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Unexpected high yields of carbonyl and peroxide products of aqueous isoprene ozonolysis and implications

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Abstract

The aqueous phase reaction of volatile organic compounds (VOCs) has not been considered in most analyses of atmospheric chemical processes. However, some experimental evidence has shown that, compared to the corresponding gas phase reaction, the aqueous chemical processes of VOCs in the bulk solutions and surfaces of ambient wet particles (cloud, fog, and wet aerosols) may potentially contribute to the products and formation of secondary organic aerosol (SOA). In the present study, we performed a laboratory experiment of the aqueous ozonolysis of isoprene at different pHs (3–7) and temperatures (4–25 °C). We detected three important kinds of products, including carbonyl compounds, peroxide compounds, and organic acids. Our results showed that the molar yields of these products were nearly independent of the investigated pHs and temperatures. These products included (1) carbonyls: 56.7 ± 6.7 % formaldehyde, 42.8 ± 2.5 % methacrolein (MAC), and 57.7 ± 3.4 % methyl vinyl ketone (MVK); (2) peroxides: 53.4 ± 4.1 % hydrogen peroxide (H_2O_2) and 15.1 ± 3.1 % hydroxylmethyl hydroperoxide (HMHP); and (3) organic acids: undetectable (< 1 % estimated by the detection limit). Based on the amounts of products formed and the isoprene consumed, the total carbon yield was estimated to be 95 ± 4 %. This implied that most of the products in the reaction system were detected. Of note, the combined yields of both MAC + MVK and H_2O_2 + HMHP in the aqueous isoprene ozonolysis were much higher than those observed in the corresponding gas phase reaction. We suggested that these unexpected high yields of carbonyls and peroxides were related to the greater capability of condensed water, compared to water vapor, to stabilize energy-rich Criegee radicals. This aqueous ozonolysis of isoprene (and possibly other biogenic VOCs) could potentially occur on the surfaces of ambient wet particles and plants. Moreover, the high-yield carbonyl and peroxide products might provide a considerable source of aqueous phase oxidants and SOA precursors. Thus, aqueous ozonolysis on the surface of plants, where carbonyls and peroxides form, might affect biogenic VOC emissions and the deposition of O_3 and SO_2 onto leaves to different extents in clean and

polluted regions.

1 Introduction

Carbonyl and peroxide compounds are important trace components in the atmosphere. In the past decade, these two compounds have received a lot of attention, because they form components or precursors of secondary organic aerosols (SOA) (e.g., Mochida et al., 2006; Tong et al., 2006; Hallquist et al., 2009), and they produce reactive radical oxidants, including OH, HO_2, and RO_2 (e.g., Jacob, 1986; Atkinson and Arey, 2003). The gas phase ozonolysis of biogenic unsaturated volatile organic compounds (VOCs) was considered to be an important pathway that simultaneously formed carbonyls and peroxides (Atkinson and Carter, 1984; Becker et al., 1990; Gäb et al., 1995; Neeb et al., 1997; Sauer et al., 1999; Zhang et al., 2002; Chen et al., 2008). The yields of carbonyls and peroxides under humid conditions were significantly higher than those under dry conditions. However, few studies (Gäb et al., 1995; Chen et al., 2008) focused on the effect of condensed water on the formation of these products, when the contribution of the gas phase reaction was eliminated. Previously, Henry's law constant was considered to be the key parameter that determined the relative importance of the aqueous phase reaction of a compound; therefore, poorly-soluble volatile organic compounds (psVOCs), including biogenic isoprene and terpenes, were excluded in analyses of aqueous phase reactions. As a result, previous studies mainly focused on the aqueous chemical processes of water-soluble organic compounds (e.g., Monod et al., 2000; Carlton et al., 2006, 2007; Altieri et al., 2008; Perri et al., 2009; Schwier et al., 2010). Thus, little is known about the aqueous phase fate of psVOCs and their potential contributions to the formation of carbonyl and peroxide compounds (Zhang et al., 2009) and aqueous SOA in the atmosphere (Ervens et al., 2011).

