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Effect of relative humidity and the presence of aerosol particles on the α-pinene ozonolysis

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ABSTRACT

The α-pinene ozonolysis under the different environmental conditions were observed in a smog chamber. The second-order rate constant (k) was determined to be (7.25 ± 0.06) × 10–^{17} cm^3/(molecule·sec) under 20% of relative humidity (RH) and room temperature. RH showed a marked influence on the α-pinene ozonolysis. The value of k increased with RH increase, which was 1.6 times faster at RH = 80% than that at RH = 20%. Additionally, the value of k apparently changed in the presence of the aerosol particles. The diesel soot increased the k value. The fly ash prohibited the reaction, however, H_2SO_4-treated fly ash promoted the reaction. The information of products gained using FT-IR and SPAMS showed that pinonic acid, 10-hydroxy-pinonic acid and pinic acid could be generated during the α-pinene ozonolysis. Water molecules could take part in the formation of the products, and play a vital role in the degradation of α-pinene. The atmospheric residence time calculation showed that the ozonolysis in the atmosphere is an important way of the α-pinene consumption as compared to that reacted with OH during daytime. The results suggested that the degradation of α-pinene *via* the ozonization in the atmosphere may be affected greatly by RH, as well as the presence of aerosol particles. The ozonolysis reaction may be an important way of the α-pinene consumption during daytime.

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Introduction

A variety of volatile organic compounds (VOCs) are emitted into the atmosphere from natural sources at a global scale, and the annual global VOCs flux was estimated to be 11.50 × 10^{14} g (Guenther et al., 1995). Among them, the annual global amount of reactive hydrocarbon emissions is 1.75 × 10^{14} g from tree foliage sources, which are much higher by 6.2 times than those from man-made sources (Rasmussen, 1972). Various monoterpenes have remarkable effects in the chemistry of the lower troposphere and the atmospheric boundary layer, their annual natural contribution is 1.27 × 10^{14} g (Guenther et al., 1995). Among monoterpnenes emitted from coniferous forests, α-pinene is the most important organic compound with the highest emission at an annual rate of ~0.66 × 10^{14} g/year (Guenther et al., 2012). It is well known that α-pinene could react rapidly with oxidants in the atmosphere (such as OH radicals, NO_3 radicals and O_3) to produce secondary organic aerosols (SOA) *via* the gas-phase reactions (Berkemeier et al., 2016; Nah et al., 2016; Rindelaub et al., 2016). Generally, OH radical is a very important photochemical oxidant during daylight hours for the degradation of α-pinene in the atmosphere, and NO_3 radical is the major during nighttime hours, whereas O_3 plays an important role on the α-pinene ozonolysis throughout the whole day. The α-pinene ozonolysis could lead to the formation of OH radical, and the measured OH yield was

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0.70 ± 0.17, which was considered to be a non-negligible source of OH (Paulson et al., 1998). The α-pinene ozonolysis produces many low-volatility compounds that could partition into particle phase and contribute prominently to the formation of SOA (Denjean et al., 2015; Gordon et al., 2015; Zhang et al., 2015).

Relative humidity (RH) is an important factor to influence the formation of SOA produced by the α-pinene ozonolysis. It was well documented that there was an inverse relationship between the equilibrium partitioning co-efficient and the activity co-efficient for a semivolatile organic compound (Pankow, 1994). Because ambient humidity could have an important influence on the activity co-efficient, the equilibrium partitioning co-efficient on many kinds of aerosols could be affected by RH (Jang and Kamens, 1999; Pankow 1994). Since atmospheric aerosols could absorb water molecules from the gas phase (Vartiainen et al., 1994), the total aerosol yield increases in the case of higher RH due to uptake of water for the experiments of the α-pinene ozonolysis (Cocker et al., 2001). In addition, the change of RH could affect the mass distribution of the products yielded during the α-pinene ozonolysis (Fick et al., 2003).

Also, the presence of aerosol shows a marked effect on the formation of SOA from the α-pinene ozonolysis. Song et al. (2011) reported citric acid significantly enhances the absorption of the oxidized products of α-pinene into particle-phase, which suggested that a well-mixed organic aerosol may be formed during the α-pinene ozonolysis. Cocker et al. (2001) found that aqueous $(NH_4)_2SO_4$ aerosols prohibit the SOA formation, whereas Czoschke and Jang (2006) confirmed that the SOA formation are enhanced apparently once the exposure to NH_4HSO_4 aerosols in the case of the α-pinene ozonolysis. The presence of $(NH_4)_2SO_4$ in organic aerosol may affect or inhibit the formation of hemiacetals and acetals, and thus cause a reduction in the aerosol yield. NH_4HSO_4 aerosols could initiate the acid catalyzed reactions forming other species (such as hemiacetals and acetals), so could have an increasing effect on the SOA formation. These studies show that different types of aerosol particles exerted the different effects on the SOA formation. Hence, a systematic research concerning the effects of aerosol particles on the SOA formation is essential. Fly ash and diesel soot are ubiquitous in the atmosphere, their effects on the SOA formation are not reported yet, and thus should be studied systematically.

