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Investigation of Thermal Properties of Carboxylates with Various Structures

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Abstract

Thermal gravimetric analysis (TGA) is the analysis of the mass of a sample as it is exposed to temperature changes. This kind of analysis looks at the mass change of a sample as a function of temperature and reveals the thermal stability of the compound being tested. TGA can also be used to look at phase transitions and kinetics of the decomposition of the tested compound. The project looked in to finding a parameter to determine the TGA properties of carboxylate salts. I used the ammonium salts of acetic acid, benzoic acid and salicylic acid. The TGA instrument was then used to obtain thermal scans of benzoic acid and salicylic acid to establish a baseline for comparison. The TGA analysis yielded the thermal properties for each salt tested. To compare these scans, excel was used to produce first derivative graphs of the mass percent versus temperature scans. The peak on these graphs is the point at which mass decrease is at its fastest, this was used as a comparison point for the salts tested. The ammonium benzoate salt peak temperature is 194.72°C with a mass loss of 88.4% There are two possible ways for the salt to lose mass: the vaporization of ammonia and the vaporization of whole salt. Based on the mass loss at the peak temperature, I determined that 86.78% of the salt was completely evaporated and the rest lost its ammonia base. The ammonium acetate salt peak is 133.8°C with a mass loss of 94.16%. The ammonium salicylate peak is 204.23°C with a mass loss of 78.08%. Using this data, a trend was discovered between the molar mass of the salt and the peak temperature of its decomposition: the heavier the salt, the more stable it is. This trend has a R squared value of 0.967.

Keywords: Thermal Gravimetric Analysis, carboxylate salt, structural dependence

1. Introduction

Thermal gravimetric analysis (TGA) monitors the mass change of a sample as it is heated to certain temperature. This analysis results in a thermal decay profile of the mass of a sample as a function of temperature. By comparing the thermal decay profiles of different chemical compounds, their thermal stability can be established.[1] Different compounds will produce different TGA thermograms based on their chemical makeups. For a salt made of cations and anions, it is possible that the chemical structures of these ions will affect the thermograms of the salt.

Another possible application of TGA is, when used in conjunction with thermal energy measurements, to reveal phase transitions of the tested compound. When a compound is heated to certain temperature, the sample may absorb more thermal energy without showing any obvious mass loss. Such observation is a strong indication that the compound undergoes a phase transition at that temperature because phase transitions involve only energy change and the sample should not loss any mass during this process.

The last but not the least, TGA results can provide clues on the kinetics and mechanism of the tested compound's decomposition. Based on principles in chemistry and the chemical structure of a compound, it is possible to list all the possible thermal decomposition reactions. The corresponding theoretical mass loss for each possible reaction can then be calculated. The peak of mass loss during a TGA analysis of the compound can be compared with all the theoretical

possibilities, and the mostly likely thermal decomposition mechanism should be the chemical reaction that matches the actual mass loss of the compound determined by TGA experiments.

Carboxylic acids are widely found in the nature. The common functional group that all carboxylic acids share is the carboxyl group (–COOH). Carboxylic acids are highly useful in many natural processes and in our daily life. For example, as the second simplest carboxylic acid (after formic acid), acetic acid has a single methyl group ($–CH_3$) connected to the carboxyl group. Acetic acid is the key ingredient of vinegar, which is vital to many of food recipes. Acetic acid is an important example of simple, aliphatic acid with straight, alkane chain directly connected to the carboxyl group.[2] As another example, the simplest aromatic carboxylic acid is benzoic acid, which has a single phenyl group ($–C_6H_5$) connected to the carboxyl group. The sodium salt of benzoic acid is a commonly used food preservative.[3] The third example is salicylic acid, which has an extra hydroxyl group (–OH) on the benzene ring of benzoic acid. Salicylic acid has applications in skin treatments and is considered one of the essential medicines.[4]

The first goal of this project was to find a parameter to determine the thermal properties of various ammonium carboxylate salts. Ammonium acetate, ammonium benzoate, and ammonium salicylate were selected to represent the salts of aliphatic, aromatic and multi-functional acids, respectively. Secondly, the thermal decomposition of ammonium acetate, benzoate, and salicylate was previously studied with a sample size of ~200 mg.[5] With the advancement of newer chemical instruments, it is possible now to conduct TGA measurements using much smaller sample size. Smaller sample size will reduce, if not eliminate potential thermal transfer processes so all the thermal energy will likely be used in chemical processes. As a result, the project also evaluated the effect of sample size on the thermal decomposition profiles of ammonium carboxylates.

