

The Structural Dependence of the Thermal Stability of Citrates

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Abstract

Citric acid is commonly found in the atmosphere, especially in aerosols (tiny particles suspended in air). This research project investigated the thermal decomposition profiles and mechanisms of a group of ammonium citrates to determine their thermal properties. Citric acid belongs to a specific class of carboxylic acids: polyacids; they are acid molecules with more than one carboxyl group on them. Since each carboxyl group can react with one ammonia molecule, polyacids can react with more than one amine. By controlling the amounts of a polyacid and ammonia added to a reaction system, fully or partially neutralized carboxylates can be synthesized. 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. This research determined thermal properties of three ammonium citrates: ammonium citrate tribasic, ammonium citrate dibasic, and ammonium dihydrogen citrate. This research measured the thermal properties of the ammonium citrates, specifically investigating the thermal decay profiles using Thermal Gravimetric Analysis method. A decay profile was obtained for each citrate. The decay profiles of the three citrates showed similar patterns. This indicated that the extra protons do not have an obvious effect on the thermal decomposition of ammonium citrates. It was determined that the ammonium citrate tribasic was the most stable of the compounds studied. The percent mass loss for each of the compounds is about the same at the first derivative peak. This mass loss suggests that each of the compounds lost a water and an ammonia during the decomposition process. The data collected indicates that there is only one step of decomposition for each of the samples that were tested.

Keywords: Thermal Gravimetric Analysis, Decomposition, Ammonium Citrates

1. Introduction

Citric acid is a naturally occurring compound that is present not only in humans but other animal and plant cells as well. It has many applications in the food industry as well as the pharmaceutical industry due to citric acid being nontoxic. The interest in this common compound has grown recently due to its ability to be used to synthesize nanopowders. This has led to the investigation of the decomposition of citric acid, originally by Barbooti and Al-Sammerrai, however there has been further investigation into the intermediates that are formed after the dehydration of citric acid during the decomposition process. The trans-aconitic acid has comparable thermal stability to citric acid while cis-aconitic acid is less stable than both compounds with a decomposition point that is about 60 K lower. The DSC results indicated that the citric acid has more complex decomposition mechanisms than was shown in the TGA graph which had indicated a single step decomposition. The same happens for the trans-aconitic acid, the TGA has a seemingly one step decomposition whereas the DSC results reveal two endothermic events occurring. Although cis-aconitic is less stable than trans-aconitic, when the cis-isomer loses another water and becomes an anhydride, it becomes relatively stable. There is an exothermic reaction present in the DSC of the cis-aconitic acid, this is indicative

of a conformational change from the anhydrous cis-isomer to the anhydrous trans-isomer. The most probable transformation scheme based on the compounds studied is a process of dehydration and decarboxylation of the intermediate products. It was determined that after the dehydration and decarboxylation, citraconic anhydride or itaconic anhydride or the mixture of the isomers were produced in the end despite the original compound.³

There are detailed kinetic studies on the solid-state decompositions of various ammonium salts. They are generally grouped together in order to emphasize the behaviors that are observed in reactions involving the NH_4^+ ion. The decomposition of many of the ammonium salts involve the loss of NH_3 and H_2O whether simultaneously or consecutively. A total of 26 ammonium salts were studied and reported by Erdey *et al* including ammonium citrate compounds. The sample size was 100–200 mg and the heating rate was $5^\circ\text{C}/\text{min}$. Ammonium citrate is included in the group of ammonium carboxylates. It was determined that many of the carboxylate salts melt or sublime before or during the breakdown of the compound. The decomposition temperatures required tend to increase with an increase in molar mass. Erdey *et al* concluded that the base strength of the anion will increase with the temperature until it reaches NH_3 . While some carboxylates proceed through amide formation or sublime without decomposition, ammonium citrate decomposes at high temperatures and leaves residual carbon. An inorganic salt with hydrates tends to lose the associated water molecules upon heating, producing water vapor in the gas phase that is very stable; such process is therefore preferred because the product leaves the reaction system to drive the reaction to completion and the overall energy of the reaction system will be lowered. The ammonium salts investigated by Erdey *et al* show similar decomposition patterns via the loss of ammonia, which are similar to the water in the hydrates for similar reasons: (1) the bond between ammonium cation and the rest of the salt is likely weak and the ammonia can be released from ammonium salts upon heating; (2) ammonia is gas under their experimental conditions and it is thermodynamically stable. The release of ammonia may be followed by other reactions with the coordinating ion or other ligands. Many ammonium compounds that undergo decomposition have a first step proton transfer which ultimately leads to the loss of a water. The process of dehydration and deamination of the ammonium salts are generally reversible, making them more complicated with solid phase transformations or sublimation.^{1,2} It is worth noting that Erdey *et al* only investigated ammonium citrate tribasic, the fully neutralized salt between ammonia and citric acid.