The accurate measurement of the rate constants for the α-pinene ozonolysis could be used to assess its atmospheric lifetimes, as well as the relative importance of its removal pathways *via* gas-phase. The rate constants for the α-pinene ozonolysis had been reported at the different environments (Atkinson et al., 1982; Gordon et al., 2015; Japar et al., 1974; Khamaganov and Hites, 2001; Munshi et al., 1989; Ripperton et al., 1972; Stewart et al., 2013; Witter et al., 2002). Ripperton et al. (1972) early reported that the rate constant of the α-pinene ozonolysis in 150-L Teflon bag was 1.70×10^{-18} cm^3/cm^3/(molecule·sec), while Japar et al. (1974) later determined the value to be $(3.3 \pm 0.3) \times 10^{-16}$ cm^3/(molecule·sec) using an evacuated 45-L bell jar reactor. Witter et al. (2002) further investigated the kinetic of the α-pinene ozonolysis under flow-tube conditions, gained the rate constant to be $(1.1 \pm 0.2) \times 10^{-16}$ cm^3/(molecule·sec). Stewart et al. (2013) measured rate constants for the α-pinene ozonolysis in a static reaction chamber at room temperature, measured the value to be $(1.07 \pm 0.13) \times 10^{-16}$ cm^3/(molecule·sec). These results show that remarkable discrepancy exists in the reported rate constants for the α-pinene ozonolysis under the different experimental conditions. Accordingly, the rate constant for the α-pinene ozonolysis under the different RH and aerosol particles should be studied systematically.

In this study, the α-pinene ozonolysis experiments were investigated in an indoor smog chamber. The rate constants of the reactions were determined individually at the different RH (20%, 50% and 80%). The influences of aerosol particles, including fly ash and diesel soot, on the rate constant of the α-pinene ozonolysis were further observed. On the basis of the product information gained by Fourier Transform infrared spectroscopy (FT-IR) and single particle aerosol mass spectrometry (SPAMS), the reaction mechanism for the α-pinene ozonolysis was proposed. The effects of RH and aerosols on relative atmospheric residence time of α-pinene were also calculated.

1. Materials and methods

1.1. Materials and reagents

Unless otherwise stated, all chemicals were purchased and used without further purification. α-Pinene (≥99.0%) was purchased from the Aladdin. Ethanol was gained from the Sinpharm chemical reagent Co. Ltd. Ozone was formed by ultrapure pure oxygen (≥99.999%, Shanghai Lou Yang Cylinder Gas Co., Ltd., Shanghai, China) through an ozone generator (Model WFG-8, Shanghai Weizhen Environmental Protection Equipment Dactory, Shanghai, China). Water was produced by Milli-Q® direct water purification system (Millipore, Bedford, USA).

The fly ash and diesel soot were used in the experiments. The fly ash was attained from rural chimney. The fly ash treated with 0.1 mol/L H_2SO_4 was called H_2SO_4-treated fly ash in this study. The absorption peaks at 1140 and 981 cm^{-1} are observed, indicating that SO_4^{2-} ions exist in H_2SO_4-treated fly ash (Givan et al., 1998; Kumar and Kanti, 2007). Diesel soot was collected from the smoke that was produced by burning diesel. The three kinds of aerosols were characterized by using a Nicolet Avatar 360 FT-IR spectrometer equipped with a MCT detector and a diffuse reflectance accessory (see SI Text S1 and Fig. S1 of the Supporting Information).

1.2. Chamber experiments

Experiments were carried out using a stainless-steel aerosol chamber equipped with a set of analytical instruments at the room temperature, which has been described in detail elsewhere (Li et al., 2015; Zhang et al., 2011; Li et al., 2017). The volume of aerosol chamber was 4.5 m^3 with a 3.4 m^{-1} surface-to-volume ratio. The interior wall of aerosol chamber was plated by a 0.3-mm Teflon inner coat. Temperature and RH inside the chamber were measued by a hygroclip monitor (model IM-4, Rotronic). A fan was installed in the bottom of the chamber to ensure the air mixed well during the experiment.

Prior to each test, the chamber was repeatedly evacuated by two vacuum pumps (Frinklin Electric, Model 1,201,006,416, USA), and restored the pressure equilibrium by the HEPA-filtrated

air. After the chamber was scrabbed using aqueous ethanol (50%, *v*/v), the chamber was evacuated and restored normal pressure once again for reducing RH. Finally the chamber was cleaned using high concentration of O_3 (3 ppm) for 12 hr.

After cleaning, the chamber was evacuated, and was restored the pressure equilibrium with ultrapure air (Shanghai Special Gas Co., Ltd., Shanghai, China). RH in the chamber was controlled by a humidifier, which was consisted of a three-necked flask half filled with Milli-Q grade water (Millipore, Bedford, USA) in the water bath pot at 80°C. Milli-Q grade water vaporized into ultrapure air stream, and then the vapors passed into chamber through a Telflon transfer line. About 2000 molecule/cm^3 polydisperse aerosol pariticles were then introduced by directly atomizing solid of the particles in the solid aerosol generator (SAG 410, Topas GmbH, Germay) into the chamber. About 600 ppb of O_3 in the chamber was generated by a flow (1 L/min) of ultrapure pure oxygen through an ozone generator and into the chamber. Finally, microliter syringe was used to measure and inject known volumes of liquid α-pinene (Aladdin, ≥99.0%) into a thermodenuder (TD) system which was kept at 180°C and vaporized α-pinene. The gas was then flushed with ultrapure air, and then passed through a Teflon line and into the chamber. The concentration of α-pinene was approximately 289 ppb in the chamber. All of the experiments were carried out in the dark. Additionally, the blank experiments of ozone and α-pinene had been done (see SI Text 2-3 and Fig. S2–S4 of the Supporting Information).

