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SECONDARY PARTICULATE FORMATION VIA PHOTO-OXIDATION OF AMINES EMPLOYED IN CO2 CAPTURING

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SECONDARY PARTICULATE FORMATION VIA PHOTO-OXIDATION OF AMINES EMPLOYED IN CO_2 CAPTURING

By:

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Abstract: This scientific article investigates the potential for the photochemical degradation of mono-ethanol amine (MEA) and 2-(methylamino) ethanol (2-MAE), two amines used for capturing carbon dioxide in traditional power plants, to produce Secondary Organic Aerosols (SOAs). SOAs are a type of fine particulate matter formed in the atmosphere by the oxidation of volatile organic compounds emitted from various sources. The study was conducted in an 8 m^3 KNU Smog Chamber under varying NO_x conditions. The main objective of the study was to compare the potential of 2-MAE and MEA to form secondary particles through OH radical-initiated photochemical degradation in the presence of NO_x. The study found that the photo-oxidation of MEA and 2-MAE produced a significant amount of SOAs. Under high NO_x conditions, the SOA yield of 2-MAE was much higher than that of MEA. The results indicate that 2-MAE has a greater potential to produce SOAs than MEA, which is important information for developing effective strategies to mitigate the adverse effects of SOAs on human health and climate. The chemistry of SOA formation is a complex process that involves multiple steps, including the oxidation of VOCs by hydroxyl (OH) radicals, ozone (O_3), and other oxidants to form intermediate products, which can further undergo reactions such as condensation, fragmentation, and oligomerization to produce low-volatility organic compounds that can participate in the formation of SOAs. The formation and properties of SOAs depend on several factors, including the chemical composition and reactivity of the precursors, atmospheric conditions, and the presence of other pollutants. Understanding the formation, properties, and impacts of SOAs is essential for developing effective strategies to mitigate their adverse effects on human health and climate.

Keywords: SOA, amines, mono-ethanol amine, 2 methylamino ethanol

Introduction

Secondary Organic Aerosols (SOAs) are a type of fine particulate matter (PM) formed in the atmosphere by the oxidation of volatile organic compounds (VOCs) emitted from various sources such as anthropogenic and biogenic activities. SOAs are complex mixtures of organic compounds, which can affect human health and climate by reducing

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visibility, causing respiratory problems, and influencing global radiation balance. The formation and properties of SOAs depend on several factors, including the chemical composition and reactivity of the precursors, atmospheric conditions such as temperature, humidity, and solar radiation, and the presence of other pollutants, such as nitrogen oxides (NO_x), sulfur oxides (SO_x), and ammonia (NH_3) [1].

The chemistry of SOA formation is a complex process that involves multiple steps, including the oxidation of VOCs by hydroxyl (OH) radicals, ozone (O_3), and other oxidants to form intermediate products, which can further undergo reactions such as condensation, fragmentation, and oligomerization to produce low-volatility organic compounds that can participate in the formation of SOAs [2]. The sources of VOCs that contribute to SOA formation include vehicle exhaust, industrial emissions, biomass burning, and natural emissions from vegetation and oceans.

Understanding the formation, properties, and impacts of SOAs is essential for developing effective strategies to mitigate their adverse effects on human health and climate. Several studies have been conducted to investigate the chemical composition, physical properties, and sources of SOAs using various analytical techniques, including mass spectrometry, chromatography, and spectroscopy. These studies have shown that SOAs are complex mixtures of thousands of organic compounds, including polycyclic aromatic hydrocarbons (PAHs), oxygenated organic compounds, and nitrogen-containing organic compounds [3-4].

The properties and health impacts of SOAs are determined by their size, composition, and ability to penetrate the respiratory system. SOAs can induce oxidative stress and inflammation in the lungs, leading to respiratory diseases such as asthma, chronic obstructive pulmonary disease (COPD), and lung cancer [5]. Moreover, SOAs can reduce visibility by scattering and absorbing light, which can have adverse effects on air quality, climate, and ecosystems.

Amines are commonly used in traditional power plants for capturing carbon dioxide (CO_2) through its absorption in aqueous solutions. However, in current technology, amines are recycled, resulting in their direct release into the atmosphere [6]. Although mono-ethanol amine (MEA) is commercially available as a solvent for carbon capture systems, it is uneconomical due to its low capacity, high regeneration cost, and corrosion rate [7]. To overcome these drawbacks of MEA, new solvents such as 2-(methylamino) ethanol (2-MAE) have been introduced [8-10]. It is crucial to assess the potential of 2-MAE to produce secondary particles or Secondary Organic Aerosols (SOA) since they can significantly impact human health and the environment. This study investigates the photochemical degradation of MEA and 2-MAE in an 8 m^3 KNU Smog Chamber under varying NO_x conditions to determine their potential to produce SOA. While some studies have examined SOA formation from MEA, this study addresses gaps related to the degradation, fate, and health and environmental impacts of new amines, specifically 2-MAE, employed in CO_2 capture processes. The primary objective of this study is to compare the potential of a new solvent (2-MAE) and a conventional solvent (MEA) used in CO_2 capture processes to form secondary particles through OH radical-initiated photochemical degradation in the presence of NO_x.

