Studies of the uptake of gaseous ethyl-3-ethoxypropionate onto ammonium sulfate and ammonium nitrate aerosol particles

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Abstract

Understanding the heterogeneous (gas-particle) interactions that occur in the troposphere is of seminal importance for modellers that assess the atmospheric fates and transport of gases. One means of understanding these interactions is to calculate the mass uptake coefficient of a gaseous species onto common anthropogenic aerosols via an experimental means. The effective uptake behavior of gaseous Ethyl–3-Ethoxy Propionate (E3EP) onto ammonium sulfate and ammonium nitrate aerosols of varying total surface areas was studied using a custom manufactured flow system. E3EP is an organic species that is commonly found in paint and paint products. Ammonium sulfate and ammonium nitrate aerosols were studied because of their abundance in the troposphere. Gas phase E3EP concentrations were obtained using a solid phase microextraction technique (SPME) coupled to a gas chromatograph with a flame ionization detector (GC-FID). Analyses of the ammonium sulfate and ammonium nitrate aerosols were carried out using a Scanning Mobility Particle Sizing system (SMPS). As expected, losses of gaseous E3EP onto the aerosol surfaces decreased with decreasing initial surface area. The calculated initial effective uptake coefficients were shown to vary, depending on aerosol composition. Due to the lack of published literature data regarding the heterogeneous interactions of organic species in the troposphere, these studies provide a significant enhancement to the overall knowledge base.

Keywords: aerosol, uptake, ethyl-3-ethoxypropionate, heterogeneous atmospheric chemistry.
1 Introduction

It is now well known that tropospheric particles consist of both inorganic and organic components that come together to form a complex mixture, Shilling and Tolbert [1]. Due to the abundance of these components in the troposphere, it is important to understand how organic compounds interact with inorganic salt aerosols, Shilling and Tolbert [1]. The uptake of gaseous species onto common anthropogenic aerosol particles present in the troposphere has been characterized in many studies, Li et al. [2]. Information regarding the uptake of various organic compounds onto common inorganic anthropogenic aerosols is of particular importance due to the fact that organic species make up a greater part of the troposphere, Warneck [3]. However, few studies have been conducted to examine the interactions between gas-phase organic species and atmospheric aerosols, Shilling and Tolbert [1]. Understanding the heterogeneous, gas–particle, interactions that occur in the troposphere is of seminal importance for modellers that assess the atmospheric fates and transport of gases.

When considering the uptake of gaseous species onto atmospheric aerosols there are several particle parameters that are relevant. Specifically, when studying the uptake of gaseous species onto aerosol particles, it has been shown that important tropospheric reactions take place at the surfaces of liquid aerosols, Vacha et al. [4]. More studies regarding surface coverage and adsorption postulates of organics at the air-water interface of aerosol particles have provided information to aid in our understanding of what occurs at the surface of particles, Donaldson and Anderson [5]. A model was proposed for gas uptake into the aqueous phase that has taken surface area indirectly into account based on the kinetics involved, Donaldson and Anderson [5]. The means by which uptake is studied and the information gained from the uptake data varies from study to study. For our purposes, uptake was studied to characterize the behavior of an organic gaseous species, ethyl-3-ethoxy propionate, (E3EP) onto ammonium sulfate (\((\text{NH}_4)_2\text{SO}_4\)) and ammonium nitrate (\((\text{NH}_4)_2\text{NO}_3\)) aerosols. E3EP is an organic gaseous species that is commonly found in paint and paint-derived products. The (\((\text{NH}_4)_2\text{SO}_4\)) and (\((\text{NH}_4)_2\text{NO}_3\)) aerosols are both abundant inorganic components of global tropospheric aerosols, Shilling and Tolbert [1]. The data presented is of utmost importance to aid in our understanding of the factors that govern the atmospheric fate of E3EP, and may be used to aid the atmospheric community in understanding the behavior of similar organic gaseous species in the troposphere. Variations in initial surface areas of ammonium nitrate and ammonium sulfate aerosols were carried out by changing the concentrations of the salt solutions that both aerosols were made from as well as changing the flow rate of the aerosols as they were studied with respect to uptake. This work has studied the relationship between uptake and surface area for this inorganic/organic complex that is formed via uptake. The resulting findings may be used make predictions as to the behavior and loss of organic gaseous species in the troposphere.
2 Experimental

The uptake of gaseous E3EP onto ammonium sulfate and ammonium nitrate aerosols generated from 1.0% wt solutions of the respective salts was studied via an experimental means.