1.3. Analysis method

The α-pinene concentration was quantitatively monitored by gas chromatograph-flame ionization detection (GC-FID, GC-9560, Shanghai Huaai Chromatography Analysis Co., Ltd., Shanghai, China) using a 30 m-long, 0.25 mm-i.d. SE-30 dimetilpolisiloxano capillary with a 0.25 μm film thickness. Samples were obtained by drawing 10 L of air through a stainless steel tube containing Tenax TA solid adsorbent. The tube was placed in the inlet of GC, and then heated to 250°C. The column temperature is maintained at 60°C for 5 min, and then ramped at 30°C/min to 270°C, finally was held at 270°C for 5 min. The concentration of α-pinene was determined from the FID response using a standard curve. Because the concentration of O_3 was much higher than that of α-pinene, thus α-pinene was almost completely consumed by O_3 finally. The O_3 concentration in the chamber was continuously monitored by an O_3 analyzer (Thermo Scientific Model 49i, USA).

The SOA formed from the α-pinene ozonolysis was sampled on the KBr particle by sampling apparatus. Infrared spectra of SOA were recorded in the spectral range from 4000 to 650 cm^{-1} using a Nicolet Avatar 360 FT-IR spectrometer which was equipped with a MCT detector cooled by liquid N_2 and a diffuse reflectance accessory. IR spectra were recorded at a resolution of 4 cm^{-1}. A 14 mg (±0.02 mg) KBr sample was placed into a ceramic crucible in the chamber.

SPAMS (Hexin Analytical Instrument Co., Ltd., Guangzhou, China) was used in this study, and the technical details of SPAMS had been reported by Li et al. (2011). Briefly, aerosols in the size range of 0.2–2.0 μm were drawn into the aerodynamic lens through a 0.1 mm critical orifice at a flow of 80 mL/min, and then focused into a collimated tiny particle beam. Then particles attained a terminal size-dependent aerodynamic velocity, which was measured by detection of light scattered from two continuous lasers (532 nm) separated by a fixed 6 cm distance in the sizing chamber. The particle arriving at the ion source region was desorbed and ionized by a pulsed laser (Q-switched Nd:YAG laser, 266 nm). The positive and negative ions of the particle were detected simultaneously by the time-of-flight mass spectrometer. Particle diameter was calculated from the measured speed and calibrated with polystyrene latex spheres (PSLs) with known diameters.

1.4. Rate constant measurements

Rate constants for the α-pinene ozonolysis under the different conditions were determined by monitoring the concentrations of α-pinene and O_3. The removal processes of O_3 and α-pinene under different conditions were following Reaction 1.

$$\alpha\text{–pinene} + O_3 \rightarrow \text{products} \quad (1)$$

The rate equation for Reaction 1 is given by,

$$\frac{dx}{dt} = k\,(a\text{–}x)\,(b\text{–}x) \quad (2)$$

where k is the rate constant, a and b are the initial concentrations of α-pinene and O_3, and x is the consumed concentrations at time t.

When the concentrations of α-pinene and O_3 are different, that is to say $a \neq b$, then the rate Eq. (2) is integrated, the equation was given by

$$\frac{1}{a-b}\ \ln\frac{b(a-x)}{a(b-x)} = kt \quad (3)$$

Clearly, a plot of $\ln\{b(a-x)/[a(b-x)]\}$ *versus* t will have a slope equal to the value of $(a-b)\,k$.

2. Results and discussion

2.1. Effect of RH on the rate constant

The dots of $\ln\{b(a-x)/[a(b-x)]\}$ *versus* t under the different RH could be drawn up, and then the values of k could be derived through the slopes of the linear least-squares best fits to the data, finally are listed in Table 1. The best-fit lines are not forced through the origin. The second-order rate constants are $(7.25 \pm 0.06) \times 10^{-17}$ at RH = 20%, $(9.78 \pm 0.59) \times 10^{-17}$ at RH = 50%, and $(1.18 \pm 0.06) \times 10^{-16}$ at RH = 80% in units of cm^3/(molecule·sec), respectively. Under this condition, one can see that the degradation of α-pinene enhances with increasing RH.

It was well known that RH could affect the mass distribution of product formed by the α-pinene ozonolysis (Fick et al., 2003). Furthermore, RH plays an important role on the mechanism of the α-pinene ozonolysis, and could impact the rate constant k value of the α-pinene ozonolysis. The increasing of RH value could decrease viscosity of the amorphous aerosol particles, and then increase the oxidant uptake due to the enhanced particle-phase diffusion (Chan and Chan,

Table 1 – Rate constants for the reaction between α-pinene and O_3 under different RH.

Reaction conditions	k (cm^3/(molecule·sec))
RH = 20%	$(7.25 \pm 0.06) \times 10^{-17}$
RH = 50%	$(9.78 \pm 0.59) \times 10^{-17}$
RH = 80%	$(1.18 \pm 0.06) \times 10^{-16}$

RH: relative humidity.

