



Thermogravimetry-mass spectrometry investigations of salicylic acid and acetylsalicylic acid desorption from montmorillonites



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ABSTRACT

Thermogravimetry-mass spectrometry is employed to characterize desorption and decomposition processes that occur when samples containing salicylic and acetylsalicylic acids absorbed to potassium, sodium, and calcium montmorillonites are heated. Whereas salicylic acid exhibits behavior similar to benzoic acid, in that the interlayer cation charge is the most important factor affecting desorption temperatures, acetylsalicylic acid decomposition is significantly affected by montmorillonite water content. When salicylic acid/clay samples are heated, desorption begins at temperatures slightly above 100 °C. At higher temperatures, decomposition produces phenol and carbon dioxide. Acetylsalicylic acid does not desorb. Instead, it reacts with water to produce salicylic and acetic acids. For both salicylic and acetylsalicylic acids, decomposition is favored for samples with low absorbate loadings, suggesting that initially absorbed molecules occupy more thermally stable environments than those subsequently incorporated into montmorillonite interlayer spaces.

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1. Introduction

Pharmaceuticals and personal care products (PPCPs) are increasingly found as contaminants in soils [1–5]. PPCPs encompass a wide range of chemical substances [6]. The role that PPCPs play in environmental contamination has been the subject of numerous research studies over the past twenty years [6–10]. Animals and people are exposed to unwanted PPCPs when contaminated crops and meat products are ingested [11,12]. Additionally, when soil bacteria are exposed to antibiotics, they can mutate and become drug resistant [13,14]. Acetylsalicylic acid (aspirin) is an abundant PPCP, approximately 40,000 tons are produced annually worldwide [15]. Roughly one-third of males over the age of 65 take it daily to reduce heart attack risk [16]. It has been ranked 43rd out of 313 selected PPCPs based on potential environmental risk [14]. In the presence of water, acetylsalicylic acid decomposes into salicylic and acetic acids. Because of the ease of this transformation, the acetylsalicylic acid environmental impact is primarily determined by its decomposition products. In addition to its environmental persistence from acetylsalicylic acid decomposition, salicylic acid

accumulates because of its use in skin care treatments [17] and as a component of some shampoos [18].

In general, polar contaminants, such as salicylic and acetylsalicylic acids, concentrate in clay soil fractions [19,20]. Unfortunately, few studies have focused on the interactions between these acids and clays. Celis, et al. investigated the sorption and leaching of aromatic acids in soils [20] and concluded that sorption behavior varied depending on absorbate functional groups and soil type. They found that salicylic acid was the least mobile of those tested and that it absorbed less strongly to soils with higher organic content. Bonina, et al. measured the absorption of salicylic acid by bentonite and found that after soaking in salicylic acid solution for two days, it retained 8% of the acid by weight [21]. For comparison, the water solubility of salicylic acid is merely 0.2% [22]. Thermal analysis of a sample comprised of bentonite with absorbed salicylic acid revealed reaction peaks at 181, 260, and 408 °C, which were not assigned [21]. Nakai et al. used x-ray diffraction, differential scanning calorimetry, and infrared spectroscopy to study absorption and decomposition of acetylsalicylic acid by sodium montmorillonite [23]. For samples containing 5% acetylsalicylic acid, they found that decomposition rates depended on humidity, with slower rates detected when samples were stored at lower humidity [23]. Montmorillonite is ubiquitous in soils and consists of inorganic oxide tetrahedral and octahedral layers in a 2:1 ratio that possess residual negative charges [24]. Spaces between

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stacked inorganic sheets contain cations that balance these residual negative charges. The identity of the interlayer cation has a significant impact on its properties. In particular, it affects the amount of water contained between inorganic layers [25]. The water content also depends on relative humidity, because montmorillonites can absorb water from the air.

Yariv et al. predicted that studies involving the use of thermal analysis techniques combined with evolved gas detection, such as thermogravimetry (TG) coupled with mass spectrometry (MS), would provide detailed information regarding organo-mineral interactions [26]. In fact, previous TG-MS studies of sodium and calcium montmorillonites containing benzoic acid were employed to assess the influence of montmorillonite interlayer cation on absorbate-mineral interactions [27]. Low temperature sample transformations primarily involve loss of water, therefore thermal analysis results reflect interactions between absorbates and interlayer water molecules [28,29]. Sample changes that occur at higher temperatures derive from absorbate desorption and decomposition processes, which depend on absorbate and montmorillonite structural features and their interactions. As described here, TG-MS analyses of samples comprised of salicylic and acetylsalicylic acids absorbed on montmorillonites containing potassium, sodium, and calcium cations provide a means for characterizing thermal reactions and their dependence on montmorillonite interlayer environment.