2. Experimental Details

Ammonium acetate (99.5%, MP Biomedicals), ammonium benzoate (99%, Alfa Aesar), and ammonium salicylate (97%, Accela ChemBio Inc.) were used without any further purification. However, all three chemicals were stored in a desiccator because they were believed to be hygroscopic according to the manufacturers' product data sheets.

This project determined the thermal properties of the three ammonium carboxylates. A Q-series 600 instrument (TA Instruments, Inc.) was used to determine the mass loss of a salt sample in an alumina sample pan when the sample was heated under a constant nitrogen flow from room temperature to 300°C. An empty sample pan was placed side-by-side with the pan with the salt sample as a reference for the internal balance. The sample sizes were 5–7 mg. The samples were heated up by 20°C/min from room temperature to 300°C with a nitrogen flow rate of 100 mL/min. Two decay profiles were obtained and averaged for each ammonium salt.

3. Results and Discussion

Since the ammonium salts in this project are hygroscopic, they have been kept in a desiccator once the bottles were open. The thermal decay profiles of the three salts were shown in Figure 1. All three salts showed very similar shape in their mass loss curves. It was clear that ammonium salicylate showed the highest thermal stability.

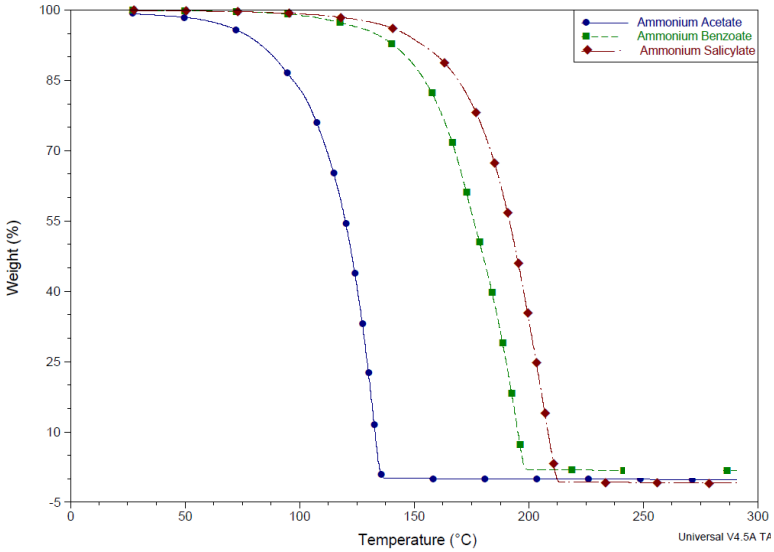


Figure 1. The overlay of thermal profiles of ammonium acetate, benzoate and salicylate.

The first derivative plots of the thermal decay profiles in Figure 1 were obtained by taking the first derivative of the %weight loss vs temperature. The resulting first derivative plots were overlaid in Figure 2.

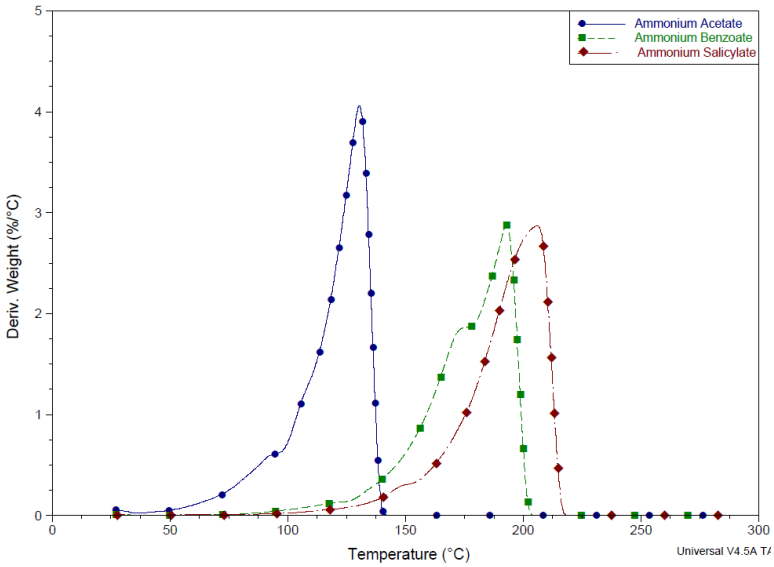


Figure 2. The overlay of first derivative graphs of ammonium acetate, benzoate and salicylate

The shapes of our first derivative plots of the three salts matched well with those found in the literature. This suggested that the sample size had little impact on the thermal decomposition mechanisms of ammonium salts.