2012; Kuwata and Martin, 2012; Liu et al., 2014). On the other hand, some researchers observed that increasing RH could prohibit the oxidant uptake due to the competition between water and oxidant uptake, because the reactive sites were taken up by water molecules (Slade and Knopf, 2014). For this study, the viscosity of the seed aerosol particles could be lowered with increasing RH, subsequently the diffusion of oxidant on particle-phase could be enhanced. Finally, the O_3 uptake could be promoted, and the rate constant of k value for the α-pinene ozonolysis increases with RH.

2.2. Effect of aerosol particles on the rate constant

The rate constant as a function of RH value in the presence of aerosol particles are shown in Fig. 1. When RH value is set at 20%, the degradation of α-pinene is promoted by diesel soot, and prohibited by fly ash. However, the α-pinene degradation is promoted by the H_2SO_4-treated fly ash. The rate constant is $(1.13 \pm 0.37) \times 10^{-16}$ cm^3/(molecule·sec) in the case of diesel soot, which is much high than that in the absence of the aerosols ($(7.25 \pm 0.06) \times 10^{-17}$ cm^3/(molecule·sec)). The rate constant changes to $(4.55 \pm 1.50) \times 10^{-17}$ cm^3/(molecule·sec), when fly ash is used. This suggests that the presence of fly ash particles apparently prohibits the α-pinene ozonolysis. However, the rate constant changes to $(1.12 \pm 0.15) \times 10^{-16}$ cm^3/(molecule·sec), when H_2SO_4-treated fly ash is used. When RH value is set at 50% and 80%, respectively, diesel soot could promote the α-pinene ozonolysis, and fly ash prohibits it. However, H_2SO_4-treated fly ash could promote the α-pinene ozonolysis.

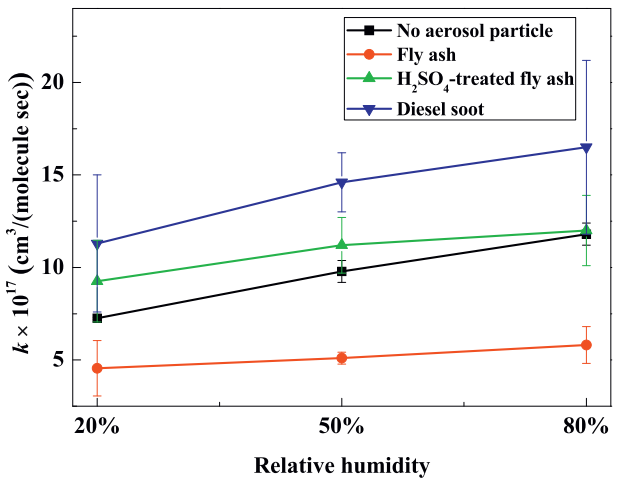


Fig. 1 – Representative curves for rate constant of the α-pinene ozonolysis with different aerosol particles as a function of RH value. RH: relative humidity.

For some solid catalysts, water molecules sometimes are detrimental, due to occupying reactive sites, and thus decrease catalytic activities (Okuhara, 2002). Diesel soot is hydrophobic, so its catalytic activity may be affected slightly, and is the highest. Hence, in the case of the diesel soot, the second-order rate constants are the biggest. Fly ash is hydrophilic, so the catalytic activity is suppressed obviously and is the lowest. As for the experiments with fly ash, the second-order rate constants are thus the smallest one. The H_2SO_4-treated fly ash is hydrophilic, so the catalytic activity is suppressed obviously. But they are treated by H_2SO_4 solution, so they could have more reactive sites, the catalytic activity is enhanced partly. Hence, in the presence of the H_2SO_4-treated fly ash, the second-order rate constants are bigger than that without aerosol particle.

Rate constants for the α-pinene ozonolysis available from the literature are compared with those from the study in Table 2. The data shown herein are in excellent agreement with those of Stewart et al. (2013), Witter et al. (2002), Atkinson et al. (1982 and 1990), Munshi et al. (1989), and Nolting et al. (1988). However, remarkable discrepancy exists in the reported rate constants from Japar et al. (1974) and Ripperton et al. (1972) and the data shown herein. The discrepancy is probably caused by systematic experimental factors.

2.3. Product identifications for the α-pinene ozonolysis

FT-IR spectra of products from the α-pinene ozonolysis at room temperature and RH = 50% are shown in Fig. 2. The functional groups corresponding to characteristic absorption peaks are assigned based upon the previous researches (Ataol and Ekici, 2014; Doroshenko et al., 2010; Gómez-Serrano et al., 1999; Ibrahim et al., 2005; Maroń et al., 2011). These infrared spectra provide valuable information on different surface species adsorbed on the KBr particles by the vibrational modes.

Table 2 – Rate constants for the α-pinene ozonolysis in literature.