In fact, the aqueous phase reaction may occur in both the bulk solution and on the surfaces of atmospheric wet particles (cloud, fog, and wet aerosols), water bodies (sea, lakes, and rivers), and wet soils. Both reactions should be considered for soluble VOCs, but only the surface reaction appears to be of importance for psVOCs (Chen et al., 2008; Huang et al., 2011). Moreover, typically, when biogenic VOCs, like isoprene and terpenes, are emitted from plant cells into the air through the wet surfaces of leaves, they first meet gas phase oxidants (e.g., ozone and OH radicals) at the wet surface. Interestingly, Hewitt et al. (1990) found that hydroperoxides were formed on or in leaves when plants were exposed to ozone. These observed hydroperoxides had to be produced from chemical reactions, particularly surface reactions, because there is no significant primary peroxide source in the atmosphere (Jackson and Hewitt, 1996). Altimir et al. (2006) proposed that an aqueous reaction on the wet surface of plants was a potentially important chemical process for exchanging ozone between the forest canopy and the atmosphere. Based on those observations, we aimed to investigate the aqueous reaction of biogenic VOCs to extend the current knowledge of the chemistry that takes place on the atmospheric surfaces of wet particles and plants.

New technology and methods, like laser induced fluorescence and spraying chambers, have been developed to explore aqueous surface reactions of organic compounds, like pyrene (Mmereki and Donaldson, 2002), and the ozonation of terpenes (Enami et al., 2010). However, it remains difficult to quantify the reaction products. Alternatively, a series of recent laboratory experiments on the aqueous oxidation of psVOCs in bulk water in the absence of gas phase interference were performed to quantitatively determine the effect of condensed water on the distribution of products that formed in the aqueous reaction of several psVOCs (Chen et al., 2008; Zhang et al., 2009, 2010; Huang et al., 2011; El Haddad et al., 2009; Liu et al., 2009, 2012). Interestingly, those studies revealed that the production of carbonyls, organic acids, and peroxides in the aqueous ozonolysis of α-pinene, β-pinene, methacrolein (MAC), and methyl vinyl ketone (MVK), and the aqueous OH radical-initiated oxidation of isoprene, MAC, and MVK significantly differed from those observed in the corresponding gas phase reaction. This suggested that a specific SOA would be produced in the aqueous phase because of the different distribution of SOA precursors (carbonyls, organic acids, and peroxides) compared to the corresponding gas phase. Moreover, several studies revealed that particle-associated semi-volatile organic compounds could be detected at a much higher concentration than predicted by gas to droplet or particle partition theory (Schweitzer et al., 1998; Liggio et al., 2005; Corrigan et al., 2008; Nguyen et al., 2010). Those results implied that the aqueous reaction of psVOCs merited a separate study that could more precisely evaluate the contributions of gas and aqueous phases to product yields.

In the present work, we were interested in the aqueous ozonolysis of isoprene, which is the most abundant biogenic VOC (Guenther et al., 2006). We aimed to determine whether the aqueous chemical processes of isoprene might be important for the production of SOA and the transformation of oxidants (Huang et al., 2011). Notably, we elucidated the precise chemical stoichiometry for the aqueous isoprene reaction with ozone, and we quantified the major products, including carbonyls, peroxides, and organic acids. Finally, we compared the mechanism of aqueous isoprene ozonolysis to that of the corresponding gas phase reaction, and discussed relative implications.

2 Experimental

The stock solution was prepared with isoprene (Fluka, 99.5 %) diluted in acetonitrile to a final concentration of 2 mM. In blank experiments, the mixture of water and isoprene stock solution was tested before the formal series of aqueous phase reactions were carried out. We ascertained that peroxides, carbonyl compounds, and organic acids were undetected in the stock solutions.