This study will investigate the effect of unreacted active protons in ammonium citrates by studying the thermal decomposition profiles of ammonium citrate tribasic, ammonium citrate dibasic and ammonium dihydrogen citrate. It is hypothesized that any extra proton may form hydrogen bonding with the oxygen in carboxylate group and increase the thermal stability of the ammonium citrate. This study also aims at providing a more quantitative analysis on the thermal decomposition mechanisms of ammonium citrates. It has been shown in the literature that there is limited understanding on the thermal properties of ammonium and amine salts⁴ (including citrates⁵), which may play an important role in the atmospheric processes such as new particle formation, aerosol aging and air pollution.⁶ As a result, the results from our study will contribute to the research community in chemistry and atmospheric sciences.

2. Experimental Details

There were three pure samples that were retested in order to investigate the thermal decomposition behaviors of ammonium citrate salts with various ammonium to citrate ratios (degrees of neutralization). The ammonium citrate tribasic (97%, Acros), ammonium citrate dibasic (99+%, Alfa Aesar), and ammonium citrate dihydrogen (95%, Enamine Ltd.) were first analyzed without any additional purification or treatment. These ammonium citrate samples were reinvestigated in what is referred to as hydration testing: Each salt was weighed in a vial which was placed in a desiccator for about two months at room temperature to dry. These samples were reweighed to determine if there was a mass loss. Further thermal analysis was also conducted to confirm that the mass loss was truly from the loss of water (details in the Results and Discussion section).

This research measured the thermal properties of the ammonium citrates, specifically investigating the thermal decay profiles using Thermal Gravimetric Analysis (TGA) method. The TGA measurements were completed using a Q-series 600 instrument. The sample sizes were about 10 mg, with an empty sample pan used as a reference. The samples were analyzed using the following protocol: the sample was heated up by $20^\circ\text{C}/\text{min}$ from room temperature to 300°C with a nitrogen flow rate of $100\text{ mL}/\text{min}$. A decay profile was obtained for each citrate.

3. Results and Discussion

The hydration testing revealed that mass loss occurred among all three ammonium citrates after two months of the samples dried in a desiccator. Each of the samples had a clear decrease in mass, which indicated that there was some process of compound loss while in the desiccator, which could be either the loss of adsorbed water or the ammonia within the salt. When thermal gravimetric analysis was conducted on the dried ammonium citrates, no observable mass loss was observed below 100°C. It can therefore be concluded that the mass loss in reference to the dried samples was adsorbed water in the vials, rather than the compounds being hydrated. As a result, all the analysis later was based on the TGA results on dried ammonium citrate samples.

Table 1. Hydration Testing of Pure Ammonium Citrates

Compound	Mass (vial+sample, g) December, 2019	Mass (vial+sample, g) February, 2019	% Change
Ammonium dihydrogen citrate	15.1598	15.0695	- 9.03
Ammonium citrate dibasic	14.8906	14.8114	- 7.92
Ammonium citrate tribasic	15.0515	14.9726	- 7.89

The TGA graphs (Figures 1–3) of the three citrates are very similar in the decomposition patterns observed. This indicated that the extra protons do not have an obvious effect on the thermal decomposition of ammonium citrates. This is contrary to our original hypothesis that any extra proton may form hydrogen bonds with the oxygen in the ammonium citrates to make ammonium dihydrogen citrate and/or ammonium dibasic thermally more stable than ammonium citrate tribasic.