2. Experimental

Montmorillonite (K-10), salicylic acid, and acetylsalicylic acid were obtained from Sigma-Aldrich. Potassium chloride and sodium chloride were obtained from Mallinckrodt. Calcium chloride was obtained from Fischer Scientific. Chloroform was obtained from JT Baker Chemical Company. All chemicals were used as received without additional purification. The K-10 montmorillonite, which has been previously characterized [30], had a $269\text{ m}^2\text{ g}^{-1}$ surface area and a 0.8 meq/g cation exchange capacity. The supplier indicated that calcium was the most abundant K-10 interlayer cation, but the identities and relative concentrations of all K-10 interlayer cations were unknown. To facilitate studies of the effects of selected interlayer cations on absorbate properties, montmorillonites enriched with K^+ (KMMT), Na^+ (NaMMT) and Ca^{2+} (CaMMT) interlayer ions were prepared from the K-10 by following previously described cation exchange procedures [31,32]. Approximately 5 g clay samples were mixed with 100 mL of 1 M metal chloride solutions. Montmorillonite/metal chloride slurries were stirred for 2–3 h at room temperature and then allowed to stand overnight. After permitting sufficient time for the solid to settle, the supernatant (salt solution) was discarded and the montmorillonite was washed 3–4 times with distilled water to remove excess salt. Samples were allowed to dry for several days under ambient conditions ($\sim 25^\circ\text{C}$ and $\sim 45\%$ relative humidity). Cation exchanged clays were loaded with absorbates by incipient wetness. Salicylic and acetylsalicylic acids were dissolved in chloroform. Samples loaded with 1.1, 3.4, 5.6, and 11% (w/w) salicylic acid were prepared by mixing 0.1 g of montmorillonite with ca. 5 mL of salicylic acid solutions containing the appropriate amounts of absorbate. After mixing for 30 min at ambient temperature, solvent was removed by roto-evaporation for 90 min at room temperature. Acetylsalicylic acid samples were prepared by the same process and contained the same molar amounts, but differed in w/w percentages because of higher molecular weight: 1.5, 4.4, 7.4, 15%. Water contents and mass loss temperature profiles for the cation exchanged montmorillonites with and without absorbates have been reported [28]. Water contents increased in the order: KMMT < NaMMT < CaMMT, consistent with primarily zero, one, and two water monolayers

respectively [28]. Variable temperature diffuse reflection infrared spectroscopy (VT-DRIFTS) [33] was employed to characterize neat montmorillonites and samples containing absorbates [29,34–36]. VT-DRIFTS infrared spectra obtained from samples containing benzoic acid absorbed on NaMMT and CaMMT contained distinct and characteristic $\text{C}=\text{O}$ stretching vibration band positions and shapes [29]. Infrared absorption bands indicated that montmorillonite absorbates were primarily in the protonated form.

TG measurements described here were made by using a Du Pont Instruments model 951 Thermogravimetric Analyzer (TGA) controlled by an IBM Personal System/2 Model 55 SX with Thermal Analyst software. TG-MS measurements were facilitated by directing the TGA effluent to a Hewlett Packard 5973 MSD quadrupole mass spectrometer, which was operated by a PC with Agilent ChemStation software. For TG-MS analyses, approximately ten mg samples were loaded into a platinum pan and heated at $5^\circ\text{C}/\text{min}$ from ambient temperature to at least 650°C in 50 mL/min helium purge. A flow splitter valve was used to divert some of the TG effluent into the mass spectrometer. TG-MS analyses for some samples were performed in duplicate to confirm repeatability.

3. Results and discussion

3.1. Salicylic acid

Ion signal temperature profiles for the most abundant volatiles evolved during TG-MS analyses of samples containing 11% (w/w) salicylic acid are shown in Fig. 1. Mass spectrometric ion signals representing water (m/z 18), carbon dioxide (m/z 44), phenol (m/z 94), and salicylic acid (m/z 120) are shown. With the exception of m/z 120, which corresponds to the salicylic acid mass spectrum base peak, ion signal temperature profiles were derived from molecular ions. The molecular ion for salicylic acid occurs at m/z 138, which was detected during TG-MS analyses of samples containing 5.6 and 11% (w/w) salicylic acid, but was below the detection limit for samples containing less salicylic acid. Fig. 1a shows the results obtained for a KMMT sample containing 11% (w/w) salicylic acid. At temperatures below 80°C , the only significant sample change was attributed to water loss, as evidenced by the fact that only the m/z 18 ion signal intensity exhibited non-zero values.

Salicylic acid (m/z 120) began to desorb above 100°C , and reached a maximum evolution rate at 153°C . Interestingly, phenol (m/z 94) and carbon dioxide (m/z 44) were detected in TG effluent at temperatures below 100°C . These substances were likely formed by salicylic acid decomposition [37,38]. TG-MS analyses of samples containing montmorillonites loaded with phenol revealed that it desorbed immediately when samples were heated, which is consistent with previous reports [39,40]. Therefore, the appearance of m/z 94 in TG-MS mass spectra obtained while heating salicylic acid/clay samples can be used to track salicylic acid decomposition. The increase in m/z 94 ion signal intensity above 100°C indicates that salicylic acid decomposition occurred along with desorption. The overlap between the m/z 120 and 94 ion signal temperature profiles indicates that there was no temperature range over which absorbate desorption occurred without some decomposition. Unlike phenol, most carbon dioxide (m/z 44) desorption from montmorillonite was detected above 400°C . Although the m/z 44 ion signal exhibited a local maximum near 250°C , which coincided with the m/z 94 ion signal maximum, the overall profile shape was very broad with a global maximum just below 500°C . According to Schaefer et al. [41], carbon dioxide is not easily intercalated by montmorillonites that are excessively dehydrated or hydrated. Apparently, carbon dioxide can be stabilized by interactions with interlayer cations, but if sufficient water is available, it can be displaced from absorption sites. Thus, unlike phenol, the carbon

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