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Discussions

Newly observed peroxides and the water effect on the formation and removal of hydroxyalkyl hydroperoxides in the ozonolysis of isoprene

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Abstract

The ozonolysis of alkenes is considered to be an important source of atmospheric peroxides, which serve as oxidants, reservoirs of HO_x radicals, and components of secondary organic aerosols (SOAs). Recent laboratory investigations of this reaction identified hydrogen peroxide (H_2O_2) and hydroxymethyl hydroperoxide (HMHP). Although larger hydroxyalkyl hydroperoxides (HAHPs) were also expected, their presence is not currently supported by experimental evidence. In the present study, we investigated the formation of peroxides in the gas phase ozonolysis of isoprene at various relative humidities on a time scale of tens of seconds, using a quartz flow tube reactor coupled with the online detection of peroxides. We detected a variety of conventional peroxides, including H_2O_2, HMHP, methyl hydroperoxide, bis-hydroxymethyl hydroperoxide, and ethyl hydroperoxide, and interestingly found three unknown peroxides. The molar yields of the conventional peroxides fell within the range of values provided in the literature. The three unknown peroxides had a combined molar yield of ~30 % at 5 % relative humidity (RH), which was comparable with that of the conventional peroxides. Unlike H_2O_2 and HMHP, the molar yields of these three unknown peroxides were inversely related to the RH. On the basis of experimental kinetic and box model analysis, we tentatively assigned these unknown peroxides to C2–C4 HAHPs, which are produced by the reactions of different Criegee intermediates with water. Our study provides experimental evidence for the formation of large HAHPs in the ozonolysis of isoprene (one of the alkenes). These large HAHPs have a sufficiently long lifetime, estimated as tens of minutes, which allows them to become involved in atmospheric chemical processes, e.g. SOA formation and radical recycling. These standards are needed to accurately specify HAHPs, although their synthesis is a challenge.

1 Introduction

Peroxides, including hydrogen peroxide and organic peroxides, are considered to be important trace compounds in the atmosphere due to their multiple roles as oxidants (Calvert et al., 1985) and reservoirs of radicals (HO_x, RO_2) (Wallington and Japar, 1990; Lightfoot et al., 1991; Vaghjiani and Ravishankara, 1990; Hatakeyama et al., 1991; Atkinson et al., 1992; Spittler et al., 2000; Ravetta et al., 2001). Furthermore, they can cause the death of vegetation (Hewitt et al., 1990; Pellinen et al., 2002) and are known to be important components of secondary organic aerosols (SOAs) (Bonn et al., 2004; Docherty et al., 2005; Hallquist et al., 2009; Chen et al., 2012). In the laboratory, organic peroxides are known to be major products of the photooxidation of isoprene by the OH radical under NO_x-free conditions (Miyoshi et al., 1994; Paulot et al., 2009). Using the iodometric spectrophotometric method, Surratt et al. (2006) quantitatively reported that total organic peroxides account for 25–60 % of SOA mass formed from the photooxidation of isoprene. Some model results suggest that organic peroxides are even more important than carboxylic acids as SOA contributors (Bonn et al., 2004). Kroll et al. (2006) suggested that the decrease in SOA mass during the photooxidation of isoprene may be attributed to the chemical reactions of organic peroxides. There are no known primary sources of peroxides. An important pathway for their formation is considered to be the bimolecular reaction between RO_2 and HO_2 radicals, while RO_2 radicals are mainly formed from the OH radical-initiated photooxidation of alkanes and alkenes under low NO_x conditions (e.g. Atkinson et al., 2006). Another pathway for the formation of hydroperoxides is the ozonolysis of alkenes (e.g. Becker et al., 1990; Hewitt et al., 1990; Gäb et al., 1995; Neeb et al., 1997; Sauer et al., 1999; Lee et al., 2000; Tobia and Ziemann, 2001). A peak in the concentration of peroxides was found at night in field measurements (Hua et al., 2008), providing evidence for the important contribution from the ozonolysis of alkenes.

Scheme 1 illustrates a summary of the major known steps in the ozonolysis of alkenes. The formation of peroxides is related to the reactions of Criegee intermediates, i.e. isomerization (R3b), reaction with water (R4a1), and reaction with organic acid (R4a2); whereas the decomposition of peroxides follows pathways of R4b1, R4a11, and R4a12. Considering the ubiquity of water molecules in the atmosphere, water plays a principal role in hydroxyalkyl hydroperoxide (HAHP) formation via the reaction of R4a1 (Gäb et al., 1985; Hatakeyama and Akimoto, 1994; Ryzhkov and Ariya, 2004, 2006). In theoretical studies, Crehuet et al. (2003) suggested that the CH_2OO biradical, the simplest Criegee intermediate, would have a two-step reaction with H_2O, first generating HMHP and then decomposing. Aplincourt and Anglada (2003a) showed that the most favorable pathway for the reaction of water and the isoprene Criegee intermediate is the formation of HAHP. The HAHP would decompose into the corresponding carbonyl and H_2O_2 (Atkinson and Arey, 2003). Very recently, Welz et al. (2012) directly determined unexpectedly large rate constants for the reactions of the Criegee intermediate with SO_2 and NO_2, indicating that Criegee intermediates may be important oxidants for SO_2 and NO_2. Vereecken et al. (2012) presented a series of loss paths for the stabilized Criegee intermediate, and found that its loss was dominated by its reaction with H_2O, NO_2, and SO_2, for which H_2O is the most efficient scavenger.

There have been only a few chamber studies focusing on hydrogen peroxide and the C1-C3 hydroperoxide formation in the ozonolysis of alkenes (Gäb et al., 1985, 1995; Hewitt and Kok, 1991; Horie et al., 1994; Neeb et al., 1997; Sauer et al., 1999; Hasson et al., 2001a, b). However, to date, the identified peroxides are mostly limited to H_2O_2 and HMHP. The larger HAHPs have been speculated in laboratory studies, although their possible decomposition products such as H_2O_2, carbonyls, and organic acids have been quantitatively observed. Moreover, there is large uncertainty for the H_2O_2 and HMHP yields obtained in chamber experiments, which usually last for tens of minutes to several hours of reaction time due to the decomposition and wall losses of the highly reactive peroxides. In addition, most experiments have been performed at either a low or high relative humidity rather than at various relative humidity values.

In the present study, we detect more peroxide types in the reaction of ozone and isoprene in the gas phase to evaluate the reaction mechanism of Criegee intermediates with water, and we study the peroxide yield dependence on the relative humidity. We conduct simulations for the ozonolysis of isoprene in a quartz flow tube reactor with a reaction time of tens of seconds at ten different relative humidities, using an online HPLC detection for the peroxides. A variety of peroxides have been identified and quantified or semi-quantified, in particular organic peroxides. A box model is used to simulate the HAHPs' formation process, and simultaneously to study the effect of water on the formation and removal of HAHPs.