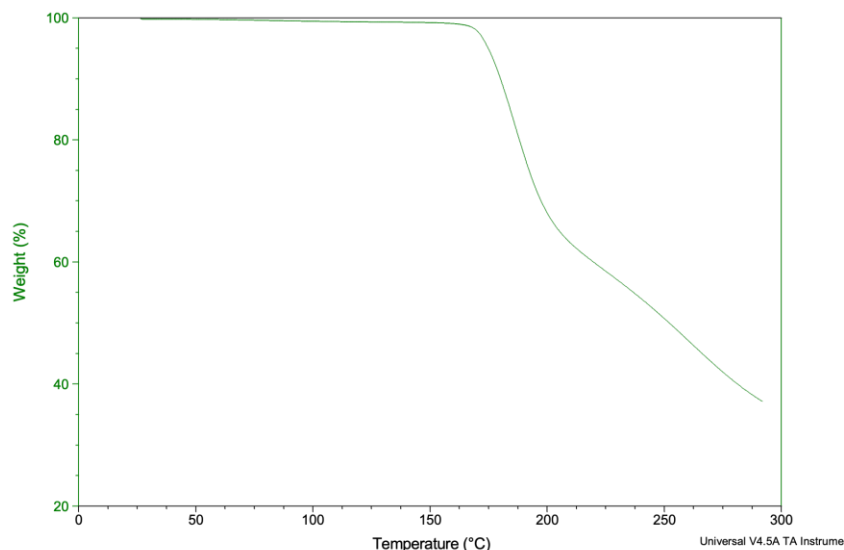


Figure 1. TGA graph of ammonium dihydrogen citrate

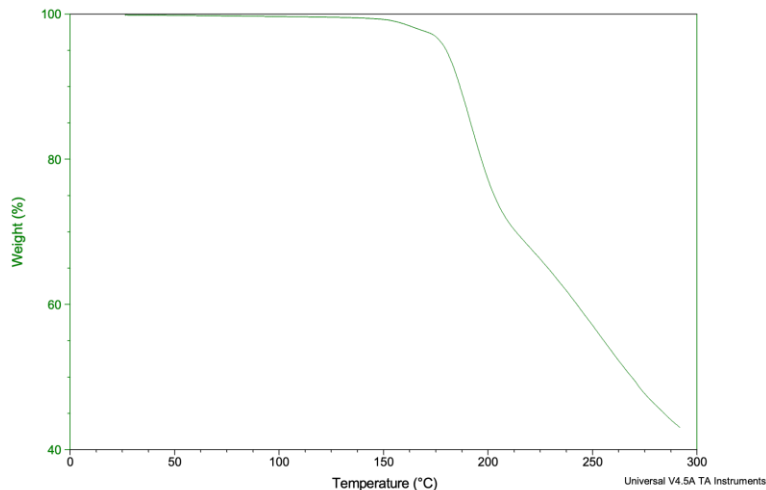


Figure 2. TGA graph of ammonium citrate dibasic

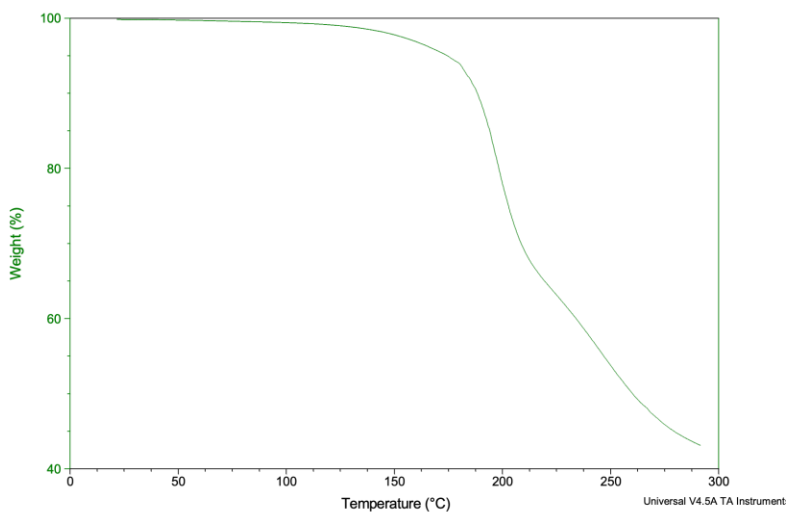


Figure 3. TGA graph of ammonium citrate tribasic.

The mass loss of the three citrates are likely due to the decomposition of these salts into ammonia, water and carbon dioxide that will then enter the gas phase. All the possible decomposition pathways for the three ammonia citrates were explored and the corresponding theoretical % mass losses were listed in Table 2.

Table 2. Possible Decomposition Pathways and the Corresponding %Mass Loss for Ammonium Citrates upon Heating.