The first derivative plots of the three ammonium salts revealed peak temperatures with the fastest mass loss. A summary of all the obvious peaks in the first derivative plots can be found in Table 1. Ammonium salicylate was the most thermally stable salt among the three, with a first derivative peak temperature of about 204 °C.

Our results in Table 1 were different from those determined in Reference 5. This is probably because Reference 5 used a scan rate of 5 °C/min, which was much slower than what was used in this project. Normally slower scan rate will lead to a first derivative peak at a higher temperature. This is reasonable because at a slower heat rate, it will take longer time to transfer the same amount of energy to the sample.

Table 1. The peaks in first derivative plots of the three ammonium salts

Ammonium Salt	Temperature, °C	Weight loss, %	Peak Type
Acetate	91.95	11.60	shoulder peak
	133.8	94.16	major peak
Benzoate	173.32	39.91	shoulder peak
	194.72	88.40	major peak
Salicylate	148.13	5.70	shoulder peak
	204.23	78.08	major peak

The mass loss of each salt is likely due to the decomposition of the salt into ammonia and the carboxylic acid. Furthermore, carboxylate salts may lose water to form amide when heated. As a result, it is important to consider the physical state of the possible products. Table 2 (on the next page) summarizes the boiling points of all the possible decomposition products for the three ammonia salts. Benzoic and salicylic acids are solid at room temperature.

Table 2. Possible decomposition products and their physical properties

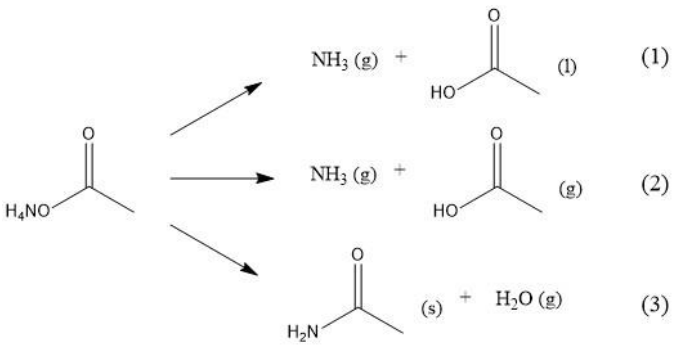
Chemical Name	Boiling point, °C	Chemical Name	Boiling point, °C
Ammonia	−33	Benzoic acid	249
water	100	Benzamide	288
Acetic acid	118	Salicylic acid	211
Acetamide	222	Salicylamide	>300

The temperature and weight loss (%) corresponding to the possible decomposition mechanisms of the three ammonium carboxylate salts were listed in Table 3.

Table 3. Possible thermal decomposition products and the corresponding theoretical weight loss (%) of the three ammonium carboxylate salts.

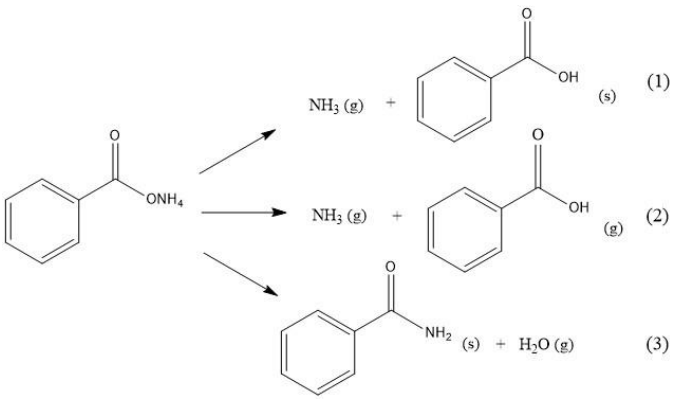
Ammonium Acetate		Ammonium Benzoate		Ammonium salicylate	
Loss	weight loss, %	Loss	weight loss, %	Loss	weight loss, %
NH_3	22.09	NH_3	12.24	NH_3	10.98
H_2O	23.37	H_2O	12.95	H_2O	11.61
Full loss	100.00	Full loss	100.00	Full loss	100.00

As an example, Schemes 1 illustrated the possible chemical reactions involved in the thermal decomposition of ammonium acetate. At the shoulder peak around 91 °C (below the boiling point of acetic acid), some of the ammonium acetate probably lost ammonia yet had acetic acid remaining in the sample pan (pathway 1 in Scheme 1). At the main peak of 133.8 °C, it is likely that multiple pathways in Scheme 1 occurred. Note that pathway 2 will lead to a full loss (100% loss) in mass while the ammonia (pathway 1) or water (pathway 3) loss will only reduce the sample mass by 22–23%. A mass loss of 94.16% was observed in our experiments. Assuming that only full loss and pathway 1 occurred at 133.8 °C, 92.5% of ammonium acetate fully evaporated into the gas phase as ammonia and acetic acid. Similarly, 92.4% of ammonium acetate fully evaporated if pathways 2 and 3 occurred at 133.8 °C.