2.1 Overview of equipment

A schematic of the overall reaction system appears in Figure 1. A flow tube was used as the reaction vessel. Gaseous E3EP was flowed through the reactor in the presence of either ammonium sulfate or ammonium nitrate aerosols that were generated using a Collison atomizer followed by drying through a customized drying column. E3EP was purchased from Aldrich with a stated purity of 99%, and is a liquid at room temperature. Thus, to admit the E3EP into the reactor in gaseous form, a flow system was utilized. E3EP was introduced into the reactor from a Teflon tube that was connected to the outlet end of a sparger that housed the liquid E3EP. A zero air generator was used to flow air (at a flow rate of 0.008 LPM) through the sparger and into the system. Air was also used to generate the aerosol particles and as a diluent for the entire system. The flow rates of air to the Collison atomizer (for aerosol generation) and for dilution were 7 LPM and 0.2 LPM, respectively. All airflow rates were controlled using Omega 5400/5500 mass flow controllers.

Figure 1: Schematic diagram of the reactor system.

The flow tube reactor is equipped with a movable injector port to disperse gaseous E3EP into the system at varying reaction distances (measured down the
flow reactor in inches). The reactor is approximately 4 ft long, with a diameter of 3.5 inches. Different reaction times were obtained by moving the injector to pre-measured and marked distances within the reactor.

Aerosol particle concentrations were analyzed using a Scanning Mobility Particle Sizer (SMPS), Model 3936 manufactured by TSI, Inc. The SMPS directly measures particle number concentration, but automatically converts these data to particle concentrations based on surface area, volume, or mass. Gaseous concentrations of E3EP were analyzed by Solid Phase Micro Extraction (SPME) and a Perkin-Elmer GC-FID Auto System XL and Finnigan Trace-Polaris GC/MS 2000 Series.

2.2 Aerosol generation and background studies

Before commencing with the uptake studies, several background studies were undertaken. First, it was important to ensure that the SMPS was properly calibrated for aerosol size (i.e. that the size that was reported was truly what was being measured). A size calibration experiment was carried out using a solution of Polymer Microsphere Suspension (PSL), a calibration standard that is used to provide accurate and traceable size calibration for particle size analysis. Immediately following the calibration of the SMPS system, background particle distribution studies were carried out for (NH₄)₂SO₄ and NH₄NO₃ aerosol particles generated from 1.0% by weight solutions of each aerosol using a Collison atomizer followed by drying. The (NH₄)₂SO₄ and NH₄NO₃ were purchased from Aldrich, Inc. and Fisher Scientific, Inc., with stated purities of 99% and 98.5%, respectively. In order to produce varying total surface areas while maintaining essentially the same distribution of particle diameters and total flow rates through the reactor, the aerosol flow was split and makeup zero air was used. The aerosols were then passed through the flow reactor for analysis by the SMPS. These studies were completed to characterize the mean diameters and total concentrations by surface area of the resulting ammonium nitrate and ammonium sulfate aerosols generated.

2.3 Gas phase E3EP analysis

Solid Phase Micro Extraction (SPME) was used to collect and subsequently quantify (using a gas chromatograph) the organic material (E3EP) at a given reaction distance. SPME is an adsorption technique that eliminates the need for solvents and allows for the quantification of results from low concentration analytes by simply exposing the SPME fiber (a 70µm Carbowaxen fiber) to the analyte of interest. Preliminary background studies were carried out to determine the optimum fiber exposure time needed to ensure reproducible results from the GC-FID or GC-MS for a series of samples. An optimal fiber exposure time was determined to be 10 minutes, based upon the reproducibility of GC peak areas. This sampling time yielded peak areas from multiple samples that were within 2% of one another, and indicated that equilibrium of the gaseous E3EP on the
fiber had been reached. The SPME background studies were used to determine GC calibration factors for E3EP. These calibration factors were subsequently used to determine the E3EP concentrations flowing through the reactor system. In order to reach low part per million concentration levels of E3EP, the temperature, and hence the vapor pressure of E3EP housed in the sparger, needed to be lowered. A low starting concentration was vital to obtaining uptake data because the lower the initial concentration level, the greater the percentage change in E3EP that could be calculated to show that uptake was indeed occurring. After several tests, it was determined that in order to achieve a low part per million level concentration of E3EP, the liquid needed to be cooled to 0ºC and held at that temperature for at least an hour. An ice bath was set up to cool the liquid prior to the vapor being flowed through the reactor. The ice bath was used continuously during the uptake studies to maintain the necessary temperature.