Reaction conditions	k (cm^3/(molecule·sec))	Reference
C_{O_3} = 1–6 ppm, $C_{\alpha-pinene}$ = 10 ppm, T = 25 ± 2°C, RH < 5%	$(1.07 \pm 0.13) \times 10^{-16}$	Stewart et al. (2013)
C_{O_3} = 0.122–1.88 ppm, $C_{\alpha-pinene}$ = 78–67 ppb, T = 23°C, RH < 5%	$(1.1 \pm 0.2) \times 10^{-16}$	Witter et al. (2002)
$C_{\alpha-pinene} \gg C_{O_3}$ T = 23°C, RH < 1%	8.7×10^{-17}	Atkinson et al. (1990)
C_{O_3} = 1391 ppm, $C_{\alpha-pinene}$ = 290 ppm, T = 25°C°C, RH < 5%	8.0×10^{-17}	Munshi et al. (1989)
C_{O_3} = 20–50 ppm, $C_{\alpha-pinene}$ = 10–200 ppb T = 28°C, RH < 5%	$(8.6 \pm 1.3) \times 10^{-17}$	Nolting et al. (1988)
C_{O_3} = 0.2–0.4 ppm, $C_{\alpha-pinene}$ = 2–4 ppm, T = 3–48°C, RH < 1%	8.4×10^{-17}	Atkinson et al. (1982)
C_{O_3} = 25–60 ppb, $C_{\alpha-pinene}$ = 214–537 ppm, T = 25°C, RH < 5%	$(3.3 \pm 0.3) \times 10^{-16}$	Japar et al. (1974)
C_{O_3} = 4.1–26.5 ppm, $C_{\alpha-pinene}$ = 64.9–121.1 ppm, T = 21°C, RH < 5%	1.70×10^{-18}	Ripperton et al. (1972)

The absorption peaks at 3427, 3438, and 3477 cm^{-1} are observed, corresponding to the O–H stretching vibration in alcohol (Doroshenko et al., 2010). The absorption peaks at 2849, 2850, 2913, and 2917 cm^{-1} are assigned as O–H stretching vibration in carboxylic acid (Maroń et al., 2011). The absorption peaks appear at 1649, 1660, 1741, and 1743 cm^{-1}, due to C═O stretching vibration (Ibrahim et al., 2005; Lee and RAC, 1999). The absorption peaks at 1384, 1385, and 1390 cm^{-1} are attributed to CH_3 the bending vibration in alkane (Gómez-Serrano et al., 1999). The spectral characteristic of C–H in the cyclobutyl appears at about 1093 cm^{-1} (Ataol and Ekici, 2014). The absorption peaks at about 930 and 914 cm^{-1} are assigned to the O–H deformation vibration for carboxylic acid (Ibrahim et al., 2005).

Also, SPAMS was used to identify the possible products from the α-pinene ozonolysis. The average negative mass spectrum of products from the α-pinene ozonolysis under 50% of RH and room temperature is shown in Fig. 3. The characteristic m/z and possible products are assigned based upon the previous studies (Camredon et al., 2010; Claeys et al., 2009; Peng et al., 2016; Jaoui and Kamens, 2001), and are shown in Table S1. In Fig. 3 average negative mass spectrum at *m/z* = −183, −185, −189, −199 and −213 could be ascribed to $C_{10}H_{16}O_3$ (Camredon et al., 2010; Jaoui and Kamens, 2001; Jenkin et al., 2000; Kristensen et al., 2013; Ma et al., 2008; Witkowski and Gierczak, 2014), $C_9H_{14}O_4$ (Camredon et al., 2010; Jaoui and Kamens, 2001; Jenkin et al., 2000; Kristensen et al., 2013; Ma et al., 2008; Witkowski and Gierczak, 2014), $C_8H_{14}O_5$ (Claeys et al., 2009; Kristensen et al., 2013; Witkowski and Gierczak, 2014; Yasmeen et al., 2010), $C_{10}H_{16}O_4$ (Camredon et al., 2010; Jaoui and Kamens, 2001; Jenkin et al., 2000; Kristensen et al., 2013; Ma et al., 2008; Witkowski and Gierczak, 2014) and $C_{10}H_{14}O_5$ (Peng et al. 2016), respectively. The functional groups in these products include OH, C═O, CH_3, cyclobutyl groups and so on. These results gained by SPAMS are in excellent agreement with those attained by FT-IR.

Fig. 4 presents the proposed mechanism of the α-pinene ozonolysis (Docherty et al., 2005; Jang and Kamens, 1999; Jenkin, 2004; Jenkin et al., 2000; Kurtén et al., 2015). Energy-rich ozonides are generated from the addition of O_3 to the double bond of α-pinene initially, and then decompose rapidly by two possible channels to form two different carbonyl-substituted Criegee intermediates of CI-1 and CI-2. CI-1 reacts with water initially, and then loses water, finally forms pinonic acid (route-1). The mechanism producing the pinonic acid shows that water takes part in the process, suggesting that water could have an important effect on the rate constant for the α-pinene ozonolysis. It was well documented that Criegee intermediate may react primarily with water vapor under atmospheric conditions (Neeb et al., 1996; Tobias and Ziemann, 2001). A theoretical study showed that the observed rate constant for the reaction of Criegee is linearly dependent on the water concentration, which increases with RH increasing (Ryzhkov and Ariya, 2004). High RH was thus lead to the increase of the rate constant for the α-pinene ozonolysis.