2 Experimental

2.1 Chemicals

Isoprene (Fluka, 99.5 %), ultrapure water (18 MΩ, Milli-pore), acetonitrile (Tedia, spectroscopically pure, ≥ 99.9 %), N_2 (≥ 99.999 %, Beijing Haikeyuanchang Practical Gas Company Limited, Beijing, China), and O_2 (≥ 99.999 %, Beijing Haikeyuanchang Practical Gas Company Limited, Beijing, China) were used as received. The source and purity of authentic standards for synthesizing peroxides are: H_2O_2 (Acros, 35 wt. %), formaldehyde (Riedel-delaen, 36.5 wt. %), acetaldehyde (Amethyst, 40 wt. %), glycoaldehyde (Aldrich, crystalline), propanal (Fluka, 99.7 %), glyoxal (Sigma-Aldrich, 40 wt. %), formic acid (Alfa Aesar, 97 %), acetic acid (Alfa Aesar, 99.9985 %), glycolic acid (Sigma-Aldrich, 99 %), propionic acid (Alfa Aesar, 99 %), acetone (Fluka, 99.7 %), hydroxyacetone (Fluka, 90 %), 2-Br-ethanol (Alfa Aesar, 97 %), 3-Br-1-proponol (Alfa Aesar, 97+ %), and 1-Br-2-proponol (Aldrich, 70 %).

2.2 Apparatus and procedure

A flow tube reactor (120 cm length, 10 cm inner diameter, quartz wall) equipped with a water jacket for temperature control was employed for performing ozonolysis experiments in the dark. Figure 1 provides the overview of the apparatus. The temperature of the reactor was controlled to 25 ± 0.5 °C. O_3 was generated by the UV irradiation

of a 0.1 $\mathrm{L\,min^{-1}}$ flow of O_2, and the concentration was controlled by the light intensity. Isoprene stock gas was prepared by injecting 4.0 µL liquid isoprene into an evacuated steel canister (15.0 L, Entech Instrument), followed by the addition of N_2 to the canister to a pressure of 30 psi. The isoprene concentration in the canister was 20.6 ppmv. Through a mass flow controller (MFC), the stock isoprene gas was introduced into the flow reactor from the canister. Water vapor was generated by passing N_2 through a glass tube containing two floors of carborundum disc submerged in ultrapure water (18 MΩ). There were two gas entrances on the reactor, and the flow through each entrance was 1.0 $\mathrm{L\,min^{-1}}$. One entrance introduced a mixture of isoprene, dry N_2, and wet/dry N_2. The other introduced a mixture of O_3, O_2, and wet/dry N_2. The residence time of the gases was estimated to be 68 s with a total flow of 2.0 $\mathrm{L\,min^{-1}}$. The final ratio of N_2 to O_2 was 80 % : 20 %. The initial concentrations of isoprene (C_{ISO}) and O_3 (C_{O_3}) in the reactor were 290 ppbv and 80 ppmv, respectively. The ratio of C_{O_3} to C_{ISO} was about 300, which is similar to the ratio in the real atmosphere. After each experiment, the reactor was rinsed out twice with water and was dried with N_2.

It is worth noting that, using the flow tube reactor, the reaction time was 68 s although each experiment lasted for several hours. The reactants and nitrogen plus oxygen were constantly added to the reactor; then an hour later, the concentrations of the products become constant. Next, the products were collected and detected either online or offline. We ensured that the reactants and the products mixture continuously contacted the reactor wall for one hour, to age the reactor wall and thus decrease the wall effect on the products.

2.3 Products analysis

The concentrations of O_3 and the major products, including peroxides, carbonyl compounds, and organic acids, were determined using methods described in our previous work (Wang et al., 2009; Hua et al., 2008; Huang et al., 2011). Generally, peroxide compounds were collected in a coil collector with an H_3PO_4 solution (pH 3.5) and were online analyzed by high performance liquid chromatography (HPLC) (Agilent 1100, USA) coupled with post-column derivatization. In this latter step, the peroxides oxidized p-hydroxyphenylacetic acid to produce a fluorescent dimer in a reaction catalyzed by hemin. The reaction mixtures were collected for 1 min at a time. We used the reaction between H_2O_2 and HCHO, both of which are the important products in the ozonolysis of isoprene, to probe the possibility of a chemical reaction occurring in the scrubbing H_3PO_4 solution. We mixed 10^{-6} M H_2O_2 with 10^{-5} M HCHO in H_3PO_4 solution, and we did not detect HMHP in the mixture 30 min later. This result implied that the chemistry occurring in the scrubbing solution inside the coil collector was unimportant. The samples for determining the carbonyls were collected using the cold trap method, in which a 2.0 L min^{-1} gas mixture from the outlet of the reactor passed through a Horibe tube in a cold trap of ethanol-liquid nitrogen at about −90 °C. In our experiments, the “Horibe tube” was made of three glass components: an inlet main tube (25 cm length, 4 cm O.D.), a coil (4–6 laps, 1 cm O.D.) linked to and around the main tube, and an outlet carborundum disc. After the sample was collected for 30 min, the Horibe tube was removed from the cold trap, and immediately 10 mL acetonitrile was used to strip the tube inside. In this process, 2 mL stripping solution was mixed with 2 mL 2, 4-dinitrophenyhydrazine (DNPH)–acetonitrile solution for 24 h derivatization, and the derivatization solution was analyzed by HPLC with UV detection (Agilent 1100, USA). The samples for the organic acids were also collected using the cold trap method, and water was used to strip the Horibe tube. The 2 mL stripping solution was immediately analyzed with ion chromatography (DIONEX 2650, USA) and an ED50 conductivity detector. During the collection process, O_3 and isoprene could not be frozen in the tube – only the reaction products were captured by the cold tube. The reaction rate of O_3 and isoprene at −90 °C was much lower than it was at 25 °C. We think the reactions during the collection process were unimportant to the formation of the observed products.

2.4 Control experiments: H_2O_2 background and peroxide wall loss

Blank runs were performed to investigate the potential H_2O_2 produced during the process of O_3 generation by UV irradiation of oxygen and trace water; that is, we passed the mixture of $O_3 + N_2 + O_2$ through the reactor in the absence of isoprene. The measured H_2O_2 was considered to be the blank background that should be subtracted from the H_2O_2 observed in the isoprene ozonolysis experiment.

The wall losses of the reactants (O_3 and isoprene) were negligible; however, the wall losses of the oxygenated products were inevitable, especially under high RH conditions. A series of peroxides, including H_2O_2, HMHP, 1-hydroxyethyl hydroperoxide (1-HEHP), peroxyacetic acid (PAA), and perpropionic acid (PPA), were selected as representatives to determine the wall losses of the oxygenated products. HMHP and 1-HEHP are proxies for 1-hydroxyl hydroperoxides, and PAA and PPA are proxies for peroxy acids. Peroxide gas with a certain concentration was obtained by passing 100 mL N_2 through a diffusion tube containing a peroxide solution. The peroxide gas was then introduced into the flow tube together with water vapor and N_2 plus O_2, which resulted in a total flow of 2.0 L min^{-1} and a peroxide concentration close to that observed in the ozonolysis experiment. The wall losses of the peroxides, which were a function of RH, were determined as the difference between the peroxide concentrations of the inlet and the outlet of the reactor after 60 min of peroxide passing (at which time the peroxide concentrations became constant). These losses were represented by the ratio $(C_{IN}-C_{OUT})/C_{IN}$. In addition, we adjusted the total gas flow passing through the reactor to reach variable gas residence times of 45 s at 3.0 L min^{-1}, 68 s at 2.0 L min^{-1}, 135 s at 1.0 L min^{-1}, and 270 s at 0.5 L min^{-1}, respectively. We then obtained the variation profiles of the wall loss with residence time for H_2O_2 and HMHP at 5 % RH.