2.4 Uptake studies

Uptake was determined by varying the position of the movable injection port in the flow reactor while introducing the dry ammonium sulfate or ammonium nitrate aerosol particles and E3EP. Two different aerosol conditions were used in the actual uptake studies. As indicated previously, to achieve the lower surface area condition for each composition studied, the aerosol flow emanating from the drying column was split, and additional zero air was used to maintain the same total flow rate through the reactor. This technique allowed for variation in total aerosol surface area while maintaining similar initial particle distributions (i.e. median diameters).

E3EP concentrations were determined twice at each of the reaction distances. These reaction distances were 14 inches, 21 inches, 28 inches, and 35 inches, corresponding to reaction times of 18.3 seconds, 27.3 seconds, 36.5 seconds, and 45.5 seconds, respectively, given a total reactor flow rate of 7.208 LPM and a cross sectional reactor tube area of 9.62 in². Variations in the injector position provided a varying reaction time because as the distance increased, the amount of time that the E3EP was exposed to the surface of the ammonium sulfate or ammonium nitrate aerosol particles also increased.

3 Results and discussion

3.1 Background particle distribution studies

Particle distribution profiles for ammonium sulfate and ammonium nitrate were obtained during the background studies. A typical plot of the particle number distribution data for aerosols made from atomization of a 1.0%wt solution of ammonium sulfate followed by drying is pictured in Figure 2.

The distribution of ammonium nitrate particles (also generated from atomization of a 1.0 wt% solution followed by drying) showed a similar
log-normal distribution profile. The two different conditions for each aerosol composition employed in the E3EP uptake studies are summarized in Table 1.

![Graph showing number distribution of ammonium sulfate aerosol particles.](image)

**Figure 2:** Number distribution of ammonium sulfate aerosol particles as made from a 1.0% wt solution of ammonium sulfate.

**Table 1:** Initial total particle surface areas and mean diameters for the ammonium sulfate and ammonium nitrate aerosols studied.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Aerosol Composition</th>
<th>Total Surface Area Concentration (nm²/cm³)</th>
<th>Total Number Concentration (#/cm³)</th>
<th>Mean Number Diameter (nm)</th>
<th>Mean Surface Area Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>NH₄NO₃</td>
<td>9.27*10¹⁰</td>
<td>3.54*10⁶</td>
<td>86.3</td>
<td>143</td>
</tr>
<tr>
<td>II</td>
<td>NH₄NO₃</td>
<td>7.54*10¹⁰</td>
<td>2.42*10⁶</td>
<td>85.4</td>
<td>142</td>
</tr>
<tr>
<td>I</td>
<td>(NH₄)₂SO₄</td>
<td>1.28*10¹¹</td>
<td>4.87*10⁶</td>
<td>87.2</td>
<td>142</td>
</tr>
<tr>
<td>II</td>
<td>(NH₄)₂SO₄</td>
<td>6.41*10¹⁰</td>
<td>2.35*10⁶</td>
<td>80.3</td>
<td>138</td>
</tr>
</tbody>
</table>

**3.2 Uptake studies**

Uptake coefficients for E3EP onto the ammonium sulfate or ammonium nitrate aerosols were obtained based on the following set of equations. Equation (1) reflects the measured flux, J, of a gaseous species into a surface, expressed in terms of the measured mass uptake coefficient, γ_\text{meas}.

$$ J = \frac{n_z \bar{C} \gamma_{\text{meas}}}{4} \tag{1} $$

where:
\( J \) = flux of the gaseous species to the aerosol surfaces
\( n_g \) = concentration of the gaseous chemical
\( \bar{C} \) = gas mean velocity

Furthermore, if examining the decrease in the gaseous E3EP concentration onto the particles, the following expression holds:

\[
- \frac{dn_g}{dt} = \frac{\bar{C} S \gamma_{meas} \cdot n_g}{4}
\]  

(2)

where:

\( S \) = initial aerosol surface area

\( - \frac{dn_g}{dt} \) = decrease in the concentration of gaseous E3EP

Integrating Equation (2) gives the following expression:

\[
\ln\left(n_g(t)\right) = -\left(\frac{\bar{C} S \gamma_{meas}}{4}\right) t + \ln\left(n_g^{\text{inlet}}\right)
\]  

(3)

where:

\( n_g(t) \) = the concentration of E3EP at reaction time, \( t \)

\( n_g^{\text{inlet}} \) = the initial concentration of E3EP

The measured uptake coefficient is readily obtained by plotting the term on the left hand side of Equation (3) versus the reaction time, \( t \), obtaining the slope of the line, and then correcting the slope for the initial aerosol surface area and the gas mean velocity.