Ammonium citrate tribasic		Ammonium citrate dibasic		Ammonium dihydrogen citrate	
Compound Loss	%Loss	Compound Loss	%Loss	Compound Loss	%Loss
H ₂ O	7.41	H ₂ O	7.96	H ₂ O	8.61
NH ₃	7.00	NH ₃	7.53	NH ₃	8.14
H ₂ O + NH ₃	14.41	H ₂ O + NH ₃	15.49	H ₂ O + NH ₃	16.75
2H ₂ O + NH ₃	21.81	H ₂ O + NH ₃ + CO ₂	34.95	H ₂ O + NH ₃ + CO ₂	37.80
H ₂ O + NH ₃ + CO ₂	32.50	2NH ₃	15.06		
2NH ₃	14.00				
3NH ₃	21.01				

The thermal decomposition profiles in Figures 1–3 of the three citrates were further processed by taking the first derivative of the % weight loss as a function of the temperature. The resulting first derivative plots were presented in Figures 4–6.

The first derivative plots of the three ammonium citrates' thermal decomposition curves revealed the temperature at which the mass loss was the most significant for each ammonium citrate. These results led to the determination that ammonium citrate tribasic was the most stable of the three salts in this study. This is evident because the peak temperature of mass loss for ammonium citrate tribasic is 200.65 °C, the highest among the three salts.

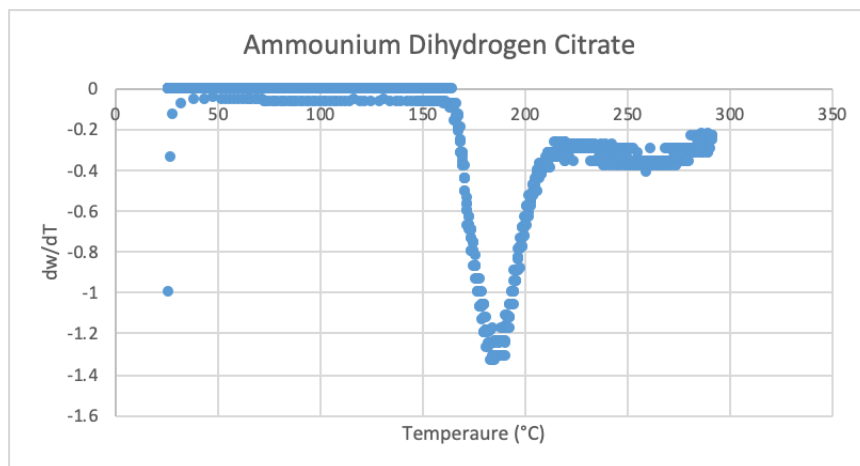


Figure 4. First derivative of the thermal decay profile of ammonium dihydrogen citrate.

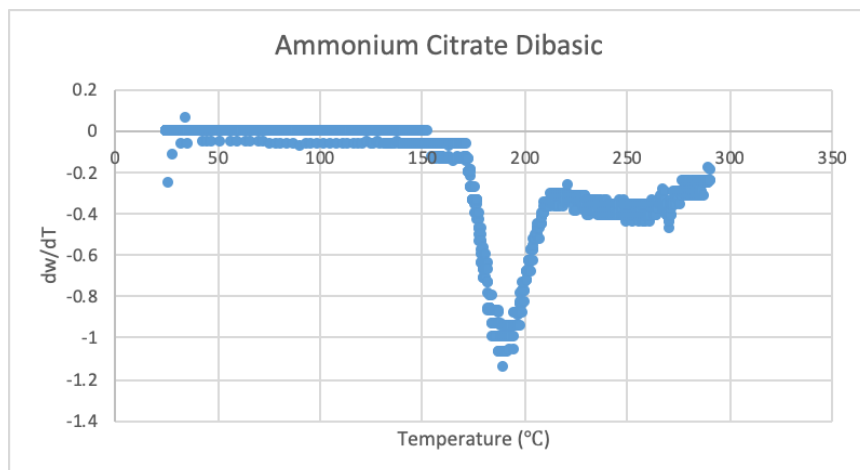


Figure 5. First derivative of the thermal decay profile of ammonium citrate dibasic.