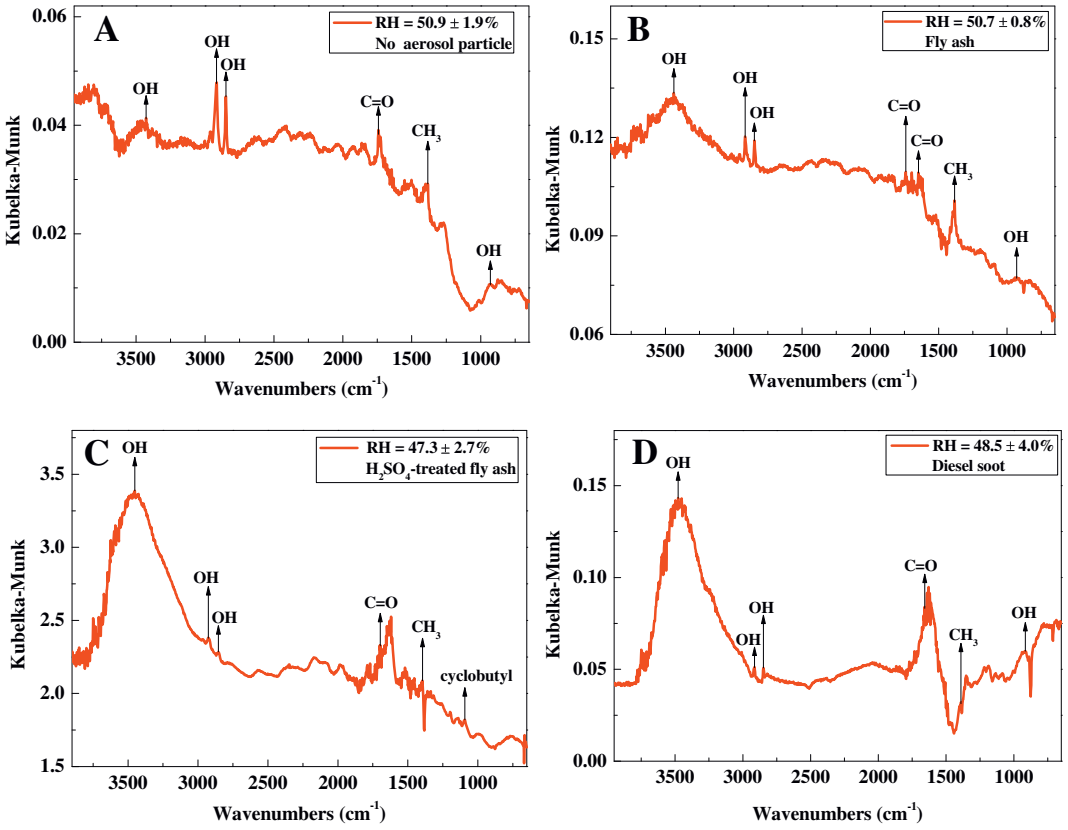


Fig. 2 – Fourier Transform infrared spectroscopy (FR-IR) spectra of the products formed by the α-pinene ozonolysis in different conditions: (A) in the absence of aerosol particle; (B) in the presence of fly ash; (C) in the presence of H_2SO_4-treated fly ash; (D) in the presence of diesel soot.

