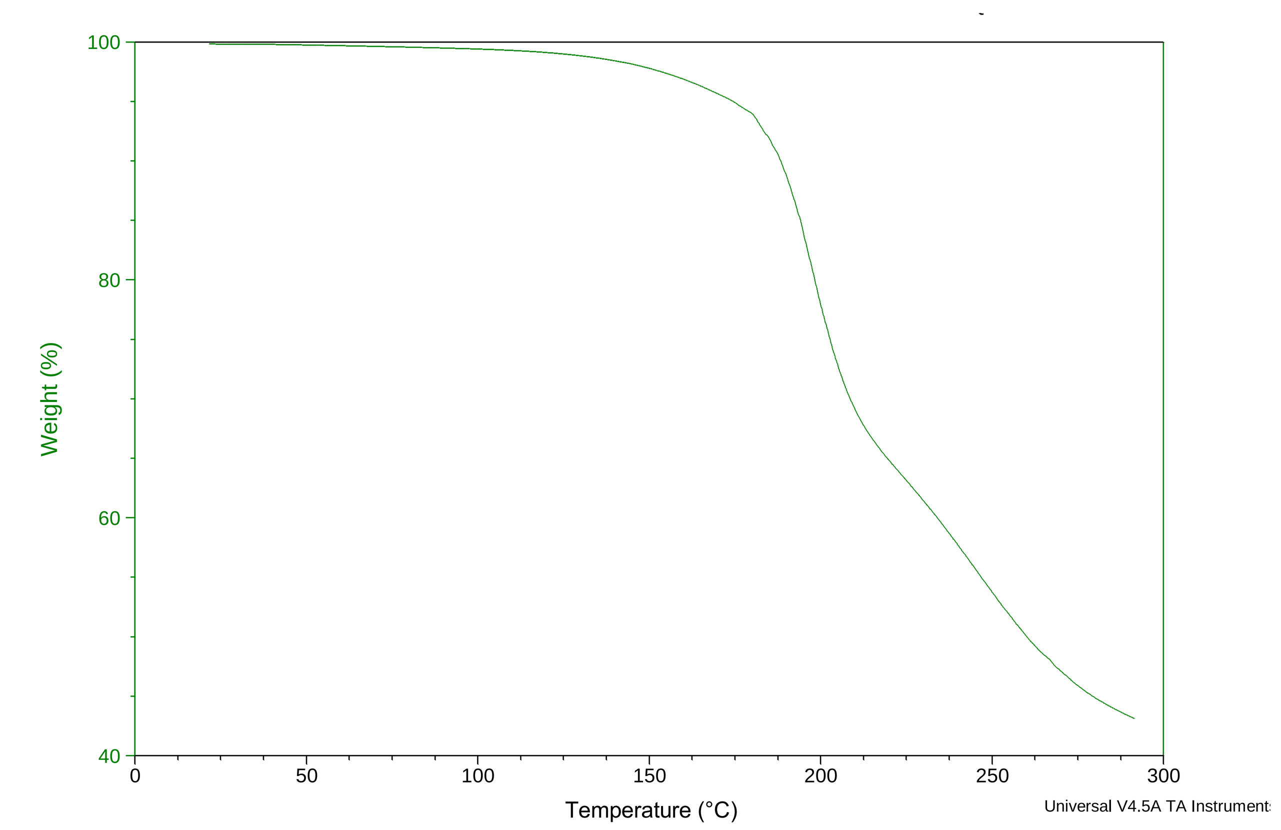

Figure 3- TGA of Ammonium Citrate Tribasic.

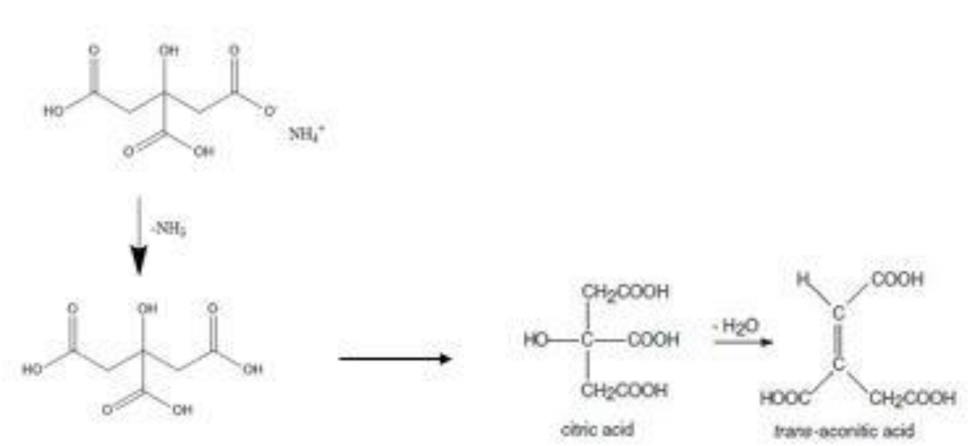

Figure 4- Possible Decomposition scheme of Ammonium Dihydrogen Citrate.

Discussion

The TGA graphs of the three citrates are very similar in the decomposition patterns observed. This indicated that the extra hydrogens do not have an obvious effect on the thermal decomposition of ammonium citrates.

The TGA graphs were analyzed by making a first derivative graph of each of the samples. This was done in order to determine the peak temperature in the decomposition of each of the compounds that were tested. This analysis lead to the determination that ammonium citrate tribasic was the most stable of the three compounds that was studied.

The first derivative peak also allowed for the analysis of the mass loss from decomposition for each of the samples studied. The mass loss of each sample was about the same. When analyzed further, the mass loss suggests there is a loss of an ammonia and a water molecule from each of the compounds. This is consistent with past research on the decomposition of citric acid in which citric acid goes through a dehydration as the first step in the process.

Table 1- Thermal Stability analysis

Compound	Temp at 1st derivative peak (°C)	mass loss at peak (%)
Ammonium Citrate Tribasic	195.25	16.49
Ammonium Citrate Dibasic	190.28	13.66
Ammonium Dihydrogen Citrate	185.93	17.26

Conclusions

The ammonium citrate tribasic compound was the most stable of the three compounds investigated. It was determined that the mass loss of each compound corresponded to the loss of one ammonium and one water molecule from each of the compounds.

This study established a baseline of known ammonium citrates. Future research will include running slow scans to determine if a slower heating will change the information collected indicating that there is something else that can happen when these compounds are heated. The results also indicated that ammonium citrate dibasic contains water at room temperature, meaning that the sample may have to be re-analyzed after proper drying.

References

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2. Erdey, L., et al. "Thermoanalytical Properties of Analytical-Grade Reagents—IVA1Sodium Salts." Talanta, vol. 11, no. 1, 1964, pp. 913–940.

Acknowledgements

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