2.5 Modeling methodology

A box model coupled with a near-explicit mechanism of ozonolysis of isoprene under NO_x-free conditions, which was extracted from the Master Chemical Mechanism version 3.2 (MCM v3.2) (website: http://mcm.leeds.ac.uk/MCM; Jenkin et al., 1997; Saunders et al., 2003), was set up to simulate the reaction processes of the O_3-initiated oxidation of isoprene occurring in the flow tube reactor. We expanded the extracted mechanism to include a dozen reactions for the formation of hydroxyalkyl hydroperoxides (HAHPs) via reactions between the gaseous water and Criegee intermediates and the reactions of the water-assisted decomposition of HAHPs. In this model, we tentatively investigated the water effect on the products' formation and removal.

3 Results and discussion

3.1 Background and wall loss quantification

In the H_2O_2 background experiment, the measured H_2O_2 concentration at the outlet of the reactor became constant after the O_3-containing gas passed through the reactor for about 30 min. Generally, the H_2O_2 background was less than 5 % of the formed H_2O_2 from the isoprene ozonolysis. Figure 2 shows the wall loss profiles of several peroxides with increasing RH. For H_2O_2, the RH dependence of the wall loss was a "V-shaped" curve, with its lowest level (0.02) occurring at 30 % RH, and its highest level (0.11) occurring at 80 % RH. For 1-hydroxyl hydroperoxides, HMHP and 1-HEHP had a wall loss curve similar to that of H_2O_2 but with a higher loss fraction. The wall loss of peroxy acids, however, linearly increased with increasing RH, and the highest value was 0.21 at 80 % RH. In general for the wall loss of peroxides, HMHP seemed to present an upper limit, while H_2O_2 showed the lower limit. In this study, the background of H_2O_2 and the wall loss of H_2O_2 and organic peroxides were considered in the data analysis.

In addition, we considered the possibility of peroxides formation on the walls. After each experiment, the reactor wall was washed with water, and then the eluate was collected for a peroxides analysis to detect if large quantities of peroxides were present. However, only H_2O_2 and HMHP were detected in the eluate. Thus, we believe that formation on the walls was an unimportant pathway for the more complicated peroxides.

3.2 Conventional products: peroxides, carbonyls and organic acids

This study identified a number of conventional hydroperoxides, which have been generally reported in the related literature, as products in the ozonolysis of isoprene. They include hydrogen peroxide (H_2O_2), hydroxymethyl hydroperoxide (HMHP), bis-hydroxymethyl hydroperoxide (BHMP), methyl hydroperoxide (MHP), and ethyl hydroperoxide (EHP). Figure 3a shows the wall-loss-corrected molar yield profiles of H_2O_2, HMHP, and BHMP as a function of RH. The wall loss of MHP and EHP was considered to be the same as that of H_2O_2, while the wall loss of BHMP was assumed to be like HMHP. The molar yield was defined as the ratio of the formed molar number of the product to the consumed molar number of isoprene. Here, the percent conversion of isoprene was estimated to be 75 %, according to the rate constant of the isoprene reaction with O_3 (Atkinson et al., 2006) and a reaction time of 68 s. The molar yields of MHP and EHP were found to be ~2 % and ~1 %, respectively, under every RH condition (not shown). HMHP and H_2O_2 increased with RH and then leveled off at 40 % RH. An increasing humidity led to a decreasing molar yield of BHMP, indicating that the water effects on the formation of BHMP were different than the water effects on HMHP and H_2O_2. All the observed organic acids and carbonyls, including formic acid (FA), acetic acid (AA), formaldehyde (FAL), acetaldehyde (AL), methyl glyoxal (MG), and glyoxal (GL), were found to be dependent on RH (Fig. 3b); that is, there was a significant yield increase with increasing RH for AL, MG, and GL, while there was a slight yield decrease with increasing RH for FAL, FA, and AA.

3.3 Unknown peroxides

Interestingly, we detected three unknown peroxides, including unknown1 (retention time in HPLC: 12.88 min), unknown2 (29.41 min), and unknown3 (27.22 min). Because of the absence of standards for the three unknown peroxides, unknown1 was quantified using the response factor of peroxyacetic acid (PAA), as the retention time of unknown1 was very close to that of PAA (13.22 min). Both unknown2 and unknown3 were quantified using the response factor of H_2O_2, since we have no standard very close to them. In our HPLC system, compared to H_2O_2 (6.25 min), compounds with longer retention times have smaller response factors. If true, the amounts of unknown2 and unknown3 would be underestimated. As for the wall losses, we applied the wall loss curve of HMHP to the yields correction for these unknown peroxides and obtained their yields upper limits. Simultaneously, the wall loss curve of H_2O_2 was used to obtain the lower limits of their yields. The largest difference between these two corrected curves was about 15 %. We averaged the wall loss ratio of H_2O_2 and HMHP and used the mean value to represent the wall losses of the unknown peroxides. Based on the semi-quantitative concentrations mentioned above, and considering the wall losses, we estimated the molar yields of these three unknown peroxides. Figure 4 shows the RH dependence for the molar yields for the unknown peroxides. Increasing the RH from 5 % RH to 90 % RH led to a 90 % decrease in the molar yield for unknown1, 98 % decrease for unknown2, and 83 % decrease for unknown3. Obviously, the formation and removal mechanism of these peroxides is worth exploring.

3.3.1 Unknown peroxides source: ozonolysis reaction or OH-initiated reaction?

To explore the source of these peroxides, we needed to determine if they were from O_3 or/and OH radical-initiated reactions. OH radicals are known to be generated in the gaseous ozonolysis of isoprene (e.g. Paulson and Orlando, 1996; Ariya et al., 2000; Kroll et al., 2001a, b). We performed an experiment of isoprene ozonolysis in the presence of the OH scavenger, cyclohexane, at 5 % RH. The added cyclohexane was estimated to scavenge 95 % of OH radicals produced from the reaction. A comparison of the initial reactant concentrations and the product yields in the presence and absence of the OH scavenger is shown in Table 1. The cyclohexane addition did not affect the molar yields of the unknown peroxides. This result suggested that the peroxides were produced via the ozonolysis reaction rather than an OH radical-initiated reaction.

3.3.2 Unknown peroxides source: cross reaction of RO_2 and HO_2 radicals?

It has been reported that Criegee radicals could produce RO_2 as well as HO_2 radicals, and the cross reaction of RO_2 and HO_2 would produce ROOH. In the MCM v3.2 mechanism for the ozonolysis of isoprene, the cross reaction of RO_2 and HO_2 resulted in the highest yield for CH_3OOH (MHP), which was produced via the reaction of CH_3O_2 with HO_2. However, a much lower yield was obtained for the more complicated ROOH compounds, about half to a tenth of the MHP yield. In the present laboratory study, we observed an MHP yield with only ~2 % at 5 % RH, which is comparable to the 4–5 % reported in the literature (Gäb et al., 1995; Neeb et al., 1997). We observed a much higher yield for the more complicated organic peroxides, e.g. ~30 % for the unknown1 peroxide as estimated using the response factor of peroxyacetic acid (PAA) in the HPLC analysis. The observed yield of MHP was much lower than that of the unknown peroxides; thus, the other ROOH compounds produced from the reactions of RO_2 and HO_2 presented a minor contribution to the formation of the observed organic peroxides.