The results obtained showed two distinct trends. If the available surface area was high enough, a measured uptake coefficient could be obtained by applying Equation (3). Results from the uptake studies using condition I (see Table I) for \((\text{NH}_4)_2\text{SO}_4\), are depicted in Figure 3. Based on these data, the measured uptake coefficient for \((\text{NH}_4)_2\text{SO}_4\) under condition I was calculated to be 2.66*10^{-03}.

If the available surface area was low, saturation of the surface by E3EP occurred, thereby producing a reverse trend than that which would be expected using Equation (3). E3EP uptake studies using \((\text{NH}_4)_2\text{SO}_4\) (at condition II), or \(\text{NH}_4\text{NO}_3\) (at conditions I and II) aerosols exhibited this reverse trend. In this case, rather than having a relatively constant value for the uptake as a function of reaction distance, the uptake value changed, and appeared to decrease as reaction
time increased. This point is illustrated in Figure 4. The decrease is attributed to the lack of available surface area for uptake of E3EP. Once all of the available sites on the aerosol particle are occupied, the concentration of E3EP coming onto/into the particle and out of the gas phase decreases.

![Uptake of Gaseous E3EP onto Ammonium Sulfate Aerosol Particles](image)

**Figure 3:** E3EP uptake study onto ammonium sulfate aerosols under condition I, plotted according to equation 3.

![Uptake Coefficients for Gaseous E3EP onto Ammonium Sulfate or Ammonium Nitrate Aerosol Particles Under Various Conditions](image)

**Figure 4:** Uptake coefficients for E3EP onto ammonium sulfate or ammonium nitrate aerosol particles (using conditions II in Table I) with respect to reaction time.
These studies illustrate that the uptake of gaseous E3EP onto ammonium nitrate or ammonium sulfate aerosol particles is dependent on the composition of the aerosol as well as the total available surface area of aerosols. The uptake coefficients that have been calculated can be used to assess the relative importance of aerosol interactions of E3EP versus the ambient gas-phase reaction of E3EP. Based on Equation (3), the effective first order collision rate for E3EP, $k_{coll}$, can be determined as (Molina and Molina [6]):

$$k_{coll} = \frac{C_{\gamma, meas}}{4} * S$$

(4)

Utilizing the experimentally determined uptake coefficient, $k_{coll}$ for E3EP onto (NH$_4$)$_2$SO$_4$ can be calculated as (0.150 * S) s$^{-1}$, where S is in m$^2$ m$^{-3}$ of air. This number can be compared to the pseudo first order rate constant for the homogeneous gas-phase reaction, $k'_E3EP+OH$, of E3EP with the primary ambient loss mechanism (i.e. reaction with hydroxyl radicals). Assuming an average ambient hydroxyl radical concentration of 10$^{06}$ molecules cm$^{-3}$ and a hydroxyl radical/E3EP rate constant of 2.29*10$^{-11}$ cm$^3$molecule$^{-1}$s$^{-1}$, the value for $k'_E3EP+OH$ is 2.29*10$^{05}$ s$^{-1}$, Baxley [7]. Given that atmospheric aerosol surface areas in polluted urban areas are on the order of 1 to 3 *10$^{03}$ m$^2$m$^{-3}$, $k_{coll}$ values range between 1.50*10$^{-04}$ to 4.5*10$^{-04}$ s$^{-1}$ for (NH$_4$)$_2$SO$_4$. Thus, the interaction with aerosol surfaces is significant in the atmosphere. Losses of E3EP onto aerosol surfaces will likely be much more important at night, when the hydroxyl radical concentration is small with an average ambient concentration of less than or equal to 2*10$^{05}$ molecules cm$^{-3}$, Baxley [7]. At this time, the pseudo first order rate constant, $k'_{E3EP+OH}$, is 4.58*10$^{-06}$ s$^{-1}$. When considering conditions I and II for NH$_4$NO$_3$ aerosols, $k_{coll}$ can be calculated based on the uptake coefficients represented in Figure 4. These values lie between 7*10$^{-01}$ and 1. Although an overall uptake coefficient cannot be calculated, Figure 4 does show the trend of uptake as reaction time increases for E3EP onto (NH$_4$)$_2$SO$_4$ or NH$_4$NO$_3$ aerosols following condition II. This trend demonstrates the surface saturation of these aerosols due to uptake of E3EP.

The studies regarding the uptake behavior of gaseous E3EP onto ammonium sulfate or ammonium nitrate aerosol particles may be used to aid the atmospheric community’s understanding of the overall fate of E3EP and other organic compounds in the atmosphere. Additional studies utilizing aerosols of different compositions and water contents are needed.

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References


