Journal of Aerosol Science 106 (2017) 120–131

Contents lists available at ScienceDirect

Journal of Aerosol Science

journal homepage: www.elsevier.com/locate/jaerosci

Secondary organic aerosol formation from ethylene ozonolysis in the presence of sodium chloride

Shuangshuang Ge[a,b], Yongfu Xu[a,c,*], Long Jia[a]

[a] State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China
[b] College of Earth Sciences, University of Chinese Academy of Sciences, Beijing 100049, China
[c] Department of Atmospheric Chemistry and Environmental Sciences, College of Earth Sciences, University of Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Keywords:
Ethylene ozonolysis
Secondary organic aerosol
Sodium chloride
Relative humidity

ABSTRACT

Secondary organic aerosol (SOA) formation from the gas-phase ozonolysis of ethylene without irradiation was studied at different levels of relative humidity (RH) in both absence and presence of sodium chloride (NaCl) in a Teflon bag reactor. Results show that a small amount of SOA was formed from the ethylene ozonolysis in the absence of NaCl. When NaCl was in the form of liquid droplets, much more SOA could be formed. With the initial concentrations of 1 ppm and 0.5 ppm for ethylene and ozone, SOA concentrations of 3.0 to 8.6 μg/m^3 were obtained after 5-h reactions under RH levels of 62% to 88% in the presence of NaCl seed particles, which were about 3~9 times higher than the results from the experiments without NaCl. The yield of SOA also increased with increasing RH, with the value being 3.0% at 88% RH in the presence of NaCl. Addition of the scavenger of OH radicals (n-hexane, ~900 ppm) into the reaction system at 86% RH resulted in a decrease of the SOA yield by 21%. The liquid water content in aerosols was a key factor to SOA formation in the presence of different seed particles, including NaCl and Na_2SO_4. An analysis of the SOA with a Fourier-transform (FT) IR spectrometer shows that the particles formed from the ethylene ozonolysis were organic compounds that contained the functional groups of O–H, C=O, C–O, C–Cl and C–OH. The heterogeneous aqueous reaction is probably an effective pathway to form SOA from the ethylene ozonolysis, which should be considered in the atmosphere.

1. Introduction

Alkenes are one important group of reactive volatile organic compounds (VOCs) in the troposphere. Atmospheric oxidation initiated by the OH radicals in the presence of NO_x can lead to tropospheric ozone formation. It has been long realized that the alkenes with relative high-molecular-weight (HMW), such as isoprene and terpenes, are the precursors of secondary organic aerosol (SOA). SOA has a great influence on the oxidation capacity of the troposphere, air quality and human health (Jacobson, Hansson, Noone & Charlson, 2000). It has been estimated through the global model simulation (Spracklen et al., 2011) that about 80% of the total organic aerosol sources are SOA. Recently, it has been considered that some reactive low-molecular-weight (LMW) VOCs can be the precursors of SOA, such as ethylene and acetylene (Sakamoto, Inomata & Hirokawa, 2013; Jia & Xu, 2016; Ge, Xu & Jia, 2016).

---

[*] Corresponding author at: State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China.
E-mail address: xyf@mail.iap.ac.cn (Y. Xu).

http://dx.doi.org/10.1016/j.jaerosci.2017.01.009
Received 14 April 2016; Received in revised form 29 December 2016; Accepted 31 January 2017

These LMW VOCs form SOA through the processes of heterogeneous photochemical oxidation (Kroll et al., 2005; Volkamer, Ziemann & Molina, 2009; Jia & Xu, 2016; Ge et al., 2016). Ethylene is reactive and the simplest symmetric alkene, and its content is several to dozens of ppb in the atmosphere (Chang, Sree, Lin & Lo, 2005).