3.3.3 Unknown peroxides variation with reaction time

Additional experiments that varied the flow were performed to investigate the reaction time dependence of the unknown peroxides. Flows of 3, 2, 1, and 0.5 $\mathrm{L\,min^{-1}}$ corresponded to reaction times of 45, 68, 135, and 270 s, respectively. In all these experiments, the initial concentrations of the reactants in the reactor were the same (290 ppbv isoprene + 80 ppmv O_3). We also determined the wall loss ratios ($(C_{IN}-C_{OUT})/C_{IN}$) of HMHP and H_2O_2 at different residence times and obtained an average wall loss variation that represented the wall loss residence time dependence of the three unknown peroxides: 8.3 % at 45 s, 12.6 % at 68 s, 16.9 % at 135 s, and 15.2 % at 270 s, respectively. These wall losses were considered in the unknown peroxides concentration calculation. The results for the peroxides concentrations are shown in Fig. 5. Once the reaction began, the unknown peroxides increased to a maximum within 100 s and then gradually decreased. This indicated that the unknown peroxides were unstable; also they possibly reacted with the other compounds in the gas phase. Unfortunately, we could not exclude the case of heterogeneous decomposition of HAHPs during the reaction.

3.3.4 Unknown peroxides decomposition in aqueous solution

When we repeatedly measured a sample collected with the H_3PO_4 solution (pH 3.5) (the sample was stored in an Agilent brown sampling bottle at room temperature, ~25 °C), we found that the concentrations of the unknown peroxides gradually decreased. Figure 6a shows the time series of the peroxides in the sample. Simultaneously, we monitored the carbonyl variation of the sample (shown in Fig. 6b). The concentration variation of methyl glyoxal (MG) mirrored that of the unknown peroxides, as it increased 30 % after 130 min of storage at room temperature. Interestingly, we did not detect any compound that had more carbon than MG (C3 dicarbonyl). Moreover, the Henry's law constant of O_3 ($1.1 \times 10^{-2}\,\mathrm{M\,atm^{-1}}$, Seinfeld and Pandis, 2006) is so small that aqueous O_3 would be negligible; thus, the aqueous ozonolysis reaction could not significantly contribute to MG production. Large radicals would be quickly stabilized by condensed water (Wang et al., 2012), and these radicals could not constantly decompose and directly produce MG over such a long time. So, the source of MG remains obscure.

As shown in Fig. 6, the unknown peroxides decrease, whereas H_2O_2 and MG increase. In the O_3-initiated reaction of isoprene, we expected that hydroxyalkyl hydroperoxides (HAHPs) would be produced from the reactions of the Criegee intermediates with H_2O (Gäb et al., 1985; Hatakeyama and Akimoto, 1994; Ryzhkov and Ariya, 2004). However, in the past decade, researchers have identified few HAHPs larger than HMHP produced through the ozonolysis mechanism. The reason has been previously attributed to the faster decomposition into a carbonyl and H_2O_2 for larger HAHPs than HMHP (Hasson et al., 2001b). Notably, most of the previous studies employed a large static chamber, so possibly these studies missed details regarding the generation of

peroxides at the beginning of the reaction as the first sample was usually collected after 10 min reaction. In the present study, we used a quartz flow tube reactor to investigate the formation of peroxides in the ozonolysis of isoprene at various RH. The reaction time was dozens of seconds and the wall losses of the peroxides were limited to a small extent; this increased the chance that we could observe some compounds that were active and short lived. The obvious opposite variations for the unknown peroxides and carbonyls and the analysis mentioned above led us to suppose that the observed unknown peroxides were the products of the Criegee intermediate reactions with H_2O (i.e. HAHPs), and the increase in the carbonyls such as MG was due to the aqueous decomposition of large HAHPs.

3.3.5 Comparison with the synthesized peroxides

Considering the inverse relationship between MG and the unknown peroxides described in Fig. 6, we attempted to evaluate whether MG was a potential precursor in the synthesis of the unknown peroxides. Unfortunately, MG polymerizes at a high concentration, and at a low concentration it did not react with H_2O_2 to generate the corresponding hydroxyl hydroperoxide. However, we tried to synthesize a series of organic peroxides including alkyl hydroperoxides, hydroxyalkyl hydroperoxides, and peroxy acids to confirm the unknown peroxides. The detailed synthetic method can be found in the literature (Kok et al., 1995). The precursors and the peroxides as well as the HPLC retention times of the peroxides are shown in Table 2. Generally, MHP (EHP) was synthesized from H_2O_2 and dimethyl sulfate (diethyl sulfate) in the presence of 40 % KOH, α-hydroxyalkyl hydroperoxide was synthesized by the reaction of H_2O_2 and various carbonyls, other hydroxyalkyl hudroperoxides were synthesized from H_2O_2 and brominated alcohols in the presence of KOH, and peroxy organic acids were synthesized by the reaction of H_2O_2 and organic acids. Unfortunately, none of these synthesized peroxides had the same retention time as one of the three unknown peroxides. Nevertheless, after comparing the retention time, carbon number, and functional groups of these synthesized peroxides, we obtained regularity about the retention time of the peroxides as follows. (1) For the hydroperoxides containing the same number of carbons: (i) the compound containing an OH group has a shorter retention time, e.g. $CH_2(OH)OOH$ 7.14 min < CH_3OOH 9.75 min; (ii) hydroxyl hydroperoxide has a shorter retention time compared with peroxy acid, e.g. $CH_2(OH)OOH$ 7.14 min < $HC(O)OOH$ 8.61 min and $CH_3CH(OH)OOH$ 11.49 min < $CH_3C(O)OOH$ 13.22 min; and (iii) the further the hydroxyl group is from the peroxy group, the shorter is the retention time for the hydroxyl group containing peroxide, e.g. $CH_2(OH)CH_2OOH$ 9.59 min < $CH_3CH(OH)OOH$ 11.49 min and $HOCH_2CH_2CH_2OOH$ 14.37 min < $CH_3CH(OH)CH_2OOH$ 16.77 min. (2) For the peroxides containing a different number of carbons: (i) one more carbon usually leads to a longer retention time, e.g. CH_3OOH 9.75 min < CH_3CH_2OOH 17.30 min; and (ii) one more C(OH) group leads to a shorter retention time, e.g. $CH_2(OH)CH(OH)OOH$ 6.72 min < $CH_2(OH)OOH$ 7.14 min. Furthermore, we determined the stability of these synthesized peroxides. Alkyl hydroperoxides and peroxy organic acids are much more stable than hydroxyalkyl hydroperoxide. When stored in H_3PO_4 solution (pH 3.5) at room temperature, alkyl hydroperoxides and peroxy acids decreased by less than 5 % at a concentration of about 10^{-5} M for 1 h of storage, while hydroxyalkyl hydroperoxides decreased by 5 % to 40 % (the larger the compound, the more stable it is). From Fig. 6a, we know that the unknown 1, 2, and 3 peroxides decreased 50 %, 40 %, and 7 %, respectively. This was very similar to the variation in the hydroxyalkyl hydroperoxides in the H_3PO_4 solution.