Materials and Methods

The experiments on photochemical degradation were conducted using a smog chamber facility at KNU, which has been described in detail elsewhere [11]. As shown in Figure 1, the facility consisted of an enclosed temperature-controlled (18-33°C) Teflon batch reactor with a radiation source composed of UVA and UVB lamps. Additionally, there was an air purification system that provided dried and purified air with concentrations of non-methane hydrocarbons, NO_x, SO_x, and ozone all less than 1 ppb. The particle number concentrations never exceeded approximately 15 cm^{-3}. In each of the ten photo-oxidation experiments (five for MEA and five for 2-MAE), a known quantity of either MEA or 2-MAE was introduced into a U-shaped stainless-steel tube and then transported into the reactor by a stream of N_2 at 80°C. Hydrogen peroxide (H_2O_2) was used as a source of OH radicals in the photo-degradation experiments. Gas and particle phase concentrations were monitored using a range of instruments, including a scanning mobility particle sizer, hygro-thermometer, and NO_x, SO_x, and O_3 analysers. The concentration of both MEA or 2-MAE and H_2O_2 was 400 ppb in each experiment, and the UV exposure time was fixed at 5 hours. The ratios of MEA or 2-MAE to NO_x were approximately 1, 4, 5.5, 10, and 15 in each experiment, respectively. All the experiments performed in this study are listed in Table-1.

Table-1: Summary of experimental conditions for MEA and MAE photooxidation experiments.

Exp. ID	Initial concentration				
	VOC (ppb)	NO (ppb)	NO_2 (ppb)	VOC/NO_x	H_2O_2 (ppb)
Monoethanol amine (MEA)					
MEA400H400NO200ND200	400	212.31	236.12	0.89	400
MEA400H400NO050ND050	400	52.14	46.31	4.06	400
MEA400H400NO040ND040	400	36.31	37.52	5.41	400
MEA400H400NO020ND020	400	21.83	18.72	9.87	400
MEA400H400NO012ND012	400	11.26	15.13	15.16	400
MEA400H400NO000ND000	400	-	-	-	400
2-methyl amino-ethanol (2-MAE)					
MAE400H400NO200ND200	400	206.3	219.5	0.93	400
MAE400H400NO050ND050	400	52.42	49.1	3.94	400
MAE400H400NO040ND040	400	43.40	30.33	5.42	400
MAE400H400NO020ND020	400	27.71	22.21	8.01	400
MAE400H400NO012ND012	400	18.20	8.31	15.08	400
MAE400H400NO000ND000	400	-	-	-	400