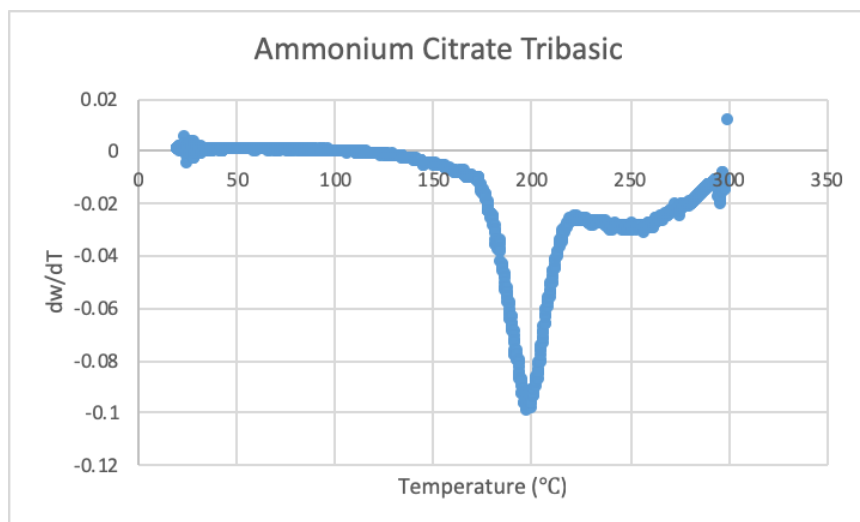


Figure 6. First derivative of the thermal decay profile of ammonium citrate tribasic.

The temperatures and % mass loss corresponding to the peaks in Figures 4–6 of the three citrates were listed in Table 3, columns 2&3, along with the most possible decomposition pathway, according to the theoretical mass loss values listed in Table 2. The difference between the theoretical and actual mass loss at each peak was calculated and listed in Table 4, column 4. In general, the % mass loss corresponding to the proposed decomposition pathway is less than 5% different from that of the measured thermal decay profile of ammonium citrates.

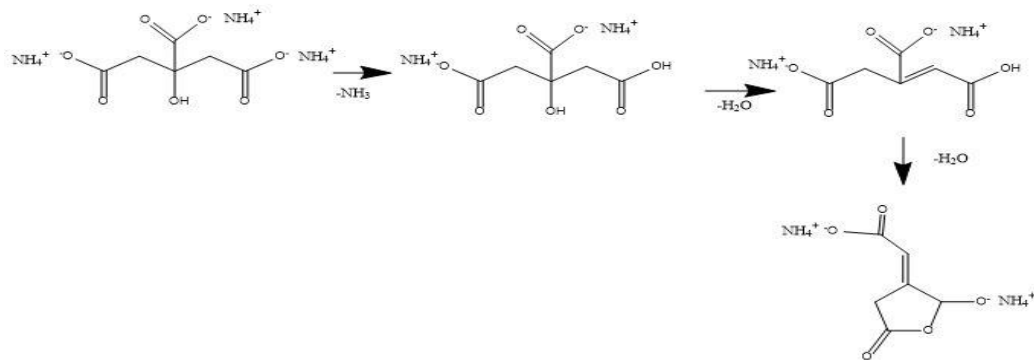
Table 3. Peak temperature and % mass loss in the first derivative plot of each ammonium citrate and the possible thermal decomposition.

Compound	First Derivative Peak (°C)	%Loss	Compound(s) Lost
Ammonium citrate tribasic	200.65	21.11	$\text{NH}_3 + 2\text{H}_2\text{O}$
Ammonium citrate dibasic	193.75	14.78	$\text{NH}_3 + \text{H}_2\text{O}$
Ammonium dihydrogen citrate	185.77	15.93	$\text{NH}_3 + \text{H}_2\text{O}$

Table 4. Difference in the % mass loss between the proposed decomposition pathway and the actual measured thermal decay.

Compound	Theoretical %Loss	Actual %Loss	% Difference
Ammonium citrate tribasic	21.81	21.11	3.21
Ammonium citrate dibasic	15.49	14.78	4.58
Ammonium dihydrogen citrate	16.75	15.93	4.90

Based on the possible decomposition pathways identified in Table 3 and confirmed in Table 4, it is possible to propose the detailed chemical reactions involved in the thermal decomposition of ammonium citrates. As an example, the proposed decomposition reaction scheme for ammonium citrate tribasic was presented in Scheme 1. It appears that all three ammonium citrates will lose small, volatile gas molecules (ammonia and water). No loss of carbon dioxide was observed under our experimental conditions.



Scheme 1. Suggested decomposition scheme for ammonium citrate tribasic.

4. Conclusion

Three ammonium citrates (ammonium citrate tribasic, ammonium citrate dibasic and ammonium dihydrogen citrate) showed one major peak between 185–201 °C when heated in an inert environment. The ammonium citrate tribasic compound was the most stable of the three compounds investigated.

It was determined that the mass loss of ammonium citrate dibasic and ammonium dihydrogen citrate corresponded to the loss of one ammonia and one water molecule from each of the compounds. The mass loss of the ammonium citrate tribasic corresponds to the loss of one ammonia and two water molecules.

5. Acknowledgements

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6. References

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