According to these empirical laws for the retention time and the stability of the synthesized peroxides, we speculated that unknown1 is a hydroxyl or a carbonyl group containing C2 hydroperoxide, or both hydroxyl and carbonyl groups containing C3 hydroperoxide. Unknown2 and unknown3 are hydroxyl groups containing C3 hydroperoxide or peroxy organic acid, or hydroxyl and/or carbonyl groups containing C4 hydroperoxide. Thus, we suggest that the MG HAHP ($CH_3C(OH)(OOH)CHO$ or $CH_3C(=O)CH(OH)OOH$) is at least one of the three unknown peroxides.

3.3.6 Possibility of peroxyhemiacetals

It has been suggested that Criegee intermediates can react with carboxylic acids to form α-acyloxyl hydropreroxides, and the α-acyloxyl hydroperoxides can subsequently react with aldehydes to form peroxyhemiacetals via heterogeneous and aqueous phase reactions (Tobias and Ziemann, 2001; Zhao et al., 2012). In the present study, formic acid (FA), acetic acid (AA), formaldehyde (FAL), and acetaldehyde (AL) were detected in the ozonolysis of isoprene performed in the flow reactor, indicating the possibility of the formation of α-acyloxyl hydropreroxides and peroxyhemiacetals. Thus, we added a pair of carboxylic acid and aldehyde with a high concentration (a few hundred ppbv), including (FA + FAL), (FA + AL), (AA + FAL), and (AA + AL), into the isoprene ozonolysis system. The results of these additional experiments show the formation of new peroxide species, which are possibly peroxyhemiacetals. On the basis of the retention time in HPLC, however, these species cannot be attributed to those three unknown peroxides.

In summary, consistent with their instability in solution, the variation of their yield with RH, and their HPLC retention time, we tentatively assigned the three unknown peroxides to be HAHPs, produced by the reaction of large Criegee intermediates with water molecules.

3.4 Mechanism and water effect modeling

To further test our hypothesis of HAHPs formation, we used a box model coupled with a near-explicit mechanism for the ozonolysis of isoprene (extracted from the MCM v3.2 mechanism) to simulate the reaction processes of the O_3-initiated oxidation of isoprene. The extracted mechanism provides the reactions of seven Criegee intermediates as they react with water, directly producing carbonyls plus H_2O_2 or organic acids plus H_2O. The seven Criegee intermediates are CH_2OO, MVKOO [$CH_3C(OO)CH{=}CH_2$], MACROO [$CH_3C({=}CH_2)CHOO$], MGLOO [$CH_3C({=}O)CHOO$], MGLYOO [$CH_3C(OO)CHO$], CH_3CHOO, and HMGLOO [$CH_2(OH)C({=}O)CHOO$]. However, a number of experimental studies have affirmed the formation of HMHP (the simplest HAHP), produced via a reaction of CH_2OO with H_2O and yielding less than 1 % to 30 % under different humidities in the gas phase ozonolysis of isoprene (Gäb et al., 1995; Neeb et al., 1997; Sauer et al., 1999). Several theoretical studies suggest that the formation of HAHPs is the main reaction path for the reactions of the Criegee intermediates with water molecules (Aplincourt and Anglada, 2003a; Hasson et al., 2003) or the water dimer (Ryzhkov and Ariya, 2004). Subsequently, the unimolecular decomposition for HAHPs is unlikely to occur in the gas phase (Aplincourt and Anglada, 2003b; Hasson et al., 2003); only the water-assisted decomposition of HAHPs is efficient in the gas phase, and it generates carbonyls plus H_2O_2 or organic acids plus H_2O (Aplincourt and Anglada, 2003b). Therefore, we added the formation and decomposition of HAHPs into the extracted MCM mechanism. We suggest that the seven Criegee intermediates react with water and produce the corresponding HAHPs as follows:

$$\mathrm{CH_2OO + H_2O \rightarrow CH_2(OH)OOH}\,\mathbf{[PO1]} \xrightarrow{\mathrm{H_2O}} \text{products}$$

$$\mathrm{CH_3C(OO)CH{=}CH_2 + H_2O \rightarrow CH_3C(OH)(OOH)CH{=}CH_2}\,\mathbf{[PO2]} \xrightarrow{\mathrm{H_2O}} \text{products}$$

$$\mathrm{CH_3C({=}CH_2)CHOO + H_2O \rightarrow CH_3C({=}CH_2)CH(OH)OOH}\,\mathbf{[PO3]} \xrightarrow{\mathrm{H_2O}} \text{products}$$

$$\mathrm{CH_3C({=}O)CHOO + H_2O \rightarrow CH_3C({=}O)CH(OH)OOH}\,\mathbf{[PO4]} \xrightarrow{\mathrm{H_2O}} \text{products}$$

$$\mathrm{CH_3C(OO)CHO + H_2O \rightarrow CH_3C(OH)(OOH)CHO}\,\mathbf{[PO5]} \xrightarrow{\mathrm{H_2O}} \text{products}$$

$$\mathrm{CH_3CHOO + H_2O \rightarrow CH_3CH(OH)OOH}\,\mathbf{[PO6]} \xrightarrow{\mathrm{H_2O}} \text{products}$$

$$\mathrm{CH_2(OH)C({=}O)CHOO + H_2O \rightarrow CH_2(OH)C({=}O)CH(OH)OOH}\,\mathbf{[PO7]} \xrightarrow{\mathrm{H_2O}} \text{products}$$

The formation rate constants for these HAHPs from the combination of Criegee radicals with water were estimated on the basis of a theoretical study by Ryzhkov and Ariya (2004), who provided the reaction rate constants of parent, mono-, and dimethyl-substituted Criegee intermediates with water. For the water-assisted decomposition of

HAHPs, only the rate constant for 2-propenyl α-hydroxy hydroperoxide (PO3) is available (Aplincourt and Anglada, 2003b), that is, $1.5 \times 10^{-30}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$. However, our model results indicate that this theoretical decomposition rate constant is too small to be consistent with experimental observations of the profile of PO3 variation with RH. Thus, we treated the exponent of the rate constant as an adjustable parameter. A sensitivity analysis was performed and 14 simulations were performed for PO3 using −30, −28, −25, −22, −21, −20, and −19 as the exponents of the rate constant at two RHs (70 % and 10 %, Fig. 7). As a result, −21, −20, and −19 could capture the variation of the concentration of HAHPs with RH. PO3 decreased by 53 % as RH increased from 10 % to 70 % at 68 s, which is similar to the 80 % decrease for unknown2 (Fig. 4). Furthermore, for exponent = −20, the simulated time series of PO3 would preferably match the observed unknown2 (Fig. 7).