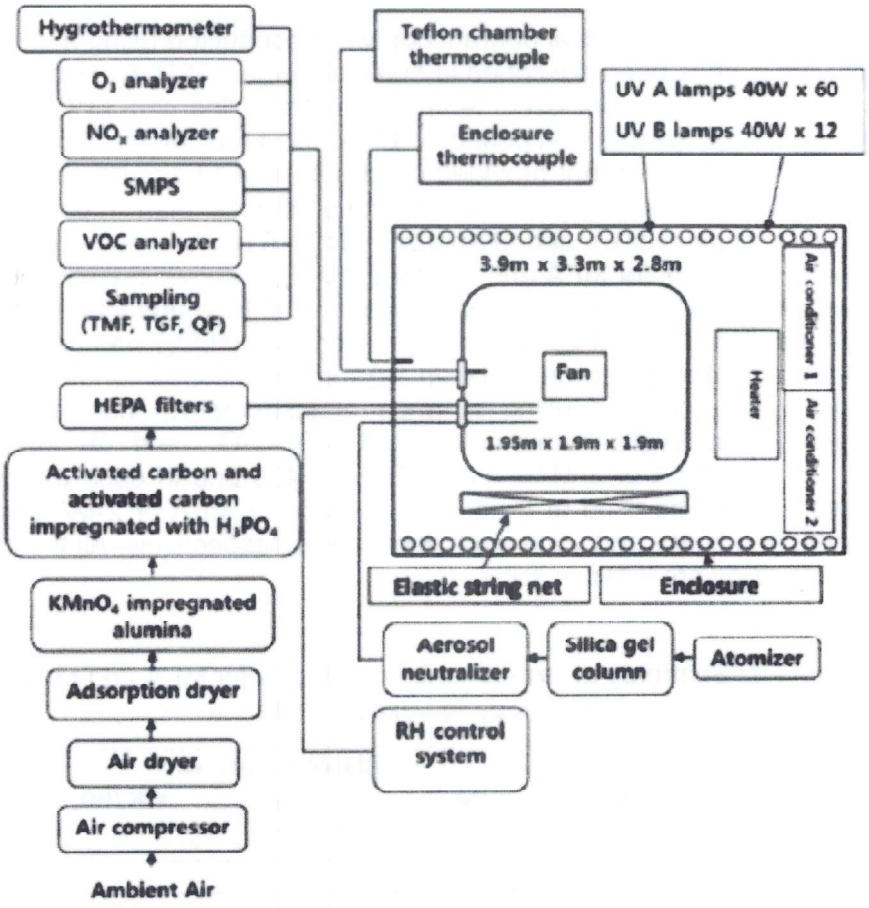


Figure-1: A schematic of KNU Smog Chamber Facility.

Results and Discussion

The quest for sustainable energy sources and minimizing the impact of greenhouse gases has led to research on carbon capture technologies, with the primary focus on identifying better solvents that can efficiently capture CO_2. MEA is the most used solvent, but it is energy-intensive, which has driven the search for alternatives such as 2-MAE. In this study, the environmental impact of these solvents was investigated by assessing the formation of secondary particles and ozone (O_3) during photo-oxidation experiments.

Monoethanolamine (MEA) is an organic compound with the chemical formula C_2H_7NO. It is a clear, colorless, viscous liquid that is widely used in various industries, including chemical, pharmaceutical, and gas processing. One of the major challenges associated with the use of MEA is its susceptibility to photooxidation.

Photooxidation is a process in which a chemical compound is oxidized in the presence of light. It occurs due to the absorption of light by the compound, which results in the formation of free radicals that react with other molecules to produce new compounds. In the case of MEA, photooxidation results in the formation of various degradation products that can negatively impact the performance of the compound and the processes it is used in.

Several studies have investigated the photooxidation of MEA and the mechanisms involved in this process. For example, a recent study investigated the photooxidation of MEA in the presence of oxygen and found that the process involved the formation of various degradation products, including formaldehyde, acetaldehyde, and acetic acid. The study also found that the rate of photooxidation increased with increasing temperature and oxygen concentration.

In another study, the photooxidation of MEA in the presence of titanium dioxide (TiO_2) nanoparticles under UV light irradiation was investigated. The study found that the TiO_2 nanoparticles acted as a catalyst and enhanced the rate of photooxidation of MEA. The study also identified the formation of various degradation products, including ethylene glycol, glycolic acid, and oxalic acid.

In addition to the negative impact on the performance of MEA, photooxidation can also result in environmental concerns. For example, the formation of formaldehyde and other degradation products can lead to air pollution, which can have adverse health effects on humans and animals.

To mitigate the negative effects of photooxidation, several strategies have been proposed. One approach is to add antioxidants to MEA to prevent the formation of free radicals and the subsequent degradation of the compound. Another approach is to use alternative solvents that are less susceptible to photooxidation, such as 2-amino-2-methyl-1-propanol (AMP).

The experiments involved varying the MEA/NO_x and 2-MAE/NO_x ratios to observe the effect on the concentration of O_3 and secondary particles. As the MEA/NO_x ratio increased from 0.9 to 5.5, the OH-initiated photochemical reaction resulted in an increase in O_3 and secondary particle mass concentrations from 4.3 ppb and 99.1 μgm^{-3} to 150 ppb and 497 μgm^{-3}, respectively. However, with further increases in the MEA/NO_x ratio from 5.5 to 15, the concentrations of O_3 and secondary particles decreased to 69.3 ppb and 270 μgm^{-3}, respectively. These results were like those observed in a recent study on the Australian National Low Emissions Coal Research and Development for MEA photo degradation at low MEA/NO_x. The SOA formation and O_3 generation potential for both MEA and 2-MAE are compared in Figure-2.

2-Methylaminoethanol (MAE) is an amino alcohol that has received attention for its potential application in carbon capture technology. Carbon capture technology involves the capture and storage of carbon dioxide (CO_2) emitted from industrial processes such as power plants, in order to mitigate greenhouse gas emissions and reduce the impact of climate change.