The experimental apparatus was described in detail in our previous work (Chen et al., 2008). The aqueous phase experiments were performed by mixing 495 ml O_3 solution with 5 ml isoprene stock solution in a 515-ml quartz aqueous reactor in darkness at different pHs (7.0, 5.4, and 3.0) and temperatures (4, 10, and 25 °C). Ozone solution was obtained by passing gaseous ozone through a 1.0 l water in a 2.1 l quartz container. After 2 h, the aqueous ozone concentration became stable. The stable ozone concentration was different at different temperatures, from 2 to 10 µM. Ozone was generated by irradiation of O_2 (≥ 99.999 %, Beijing Analytical Instrument Factory, Beijing, China) at a flow rate of 100 ml min^{-1}. The concentrations of ozone and the major products, including carbonyl compounds, peroxide compounds, and organic acids, were determined with methods described previously (Wang et al., 2009; Hua et al., 2008). Briefly, the aqueous ozone concentration was determined by indigo disulphonate spectrophotometry before ozone solution was used for mixing with isoprene solution. After mixing, 5 ml sample was extracted from the mixture at 5, 15, 30, 60, and 90 min for determining the concentrations of ozone, carbonyls, peroxides, and organic acids. After the sample was extracted, the sample was divided immediately into 4 parts for pretreatment or online analysis (within 2 min): 1 ml for determining the aqueous ozone; 1 ml for the peroxides; 2 ml for the carbonyl compounds; and 1 ml for the organic acids. Peroxide compounds were online analyzed with high performance liquid chromatography (HPLC) (Agilent 1100, USA) coupled with post-column derivatization. In this step, the peroxides oxidized hydroxyphenylacetic acid to produce a fluorescent dimer in a reaction catalyzed by hemin. Carbonyl compounds were analyzed by mixing 2 ml sample with 2 ml 2,4-dinitrophenyhydrazine (DNPH)–acetonitrile solution for derivative and then for off line analysis of HPLC with UV detection (Agilent 1100, USA) after 12–24 h derivatization. Organic acids were analyzed with ion chromatography (DIONEX 2650, USA) and an ED50 conductivity detector. Considering the gas space above the liquid mixture in the quartz reactor, the upper limits for the loss of aqueous ozone and isoprene into the gas phase were estimated to be about 10.7 % and 8.6 %, respectively, at 298 K (Sander, 1999) based on their Henry's law constants. Therefore, the contribution of the gas phase reaction was mostly eliminated, and the reaction could be regarded as an aqueous phase reaction. A small amount of H_2O_2 (< 10 % of the H_2O_2 produced from the isoprene and ozone reaction) was found in the ozone solution. The H_2O_2 formed in the ozone solution was measured in each experiment and was considered in the data analysis.

The rate constants for the aqueous ozonolysis of isoprene, methacrolein (MAC) and methyl vinyl ketone (MVK) ($k_{ISO} = 4.1 \times 10^5\ M^{-1}\ s^{-1}$; $k_{MAC} = 2.4 \times 10^4\ M^{-1}\ s^{-1}$; and

$k_{MVK} = 4.4 \times 10^4\,M^{-1}\,s^{-1}$, respectively, at 298 K) (Pedersen and Sehested, 2001) indicated that the ozonolysis of isoprene occurred prior to the ozonolysis of MAC and MVK, when the concentrations of isoprene, MAC, and MVK were comparable in the aqueous phase. In the present study, the concentration of isoprene was ~ 20 µM and the concentration of ozone was 2–10 µM; that is, isoprene was in excess. Therefore, under the present experimental conditions, we expected the ozonolysis of isoprene to dominate the aqueous phase reaction, and the ozonolysis of MAC and MVK, two major first-generation products in the aqueous ozonolysis of isoprene, should be negligible.