We hypothesized that all seven HAHPs (PO1–PO7) have the similar rate constant of $1.5 \times 10^{-20}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$. We then used the modified mechanism to simulate the concentration variations of the seven HAHPs with RH at 68 s (Fig. 8). The simulation results displayed that PO1, PO2, PO3, PO4, PO5, PO6, and PO7 decreased by 91 %, 80 %, 95 %, 76 %, 53 %, 84 %, 81 %, and 87 %, respectively, with RH increasing from 10 % to 90 %. These decreases showed good agreement with the observed decreases for the unknown peroxides, that is, 90 % for unknown1, 98 % for unknown2, and 83 % for unknown3 with RH increasing from 10 % to 90 % (see Sect. 3.3). Interestingly, for the concentration curves, PO2 and PO3 agreed well with unknown2 (Fig. 8a), and PO4, PO5, and PO6 agreed well with unknown3 (Fig. 8b). Meanwhile, all of the POs were much lower than unknown1, although their variation trends were similar. This discrepancy between the POs and unknown1 seems to indicate an overestimation of the decomposition rate constant for some PO, or an overestimation of the unknown1 concentration due to the absence of its standard calibration in HPLC analysis.

The expected dependence of PO1 (i.e. HMHP) on RH was significantly different from that observed in the experiment. The modeled HMHP decreased with increasing RH (Fig. 8a), while the observed HMHP increased gradually with increasing RH and then leveled off (Fig. 3a). This may have been due to the chemistry of BHMP. Gäb et al. (1985) reported that HMHP would react with HCHO to generate BHMP in the gas phase, and BHMP would produce HMHP by hydrolysis. Our experimental results indicated that BHMP formed during the ozonolysis of isoprene. As the humidity increased, the reaction of BHMP with water became more important and produced HMHP to offset the decrease in HMHP formed via the ozonolysis of isoprene. Unfortunately, because there are no available data for the rate constants of BHMP formation and hydrolysis, we cannot confirm this speculation through a model simulation.

In summary, the simulation results were consistent with the speculation that the detected unknown peroxides are HAHPs produced from the reaction of Criegee intermediates and water molecules.

4 Conclusions and atmospheric implications

We investigated the formation of peroxides in the gas phase ozonolysis of isoprene at various relative humidities on a reaction time scale of tens of seconds using a quartz flow tube coupled with an online HPLC detection. This relatively quick detection method enabled the detection of both conventional and unknown organic peroxides formed during the reaction. The conventional peroxides, including H_2O_2, HMHP, BHMP, and MHP, were identified and quantified, and they showed good agreement with previous studies. Interestingly, three unknown peroxides were detected and were characterized as follows: (1) their molar yields decreased significantly with increasing relative humidity (RH); (2) their concentrations varied with the reaction time, indicating their instability; (3) they decomposed into carbonyls plus H_2O_2 in an aqueous solution; and (4) they were C2–C4 species and contained a hydroxyl and/or carbonyl group, but could not be attributed to peroxyhemiacetal species. These characteristics are consistent with those of hydroxyalkyl hydroperoxides (HAHPs). As illustrated in Scheme 1, the Criegee intermediates produced from the reaction of ozone with isoprene reacted with water and generated a series of HAHPs. Thus, HAHPs are the likeliest candidates for the

unknown peroxides. We used a box model coupled with a modified near-explicit mechanism extracted from MCM v3.2 to try to produce the HAHPs profiles with RH variation. The modeled HAHPs profiles showed good agreement with those of the three unknown peroxides observed in the experiments. This provided evidence in support of our suggestion that these unknown peroxides are the products of the Criegee intermediates reaction with water. Obviously, synthesizing the standards of HAHPs is urgently needed.

The present study may experimentally prove that, instead of a one-step reaction, Criegee intermediates react with water and then generate carbonyls plus H_2O_2, or organic acids plus H_2O, via the formation of hydroxyalkyl hydroperoxide. On the basis of the experimental results of the formation kinetics and the RH-dependent molar yield of HAHPs, and the model-fitted HAHP−H_2O reaction rate constant of $1.5 \times 10^{-20}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$, we estimate that the lifetime of HAHPs due to their reaction with water is 10 to 90 min at 25 °C and 10−90 % RH. This lifetime favors the reaction of HAHPs with other species (such as carbonyls and acids) to produce peroxyhemiacetals, and thus contributes to the formation of SOAs. Moreover, HAHPs will have enough time to distribute between the gaseous and aqueous phases. Because they are soluble, they will participate in the chemistry of atmospheric aqueous phases, including cloud, fog, and wet aerosols.

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Table 1. The molar yields of the determined peroxides in the ozonolysis of isoprene in the presence and absence of the OH scavenger.

Reactants	$Y_{H_2O_2}$	Y_{HMHP}	$Y_{unkown1}$	$Y_{unknown2}$	$Y_{unknown3}$
80 ppmv O_3 + 290 ppbv ISO	0.051	0.185	0.263	0.018	0.005
80 ppmv O_3 + 290 ppbv ISO + 652 ppmv CH	0.043	0.207	0.249	0.018	0.004
80 ppmv O_3 + 290 ppbv ISO + 1956 ppmv CH	0.040	0.194	0.257	0.019	0.005

Note: ISO, isoprene; CH, cyclohexane.

Table 2. Synthesized peroxides and their retention time, carbon number, and response factors. H_2O_2 and the three unknown peroxides are listed for comparison.

Precursor	Peroxide	RT	C	RF
H_2O_2	H_2O_2	6.25	0	1
Glycoaldehyde	$CH_2(OH)CH(OH)OOH$	6.72	2	
Formaldehyde	$CH_2(OH)OOH$ **[HMHP]**	7.14	1	1
Glyoxal	$HOOCH(OH)CH(OH)OOH$	7.30	2	
Formic acid	$HC(O)OOH$	8.61	1	
Glycolic acid	$CH_2(OH)C(O)OOH$	8.72	2	
Formaldehyde	$HOCH_2OOCH_2OH$ **[BHMP]**	8.81	2	
2-Br-ethanol	$CH_2(OH)CH_2OOH$ **[2-HEHP]**	9.59	2	
Hydroxyacetone	$CH_2(OH)C(OH)(OOH)CH_3$	9.61	3	
Dimethyl sulfate	CH_3OOH **[MHP]**	9.75	1	0.07
Acetaldehyde	$CH_3CH(OH)OOH$ **[1-HEHP]**	11.49	2	
–	**Unknown1**	12.88		
Acetic acid	$CH_3C(O)OOH$ **[PAA]**	13.22	2	0.33
3-Br-1-proanol	$HOCH_2CH_2CH_2OOH$	14.37	3	
1-Br-2-proanol	$CH_3CH(OH)CH_2OOH$	16.77	3	
Diethyl sulfate	CH_3CH_2OOH	17.30	2	0.05
Acetone	$CH_3C(OH)(OOH)CH_3$	18.66	3	
Propanal	$CH_3CH_2CH(OH)OOH$	26.28	3	
–	**Unknown 3**	27.22		
–	**Unknown 2**	29.41		
Propionic acid	$CH_3CH_2C(O)OOH$ **[PPA]**	31.77	3	

Note: RT, peroxide retention time (min) in HPLC analysis; C, carbon number; RF: response factor in HPLC analysis; **[ ]** represents the abbreviation of the peroxide.