Scheme 1. Possible decomposition scheme for ammonium acetate.

Similar analysis can be made on the thermal decomposition ammonium benzoate and salicylate. As an example, Scheme 2 listed the possible pathways for ammonium benzoate to lose mass at higher temperature. Ammonium salicylate is expected to decompose in similar ways. While benzoic and salicylic acid has boiling points above 200 °C, it is important to also consider the possibility of sublimation: benzoic acid may sublime at 25 °C and above while salicylic acid starts sublimation at 76 °C. Similar analysis on reaction mechanisms can be made and the percent of ammonium salt that was fully lost can be estimated.



Scheme 2. Possible decomposition scheme for ammonium benzoate.

Table 4 summarized the possible thermal decomposition mechanisms. Two scenarios were considered: (1) full loss and loss of ammonia (forming free acid) and (2) full loss and loss of water (forming amide). The loss of ammonia and water result in very similar weight loss so it is difficult to conclude the actual reaction mechanisms for the thermal decomposition of the three ammonium carboxylate salts in this project. However, it can be concluded that the majority of the three ammonium salts will fully evaporate at their peak decomposition temperatures.

Table 4. Analysis on the thermal decomposition mechanisms of the three ammonium carboxylate salts at their main peak temperature.

	% of ammonium acetate fully lost	% of ammonium benzoate fully lost	% of ammonium salicylate fully lost
Scenario 1: full loss and loss of ammonia	92.50	86.78	75.38
Scenario 2: full loss and loss of water	92.38	86.67	75.20

A trend was discovered between the major peak temperatures in the first derivative curves and the molecular masses of ammonium acetate, benzoate and salicylate (Figure 4). Such trend showed an excellent correlation (R^2 value of

0.999) and may be used to predict the peak temperature for other ammonium carboxylate salts. This finding suggests that the heavier the ammonium salt, the more stable it is.

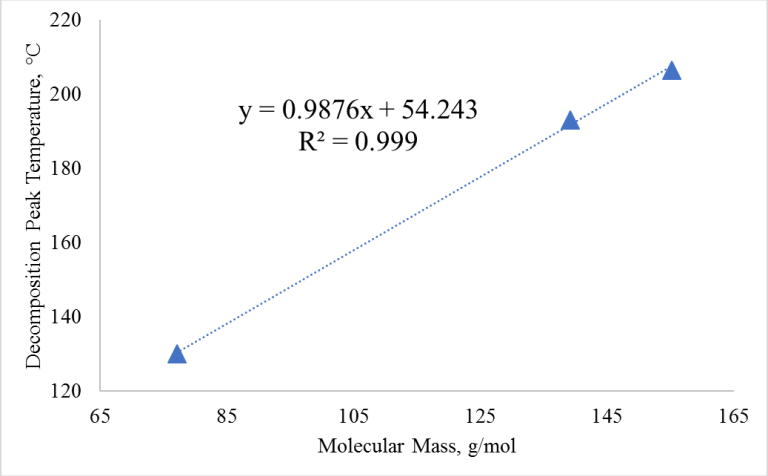


Figure 3. Linear dependence between the first derivative major peak temperatures and the molecular masses of ammonium acetate, benzoate and salicylate.

4. Conclusion

The thermal decay of three ammonium carboxylates (ammonium acetate, ammonium benzoate and ammonium salicylate) were studied using thermal gravimetric analysis instrument and small sample size (~7 mg). Our results were comparable to those in literature using ~200 mg sample size, suggesting that the initial mass sample will not affect the measurement results of these salts.

All three ammonium salts showed one major peak between 133–204 °C and ammonium salicylate was the most stable one. A linear dependence was discovered between the peak temperatures and the molecular masses of the ammonium salts. As a result, heavier ammonium carboxylate salts are likely to be thermally more stable.

The thermal decomposition mechanisms of the three ammoniums salts were studied and the three salts likely lost majority (75–93%) of their mass. The mass loss due to the loss of ammonia or water cannot be distinguished using our approach.

5. Acknowledgements

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