The alkenes in the atmosphere can be oxidized by oxidants, such as O_3, OH, etc. There have been a lot of studies on the mechanisms of ethylene ozonolysis and the determination of its rate constants (Neeb, Horie & Moortgat, 1998; Anglada et al., 1999; Chan & Hamilton, 2003; Xu et al., 2006; Qi et al., 2006; Alam et al., 2011; Copeland, Ghosh, Shallcross, Percival & Dyke, 2011; Womack, Martin-Drumel, Brown, Field & McCarthy, 2015). SOA formation from the ozonolysis of HMW VOCs, such as α-pinene, limonene and monoterpenes, has been studied (Saathoff et al., 2003; Bernard et al., 2012; Jonsson, Hallquist & Saathoff, 2007). Although the products from the ozonolysis of ethylene were considered too volatile to form SOA (Seinfeld & Pankow, 2003), a recent study showed that SOA can be formed from ethylene ozonlysis under some certain conditions (Sakamoto et al., 2013). A chamber study under the condition of irradiation with sodium chloride (NaCl) seed particles also confirmed that the ethylene-NO_x system can form SOA when relative humidity (RH) exceeds the efflorescence RH of NaCl (Jia & Xu, 2016). A model study indicated that the main oxidation product of ethylene is glycolaldehyde that can be further oxidized in the cloud to form glyxolic acid and oxalic acid, leading to the formation of SOA (Huang, Ip & Yu, 2011). Another model study by Warneck (2003) estimated the amount of oxalic acid from ethylene and acetylene in the cloud droplets in the marine atmosphere, which was about several to dozens of ng/m^3. In the study by Sakamoto et al. (2013), the formation of SOA is due to the Criegee intermediate (CH_2OO) from ethylene ozonolysis through its oligomerization reactions in the absence of any seed aerosols under dry condition ($<$ 1% RH). Nevertheless, the study of ethylene ozonolysis through heterogeneous reactions with artificial seeds under different RH conditions has not been reported.

Sea salt aerosols have a significant influence on atmospheric chemistry. NaCl is a major component of sea salt aerosols, which accounts for 55.0% Cl and 30.6% Na by weight in sea water, respectively (Seinfeld & Pandis, 2006). Thus, researches about the heterogeneous reaction of alkenes with NaCl as the seed particles are important for coastal cities. Meanwhile, humidity is an important factor that affects the processes of heterogeneous reactions, as humidity can change the physical state of NaCl, whose efflorescence RH is ~45% (Gao, Chen & Yu, 2007).

As a representative of typical LMW alkenes, how ethylene can contribute to the total particles in the atmosphere, particularly during the night time, is unclear. In this study, we selected NaCl as seed particles to study the heterogeneous reaction of C_2H_4 ozonolysis under the condition of without irradiations. The influences of RH on the SOA formation from C_2H_4 were studied. The chemical compositions of SOA were analyzed with FTIR spectra. To our knowledge, this is the first time to identify the SOA formation from C_2H_4-O_3-NaCl without irradiations.

2. Experimental

2.1. Equipment and reagents

All the experiments of ethylene ozonolysis were performed in a 650-L Teflon bag reactor, which had a minimum surface/volume (S/V) of 7.7 m^{-1}. Fig. 1 shows the experimental setup. The background gas during all the experiments was zero air, which was produced by Zero Air Supply (Model 111 and Model 1150, Thermo Environmental Instruments, USA) and the RH was about 6%. Two big hydrocarbon traps were used to further purify zero air (BHT-4, Agilent, USA). C_2H_4 was from the Beijing AP BAIF Gases Industry Co., Ltd. (Beijing, China) with the purity of 99.5%. Ozone was produced by ionizing zero air through an ozone generator (Love Beijing Environmental Protection Technology Co. Ltd.), which can produce 2–4 ppb NO_2 during the process of arc discharge to produce ozone. The reactant of prepared gas C_2H_4 during the experiments was introduced into the bag reactor directly by a syringe. The humidity of the background air was controlled by bubbling dry zero air through a bottle of high-purity water. The humidity in all the experiments was measured with a hygrometer (Model 645, testo AG, Germany). To make sure that background gas was clear enough, a blank experiment in the absence of ethylene but only with ozone and NaCl in the reactor was conducted. The FTIR spectrum result shows that no organic functional groups were detected, which demonstrates that the background gas in our experiments is clear. The purity of the reactant gas C_2H_4 used in our experiment was also checked by FTIR under the background gas condition, in which the spectrum of the sample is consistent with the FTIR spectra of standard gas of C_2H_4 and shows no other obvious peaks from other

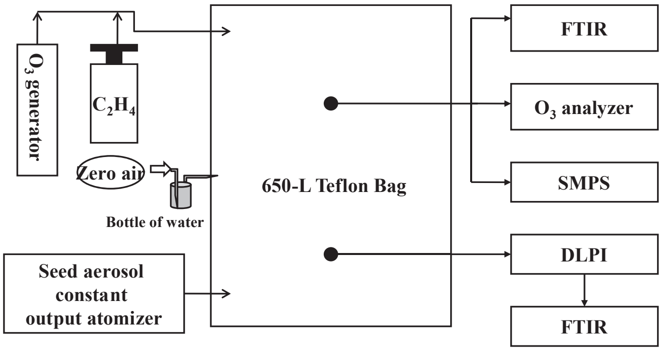

Fig. 1. Schematic diagram of the experimental setup of ethylene ozonolysis.