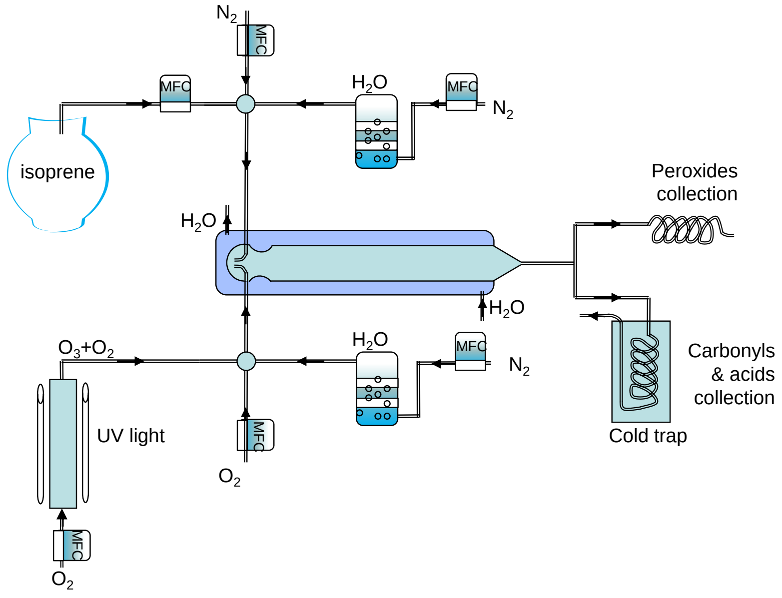


Fig. 1. Schematic diagram of the flow tube reactor and the gas path system. MFC: mass flow controller.

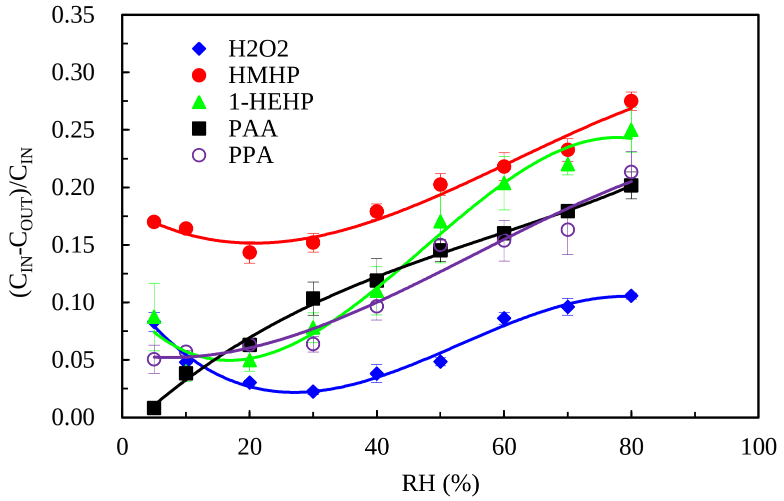


Fig. 2. The variation of peroxides wall losses, $(C_{IN}-C_{OUT})/C_{IN}$, with increasing relative humidity (RH). H_2O_2: hydrogen peroxide; HMHP: hydroxymethyl hydroperoxide; 1-HEHP: 1-hydroxyethyl hydroperoxide; PAA: peroxyacetic acid; PPA: perpropionic acid.

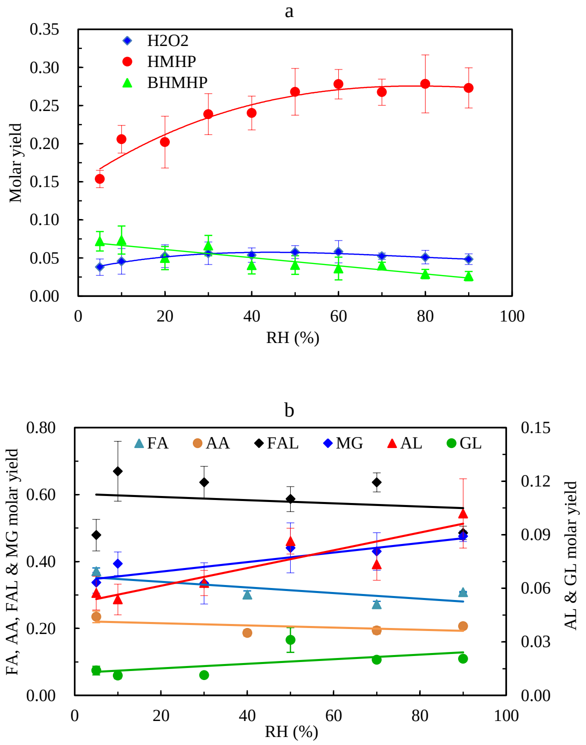


Fig. 3. Dependence of the product yields for **(a)** peroxides and **(b)** carbonyls and acids on relative humidity (RH). FA: formic acid; AA: acetic acid; FAL: formaldehyde; MG: methyl glyoxal; AL: acetaldehyde; GL: glyoxal.

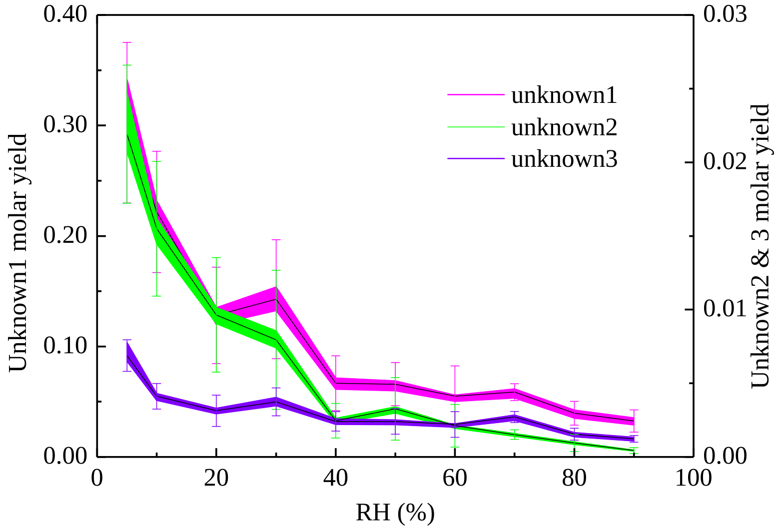


Fig. 4. Dependence of the product molar yields for the unknown peroxides on relative humidity (RH). The upper edge of the filled area represents the corrected unknown peroxide yields using the wall loss curve of HMHP. The lower edge of the filled area represents the corrected unknown peroxide yields using the wall loss curve of H_2O_2. The black line represents the mean value, and the error bar represents 2σ of the detected concentrations of unknown peroxides.