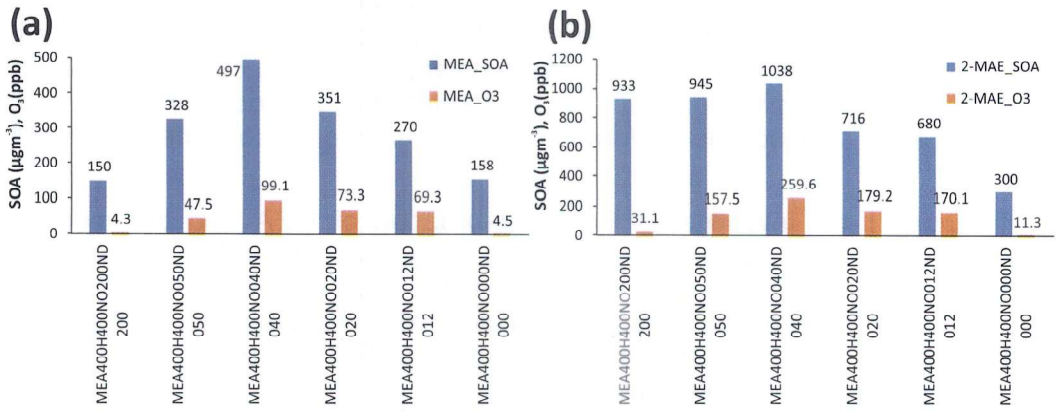


Figure-2: A comparison of the SOA formation and O_3 generation potential for both MEA and 2-MAE.

MAE has several properties that make it a promising candidate for CO_2 capture. Firstly, it has a high reactivity towards CO_2 due to the presence of amino and hydroxyl groups in its molecular structure. This allows it to effectively absorb CO_2 from gas streams. Secondly, MAE has a low volatility and a high boiling point, which makes it suitable for use as an absorbent in liquid-based carbon capture processes.

Several studies have investigated the use of MAE for CO_2 capture. For example, a study by Bara et al. (2012) investigated the use of MAE in combination with monoethanolamine (MEA) for CO_2 capture. The study found that the addition of MAE to the MEA solvent resulted in a significant increase in CO_2 absorption capacity. This was attributed to the enhanced reactivity of MAE towards CO_2 and the improved solvent properties of the MAE-MEA mixture [12].

Another study by Zhang et al. (2015) investigated the use of MAE as a solvent for CO_2 capture. The study found that MAE had a high CO_2 absorption capacity and a low energy requirement for regeneration, making it a promising candidate for use in industrial carbon capture processes [13].

The use of MAE for CO_2 capture has several potential benefits. Firstly, it can result in significant reductions in greenhouse gas emissions, which can help to mitigate the impact of climate change. Secondly, it can help to reduce the cost of carbon capture technology, as MAE is a relatively inexpensive and readily available material.

Similarly, in the case of 2-MAE photo-oxidation, as the 2-MAE/NO_x ratio increased from 0.9 to 5.5, the concentrations of O_3 and secondary particles increased from 31 ppb and 934.7 μgm^{-3} to 359 ppb and 1038.4 μgm^{-3}, respectively. However, with further increases in the 2-MAE/NOx ratio from 5.5 to 15, the concentrations of O_3 and secondary particles decreased to 170 ppb and 680 μgm^{-3}, respectively. Notably, the concentration of secondary particles and O3 was significantly higher in the 2-MAE experiments compared to those observed in the MEA experiments, regardless of the NOx concentration. For instance, at low 2-MAE/NOx (i.e., 0.9) and high 2-MAE/NOx (i.e., 15), the secondary

particle formation was approximately 9.5 and 9.8 times higher than that obtained for MEA (i.e., 99.1 μgm^{-3} and 69.3 μgm^{-3}, respectively).

Therefore, while 2-MAE may be an attractive alternative to MEA due to its similar physical properties such as vapor pressure, density, and boiling point, its environmental impact must be carefully assessed. The significant increase in secondary particle formation and O_3 concentration during 2-MAE photo-oxidation implies that it may contribute substantially to visible air pollution such as particulate matter and smog. This is of concern since secondary particles are known to have negative health and environmental impacts, including respiratory problems, reduced visibility, and cardiovascular issues.

In summary, the study highlights the importance of considering the environmental impact of alternative solvents in carbon capture technologies. The results suggest that although 2-MAE has comparable physical properties to MEA, its potential to form secondary particles during photo-oxidation is significantly higher. Therefore, further research is needed to investigate ways to mitigate the environmental impact of 2-MAE and other alternative solvents to ensure the development of sustainable carbon capture technologies.

Conclusions

Using comparable experimental settings for photo-oxidation in the presence of NO_x, it was observed that the level of secondary particulates formed from MAE was considerably higher (~9-10 times) than that of MEA. While there have been studies conducted on the secondary formation resulting from MAE, no research has yet been conducted to evaluate the impact on the environment of 2-MEA. Thus, this study aims to address the deficiencies in the knowledge regarding the degradation, destiny, and health and environmental consequences of new amines, such as MAE, used in CO_2 capture technologies.

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