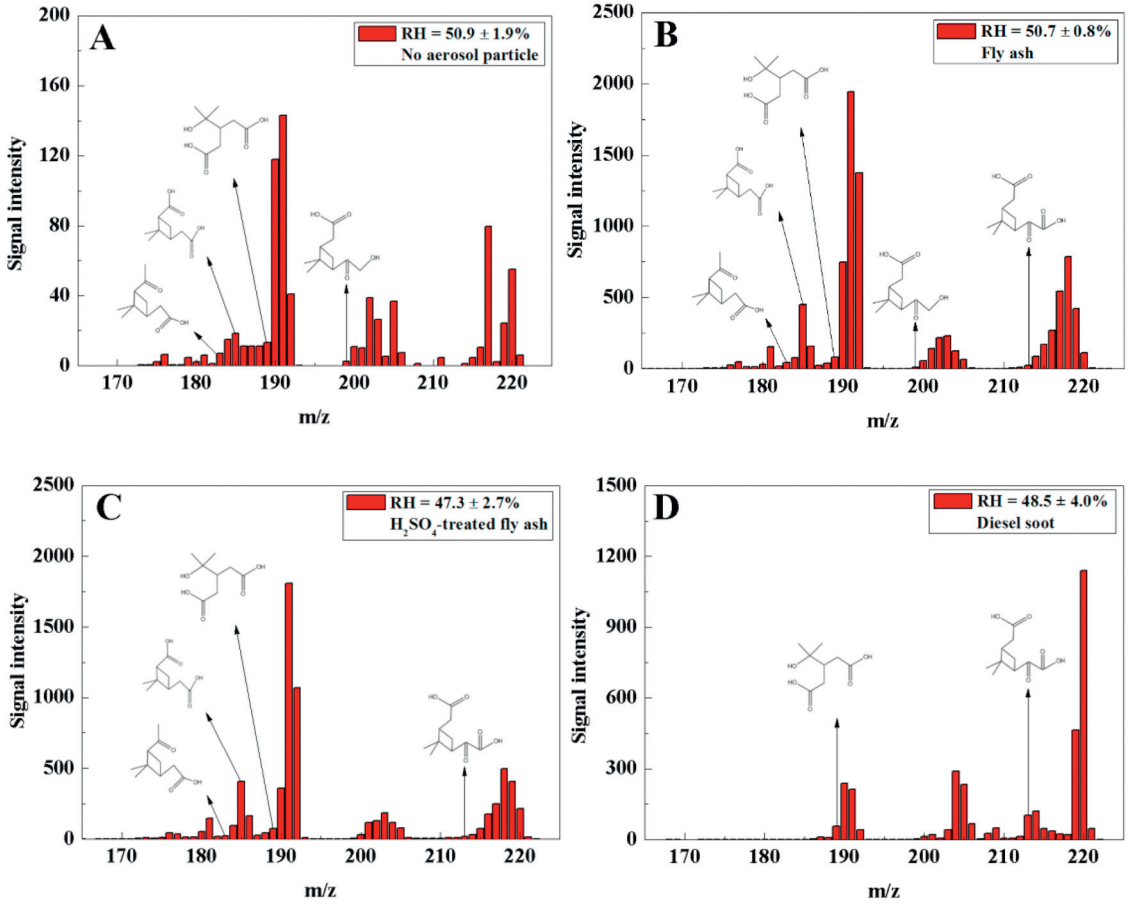


Fig. 3 – Average negative mass spectrum for SOA formed from the α-pinene ozonolysis under different experimental conditions: (A) in the absence of aerosol particle; (B) in the presence of fly ash; (C) in the presence of H_2SO_4-treated fly ash; (D) in the presence of diesel soot.

1,4H shifts of CI-2 generate a vinylhydroperoxide, which dissociates to produce a OH radical and a vinoxy radical. The addition of O_2 to the vinoxy radical leads to a peroxy radical. The reaction of the peroxy radical with RO_2 produces a C_{10} alkoxy radical, which forms the C_{10} acyl radical *via* the isomerisation reaction of 1,8H atom shift. The addition of O_2 to the C_{10} acyl radical leads to a C_{10} acyl peroxy radical, which reacts with the RO_2/HO_2 to generate a C_{10}-hydroxypinonic acid (route-2).

The thermal decomposition of the C_{10} alkoxy radical produces a formaldehyde (HCHO) and a C_9 acyl radical. The addition of O_2 to the C_9 acyl radical produces a C_9 acyl peroxy radical, which reacts with the RO_2 to generate a C_9 acyloxy radical. The acyloxy radical transforms into a C_9 acyl radical *via* isomerization by a 1,7H shift. The addition of O_2 to the C_9 acyl radical forms the C_9 acyl peroxy radical, which reacts with the RO_2/HO_2 to produce pinic acid (route-3).

2.4. *Relative atmospheric residence times*

Relative atmospheric residence time for a kind of VOC is time remaining in the atmosphere. It is relevant with kinds and concentration of oxidants. From the rate constants obtained in this work and references, atmospheric lifetime oxidation by O_3, OH and NO_3 could be calculated for α-pinene from the following equation:

$$\tau_{oc} = \frac{1}{k \times [\text{oxidant}]} \quad (4)$$

In the present work, 40 ppb (9.84×10^{11} molecule/cm^3) was chose as a background value of O_3 concentration (Singh et al., 1978), 1×10^6 molecules/cm^3 was assumed as OH radical concentration during day-time (Finlayson-Pitts and Pitts, 2000), and 10 ppt (2.46×10^8 molecule/cm^3) was selected as a NO_3 radical concentration during night-time (Stewart et al., 2013). The lifetimes for α-pinene are shown in Table 3.

Comparing with the value for the experiment without aerosol particle, atmospheric lifetime of α-pinene increased in the presence of the fly ash, whereas decreased in the presence of the H_2SO_4-treated fly ash and diesel soot at RH = 20%, 50% and 80%.

Under different conditions, the atmospheric lifetime of α-pinene oxidized by O_3 which is dependent on RH and aerosol particles, varies from 1.71 to 6.43 hr. On the basis of the data reported by Stewart et al. (2013) and Hallquist et al. (1999), the atmospheric lifetime of α-pinene oxidized by OH and NO_3 radicals are 5.22 and 0.22 hr, respectively. Thus, the

