

The OH-initiated oxidation of atmospheric peroxyacetic acid: Experimental and model studies



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HIGHLIGHTS

- First experimental rate constant of OH radical reaction with peroxyacetic acid.
- OH-oxidation is an important sink of atmospheric peroxyacetic acid, which may be underestimated in previous models.
- There should exist the channel of methyl H-abstraction for the OH-oxidation of peroxyacetic acids.

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ABSTRACT

Peroxyacetic acid (PAA, $\text{CH}_3\text{C}(\text{O})\text{OOH}$) plays an important role in atmospheric chemistry, serving as reactive oxidant and affecting radical recycling. However, previous studies revealed an obvious gap between modelled and observed concentrations of atmospheric PAA, which may be partly ascribed to the uncertainty in the kinetics and mechanism of OH-oxidation. In this study, we measured the rate constant of OH radical reaction with PAA ($k_{\text{PAA}+\text{OH}}$) and investigated the products in order to develop a more robust atmospheric PAA chemistry. Using the relative rates technique and employing toluene and meta-xylene as reference compounds, the $k_{\text{PAA}+\text{OH}}$ was determined to be $(9.4\text{--}11.9) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and 1 atm, which is about (2.5–3.2) times larger than that parameter used in Master Chemical Mechanism v3.3.1 (MCM v3.3.1) ($3.70 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). Incorporation of a box model and MCM v3.3.1 with revised PAA chemistry represented a better simulation of atmospheric PAA observed during Wangdu Campaign 2014, a rural site in North China Plain. It is found that OH-oxidation is an important sink of atmospheric PAA in this rural area, accounting for ~30% of the total loss. Moreover, the major terminal products of PAA–OH reaction were identified as formaldehyde (HCHO) and formic acid (HC(O)OH). The modelled results show that both primary and secondary chemistry play an important role in the large HCHO and HC(O)OH formation under experimental conditions. There should exist the channel of methyl H-abstraction for PAA–OH reaction, which may also provide routes to HCHO and HC(O)OH formation.

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1. Introduction

Peroxyacetic acids ($\text{RC}(\text{O})\text{OOH}$) are considered as important intermediates in the oxidation of volatile organic compounds (VOCs) in the atmosphere (i.e., Kirkby et al., 2016) and account for

40–50% of the total global organic peroxides (ROOH) (Khan et al., 2015). Peroxyacetic acid (PAA, $\text{CH}_3\text{C}(\text{O})\text{OOH}$) is a simple and abundant example of this kind of species, which has been widely detected in field measurements. The concentration of atmospheric PAA ranged from tens to several hundreds of pptv in both remote and urban areas (Lee et al., 1995; Crounse et al., 2006; Hua et al., 2008; He et al., 2010; Zhang et al., 2010; Liang et al., 2013), occasionally reaching to one ppbv level over forests (Phillips et al., 2013; Nguyen et al., 2015). As a ubiquitous peroxyacetic acid in the atmosphere, PAA plays a significant role as reactive oxidant, affects radical recycling, and competes with the formation of peroxyacyl

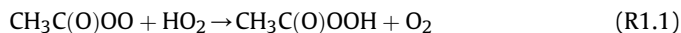
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nitrate (PAN, $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$) which serves as the reservoir of NO_2 and peroxyacetyl radical ($\text{CH}_3\text{C}(\text{O})\text{OO}$) (Lee et al., 2000; Phillips et al., 2013; Zhang et al., 2015).

The atmospheric PAA is contributed by both primary emission (i.e., biomass burning and industrial emission) (Yokelson et al., 2009) and secondary formation, and the latter is the dominant source. It is reported that the major PAA formation pathway is the reaction of HO_2 with $\text{CH}_3\text{C}(\text{O})\text{OO}$ radical (R1.1) (Niki et al., 1985; Lightfoot et al., 1992; Jenkin et al., 2007; Gross et al., 2014; Winiberg et al., 2016), which is largely produced from the oxidation of hydrocarbons or other organic species (Jackson and Hewitt, 1999).



The important removal pathways of atmospheric PAA include gas-phase chemical reactions (photolysis, OH-oxidation), dry deposition and potential heterogeneous reaction (Hall and Claiborn, 1997; Hall et al., 1999; Orlando and Tyndall, 2003; Guo et al., 2014; Wu et al., 2015). However, previous study found that the simulated atmospheric PAA was still higher than the observation even considering the heterogeneous uptake in a box model, which was more distinct in the daytime (Wang et al., 2016). The discrepancy is likely to be partly caused by the uncertainty of OH-oxidation related to PAA in models (Sarwar et al., 2013). Because of the difficulty in synthesis of organic peroxides and their labile nature, for those widely detected organic peroxides, only methylhydroperoxide (MHP, CH_3OOH) (Niki et al., 1983), ethylhydroperoxide (EHP, $\text{CH}_3\text{CH}_2\text{OOH}$) (Wang and Chen, 2008) and a few multifunctional peroxides (Wolfe et al., 2012; St. Clair et al., 2016) have experimental data for OH-oxidation. And, the PAA–OH reaction rate constant displayed in a theoretical calculation study (Rypkema and Francisco, 2013) is about three times higher than the hypothetical data in Master Chemical Mechanism version 3.3.1 (MCM v3.3.1). It should be noted that the rate constant of OH radical reaction with PAA is controversial, because there is no laboratory experiment providing further information. Furthermore, the kinetics and mechanism of PAA–OH reaction considered in models may also impact the budgets of other species, which are closely related to PAA in atmospheric chemistry. For instance, employing different mechanism (i.e. CBIV, SAPRC99 and CB05) in models, with the variation in PAA kinetic parameters, potentially leads to the different simulated percent contributions of PAA-oxidation pathway to the total sulfate formation (Stein and Saylor, 2012). It is also reported that the input of PAA-related atmospheric chemistry would initiate obvious impact on the predictions of HO_2 and $\text{CH}_3\text{C}(\text{O})\text{OO}$ radicals under low- NO_x condition (Zhang et al., 2010).