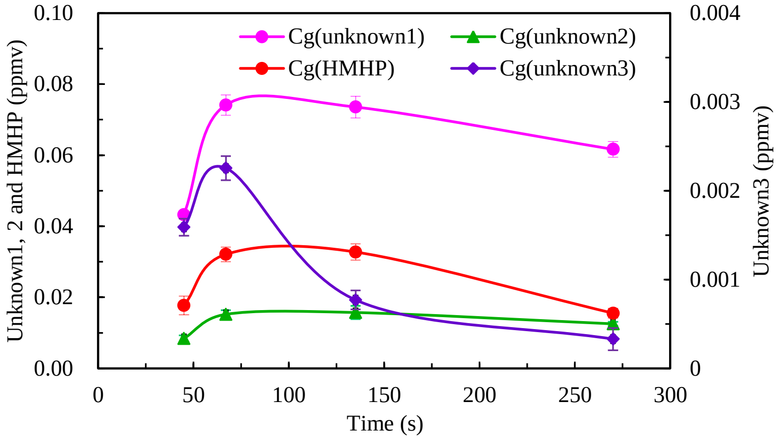


Fig. 5. The temporal profiles of HMHP and the three unknown peroxides.

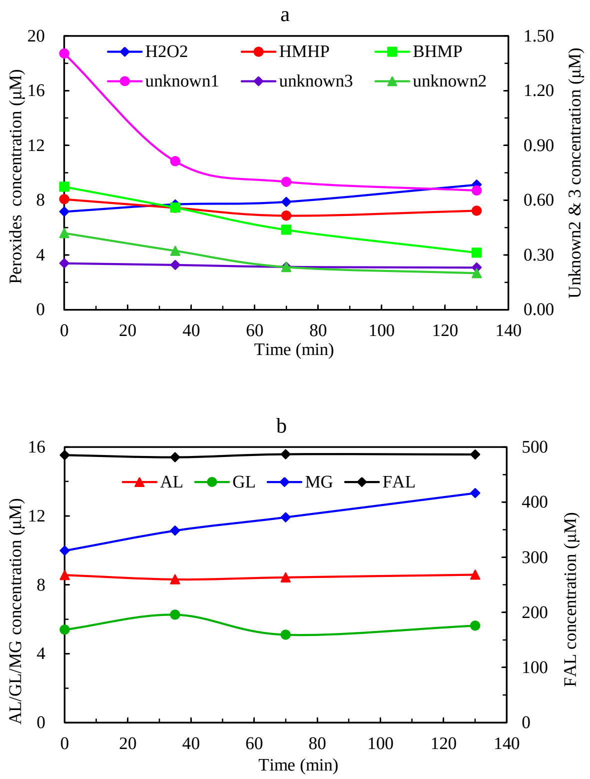


Fig. 6. Temporal profiles of **(a)** peroxides and **(b)** carbonyls of a sample collected with H_3PO_4 solution and stored at room temperature (~25 °C). AL: acetaldehyde; GL: glyoxal; MG: methyl glyoxal; FAL: formaldehyde.

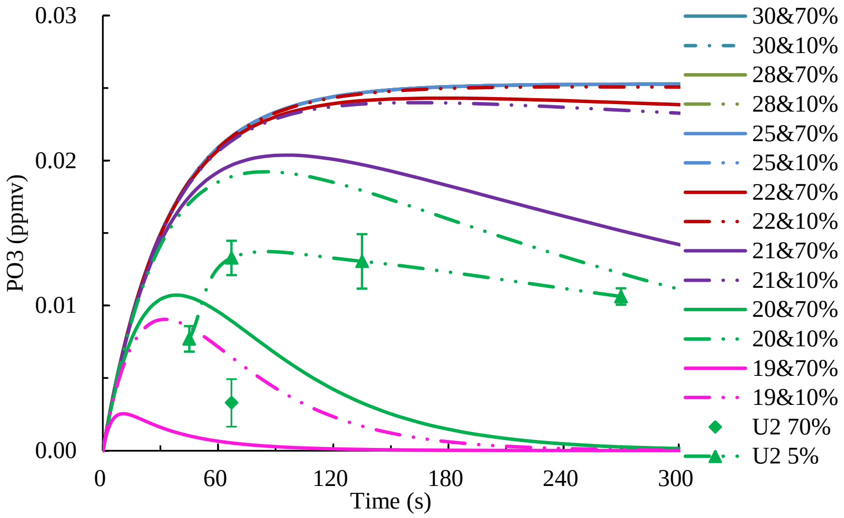


Fig. 7. Sensitivity simulation for the exponent of the reaction rate constant of PO3 and water. The number before "&" is the negative exponent, and the number after "&" is the relative humidity (RH). For example, 30 & 70 % means the model is performed with a rate constant of 1.5×10^{-30} cm^3 $molecule^{-1}$ s^{-1} and a RH of 70 %. U2 70 % and U2 5 % represent the observed unknown2 time series at 70 % RH and 5 % RH, respectively.

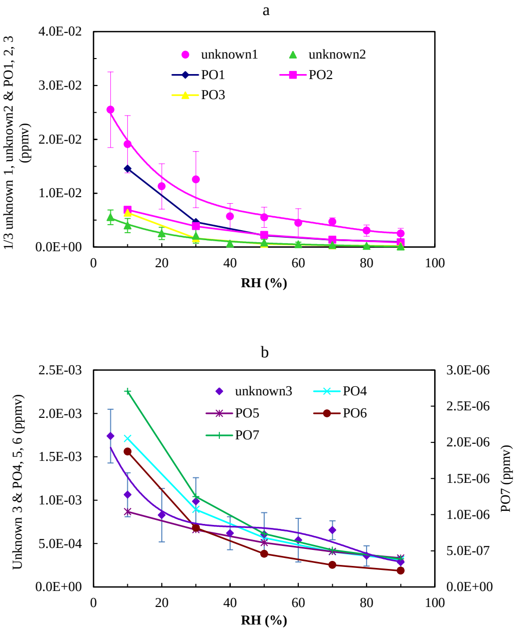
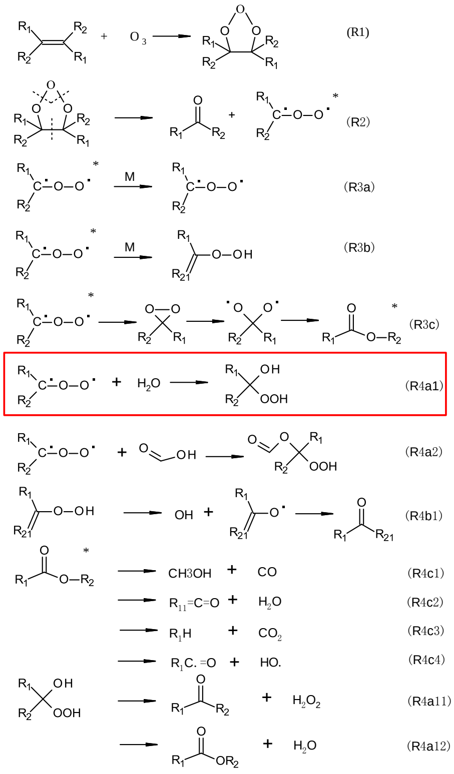


Fig. 8. The simulated dependence of the concentrations of seven POs on the relative humidity (RH), and comparisons between the modeled PO and the observed unknown peroxides. **(a)** Observed unknown1, unknown2, and modeled PO1, 2, and 3. **(b)** Observed unknown3 and modeled PO4, 5, 6, and 7.



Scheme 1. The major steps for the ozonolysis of alkenes in the gas phase.