3 Results and discussion

3.1 Products and chemical stoichiometry

The reaction of aqueous isoprene with ozone was complete within 5 min. After this, no change was observed in the amounts of products. We then determined the amounts of carbonyls, peroxides, and organic acids for this aqueous ozonation system. We identified and quantified five products, including formaldehyde (HCHO), MAC, MVK, hydroxylmethyl hydroperoxide (HMHP), and H_2O_2. No organic acids were detected above the detection limit of ~ 0.05 µM. Figure 1 shows the temporal profiles of the products at $T = 4\,^{\circ}C$, pH = 7.0, and an initial concentration ratio of $C_{ISO} : C_{O_3} = 2 : 1$. It was clear that, once the isoprene and ozone solutions were mixed, a number of products formed rapidly, and then reached a plateau. Of note, a minor amount of methylglyoxal (MG) was observed when the concentration of isoprene was below or close to the concentration of ozone; in contrast, MG was not observed when the isoprene was in large excess to ozone (e.g., $C_{ISO} : C_{O_3} > 10 : 1$). MG is considered to be formed by the ozonolysis of MAC and MVK, which are first-generation products in the aqueous isoprene–O_3 reaction system.

Next, we derived the stoichiometric ratio between isoprene and ozone in an aqueous reaction. First, we knew that, in the reaction system, the ozone would be consumed by isoprene and by its first-generation products, MAC and MVK. The aqueous ozonolysis of MAC and MVK could produce MG with yields of 98.6 % and 75.4 %, respectively, and proceed at a 1 : 1 stoichiometric ratio of MAC (or MVK) : O_3 (Chen et al., 2008). Given the rate constants of MAC–O_3 and MVK–O_3 in the aqueous phase mentioned previously (Pedersen and Sehested, 2001), one mole of MG formation in the isoprene-O_3 reaction system would indicate that 0.42 mol of MAC and 0.77 mol of MVK had been consumed by O_3, assuming comparable concentrations of MAC and MVK in the reaction system. Thus, one mol of MG formation indicates that 1.19 mol of O_3 were consumed by the first generation products MAC and MVK. Based on this analysis, the amount of MG detected in the reaction system indicates the amount of O_3 consumed by non-isoprene constituents This will be equal to the amount of consumed (MAC + MVK) in a reaction with O_3, which occurs in a 1 : 1 ratio Because the amount of O_3 consumed by isoprene was directly proportional to the amount of (MAC + MVK) produced by isoprene, a simple linear regression was set up between ozone consumed by isoprene and (MAC + MVK) produced by isoprene (Fig. 2). The data in Fig. 2 were yielded from 72 experiments at different pHs (7.0, 5.4, and 3.0) and temperatures (4, 10, and 25 °C). X-axis represented the amount of consumed O_3 ($\Delta C_{C,O_3}$) in the reaction. For each experiment, isoprene was in excess and thus all the ozone was consumed within 5 min. Hence, $\Delta C_{C,O_3}$ was the difference between the measured initial concentration of ozone and its concentration at 5 min (actually, it was zero). Y-axis represented the determined total amount of MAC + MVK ($C_{P,MAC+MVK}$) in the reaction. This linear regression indicated that the amount of O_3 consumed directly by isoprene was equal to the amount of (MAC + MVK) produced. Furthermore, it can be presumed that the consumed concentration of ozone ($\Delta C_{C,O_3}$) or isoprene ($\Delta C_{C,ISO}$) was related to the produced concentration of MAC + MVK ($C_{P,MAC+MVK}$) as follows: $\Delta C_{C,O_3} \geq \Delta C_{C,ISO} \geq \Delta C_{P,MAC+MVK}$. Combining the result shown in Fig. 2 ($\Delta C_{P,MAC+MVK}$: $\Delta C_{C,O_3} = 1.04$, approaching 1, within experimental error), we assumed that $\Delta C_{C,O_3} = \Delta C_{C,ISO}$, that is, the aqueous oznonolysis of isoprene would proceed at a stoichiometric O_3 : isoprene ratio of 1 : 1.