Obviously, experimental studies on the kinetics and mechanism of OH radical reaction with PAA are required. In the present study, we employed a flow tube reactor to investigate the PAA–OH reaction under NO_x -free condition. We determined the rate constant and terminal products, and investigated the effect of relative humidity (RH) on the mechanism. We also adopted a box model and MCM v3.3.1 with revised PAA chemistry to improve the simulation of atmospheric PAA in field measurement and to evaluate its sinks.

2. Experimental methods

2.1. Preparation and detection of gaseous reactants

Initial PAA solution was synthesized according to the method of Keller et al. (2008). H_2O_2 (Alfa Aesar, 35% water solution) was added drop-by-drop into the concentrated sulfuric acid (H_2SO_4 , Beijing Chemical Plant, 95–98%) in a flask placed in an ice water bath, followed by the addition of acetic acid ($\text{CH}_3\text{C}(\text{O})\text{OH}$, Alfa Aesar,

$\geq 99.7\%$). After the reaction flask was kept in the dark for 12–15 h at room temperature, the reaction yield reached the maximum and was 75–80% in the conversion of $\text{CH}_3\text{C}(\text{O})\text{OH}$ to PAA. The purified PAA solution was prepared by removing H_2O_2 and $\text{CH}_3\text{C}(\text{O})\text{OH}$ from pristinely diluted initial PAA solution. Dry N_2 was continuously introduced into the diluted initial PAA solution in the bubbler and the outflow was collected to a Horibe tube at about 183 K. After collecting for 8–9 h, 8 ml ultrapure water was used to strip the tube inside to get the purified PAA solution that was stored at 277 K. The gaseous PAA was generated by passing dry N_2 under a certain gas flow rate over the diluted purified PAA solution in the bubbling tube kept at (277 ± 0.2) K. The gaseous H_2O_2 was prepared using H_2O_2 solution in the same way as PAA. The reactants of PAA and H_2O_2 in the reactor were collected in a glass scrubbing coil with orthophosphoric acid (H_3PO_4 , Fluka, 85%) solution (pH 3.5) and were then measured online using high-performance liquid chromatography (HPLC, Agilent 1100) coupled with a post-column derivatization module and fluorescence detection. The details of this method can be found in our previous work (Hua et al., 2008).

Water vapor was produced by passing dry N_2 through a glass tube containing two floors of carborundum disc submerged in ultrapure water (18.2 M Ω , Millipore). The RH of the gas mixture was adjusted by changing the flow rate of N_2 and determined using hygrometer (Vaisala HMT100) at the outlet of the reactor. Gaseous cyclohexane was generated using liquid cyclohexane (C_6H_{12} , Sigma-Aldrich, $\geq 99.7\%$) in the same way as PAA. Toluene (Merck, $\geq 99.9\%$) and meta-xylene (Alfa Aesar, $\geq 99.9\%$) were used to prepare gaseous reference compounds by injecting certain amounts of standard reagents (4.0 μL liquid toluene and 4.0 μL liquid meta-xylene) into vacuum steel canisters (15.0 L, Entech Instrument), followed by adding N_2 into the canisters to the pressure of 30 psi. The concentrations and changes of reference compounds in the reactor were monitored by a gas chromatography with flame ionization detector (GC-FID, Agilent 7890A).

2.2. Apparatus and procedures

This study contains two types of experiments: determination of the rate constant of PAA–OH reaction (Ex1), and detection of the products during OH-oxidation of PAA at different RH (Ex2). All experiments were conducted in a quartz flow tube reactor with a length of 100 cm and an inner diameter of 5 cm in 760 torr of synthetic air (O_2 : $\text{N}_2 \approx 20\%: 80\%$). The UV-B fluorescent lamps were evenly placed around the reactor and these lamps emit light in the wavelength region mainly from 294 nm to 400 nm, with the maximum intensity at 312 nm. All experiments were carried out under the same illumination intensity condition. The temperature was controlled at (298 ± 0.5) K by equipping the reactor with a circulating water system. Each experiment lasted for several hours, with reactants constantly added into the reactor. Flow rates of all gases were controlled by mass flow controllers (MFCs).

The PAA–OH reaction was initiated by OH radical, which was generated from the photolysis of H_2O_2 , shown as in reactions R2.1–R2.3.



The OH reaction experiments induced the direct photolysis of PAA in the meantime, which should be considered. Thus, the PAA photolysis experiments were first performed in both the absence and presence of cyclohexane that served as OH scavenger, and this

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