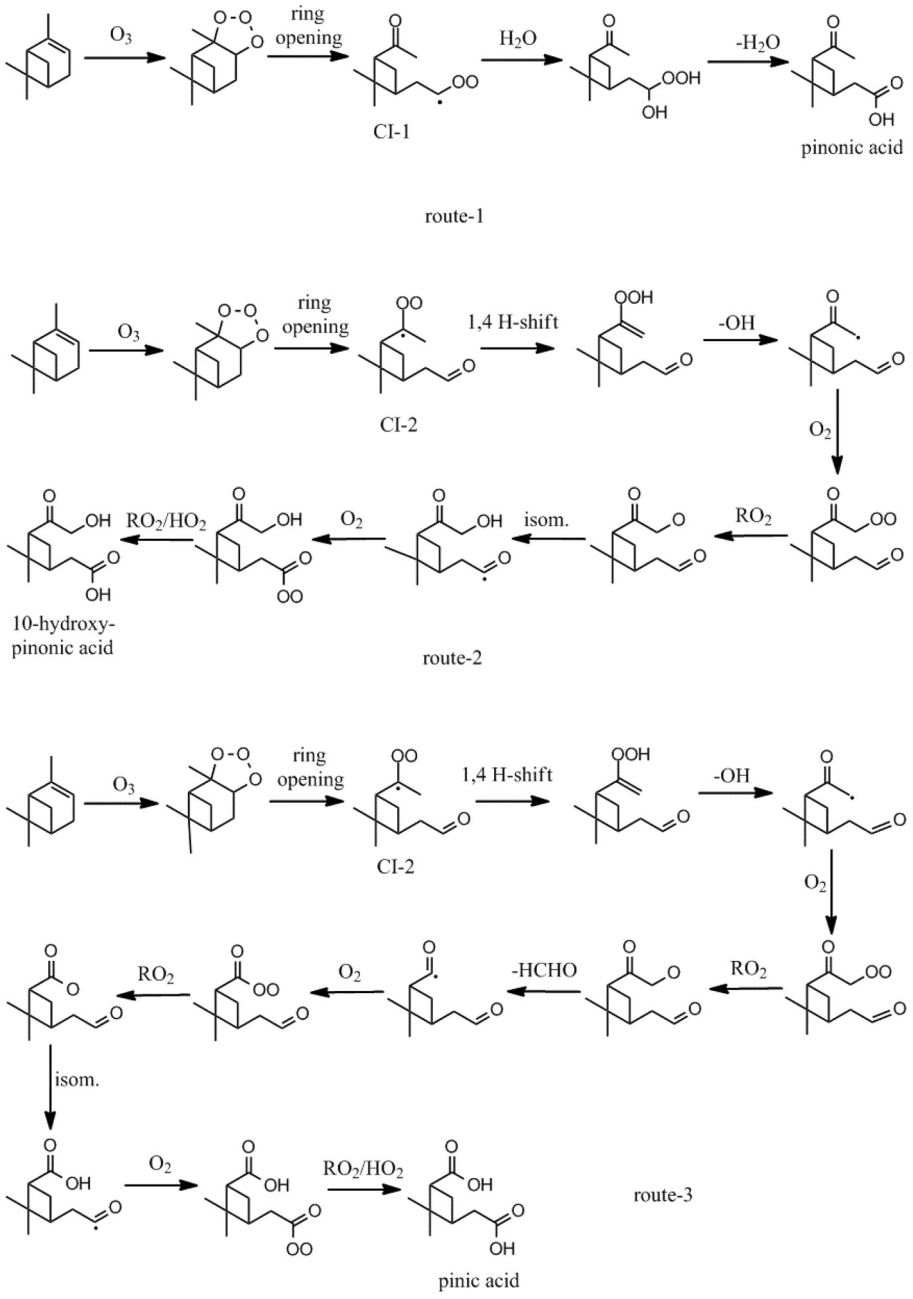


Fig. 4 – The reaction mechanism of the α-pinene ozonolysis.

ozonolysis in the atmosphere is an important way of the α-pinene consumption as compared to that *via* the reaction of α-pinene and OH during daytime, while α-pinene is primarily oxidized by the NO_3 radical at night.

3. Conclusions

In this study, the α-pinene ozonolysis had been investigated using a chamber at the different experimental conditions. RH and aerosol particles both have important effects on the rate constant for the α-pinene ozonolysis under the investigated conditions. The second-order rate constant (*k*) of the α-pinene ozonolysis increases with the increasing of RH. *k* of the α-pinene ozonolysis increased in the presence of diesel soot and the H_2SO_4-treated fly ash, however, the value decreased in the case of the untreated fly ash. FT-IR results show that the α-pinene ozonolysis could form the products with OH, C═O and COOH groups, leading to poly(carboxylic acid)s. SPAMS data show that pinonic acid, pinic acid, diaterpenylic acid, OH-pinonic acid, and $C_{10}H_{14}O_5$ may be involved in the α-pinene ozonolysis. The proposed reaction mechanism for the α-pinene ozonolysis shows water molecules may play an important role in the degradation rate of α-pinene. Calculated atmospheric lifetimes suggest the α-pinene ozonolysis to be an important loss way for α-pinene during daytime.

This study has very significant atmospheric implications. The concentration measured in the field measurements and

Table 3 – Calculated atmospheric lifetimes of α-pinene with respect to oxidation by O_3, NO_3 and OH radicals.

Rate constants (cm^3/(molecule·sec))	Oxidant concentration (molecules/cm^3)	Atmospheric lifetimes of α-pinene (hr)
No aerosol particle $k = (0.725, 0.978, 1.18) \times 10^{-16}$	9.84×10^{11}	3.89, 2.89, 2.39
Fly ash $k = (4.55, 5.1, 5.81) \times 10^{-17}$	9.84×10^{11}	6.20, 5.54, 4.89
H_2SO_4-treated fly ash $k = (0.926, 1.12, 1.20) \times 10^{-16}$	9.84×10^{11}	3.05, 2.52, 2.35
Diesel soot $k = (1.13, 1.46, 1.65) \times 10^{-16}$	9.84×10^{11}	2.5, 1.93, 1.71
$k_{OH} = 5.32 \times 10^{-11}$ (Stewart et al., 2013)	1×10^6	5.22
$k_{NO_3} = (5.17 \pm 0.62) \times 10^{-12}$ (Hallquist et al., 1999)	2.46×10^8	0.22

the relative atmospheric residence time for α-pinene may be affected by RH and aerosol particles in the troposphere.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jes.2017.10.011.

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