Considering the stoichiometric ratio of 1 : 1 between the isoprene and ozone, the consumed ozone (ΔC_{O_3}) can be used to represent the amount of isoprene that participated in the reaction, when isoprene is in excess, and MG is limited to a low concentration that can be considered a minor component. Consequently, the molar yields of the products can be estimated relative to the consumed isoprene. The experimental results under different pHs (pH = 7.0, 5.4, and 3.0) and temperatures (T = 4, 10, and 25 °C) are summarized in Table 1. Of note, the minor amount of MG formed in the reaction system was converted to MAC and MVK yields; in addition, the minor amounts of HMHP and HCHO generated from the aqueous ozonolysis of MAC and MVK were subtracted from the yields of HMHP and HCHO produced in the aqueous isoprene ozonolysis based on the chemical stoichiometry of the aqueous ozonolysis of MAC and MVK reported in our previous work (Chen et al., 2008) as follows:

$$\mathrm{MAC} + \mathrm{O_3} \xrightarrow{\mathrm{(aq)}} 0.99\,\mathrm{MG} + 0.70\,\mathrm{HMHP} + 0.32\,\mathrm{HCHO} \tag{1}$$

$$\mathrm{MVK} + \mathrm{O_3} \xrightarrow{\mathrm{(aq)}} 0.75\,\mathrm{MG} + 0.24\,\mathrm{PYA} + 0.69\,\mathrm{HMHP} + 0.13\,\mathrm{HCHO} + 0.18\,\mathrm{C_1}\ \text{unknown} \tag{2}$$

Where PYA represents pyrovic acid. It was clear that the yields of peroxides and carbonyl compounds were nearly independent of the investigated pH and temperature conditions for the aqueous isoprene ozonolysis. Note that the carbon yield (95 ± 4 %) approached 100 % for the investigated reaction system; this implied that most of the products were detected.

In summary, the experimental results showed that the aqueous ozonolysis of isoprene proceeded at a stoichiometric ratio of 1 : 1; furthermore, in the aqueous isoprene ozonolysis, the consumption of one mol of ozone produced 0.68 mol of peroxides (H_2O_2: 0.53; HMHP: 0.15), 1.6 mol of carbonyl compounds (HCHO: 0.57; MAC: 0.43; MVK: 0.57), and organic acids were not detected. Moreover, the results of our previous study for the aqueous ozonolysis of MAC and MVK (Chen et al., 2008) showed that MAC and MVK can also be oxidized by ozone. This yielded more peroxides and second-generation carbonyl and acid compounds. Taken together, these results indicated that, when ozone is in excess in the earth's atmosphere, one mol of isoprene can consume 2 mol of ozone, and produce 1.38 mol of peroxides, 1.67 mol of carbonyl

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compounds, and 0.14 mol of pyruvic acid (PYA). Therefore, the chemical stoichiometry of aqueous isoprene ozonolysis can be described as follows:

(i) First generation products of isoprene with O_3:

$$\begin{aligned}\text{Isoprene} + O_3 \xrightarrow{(aq)}\ & 0.54\text{HCHO} + 0.43\text{MAC} + 0.57\text{MVK}\\ & + 0.53H_2O_2 + 0.15\text{HMHP} + 0.31C_1\text{unknown}\end{aligned} \tag{3}$$

(ii) Complete reaction of isoprene and products with O_3:

$$\begin{aligned}\text{Isoprene} + 2O_3 \xrightarrow{(aq)}\ & 0.81\text{HCHO} + 0.86\text{MG} + 0.53H_2O_2\\ & + 0.85\text{HMHP} + 0.14\text{PYA} + 0.42C_1\text{unknown}\end{aligned} \tag{4}$$

Notably, a minor amount of carbon was not accounted for in these equations (Eqs. 3 and 4). Here, we tentatively attributed this to C_1 compounds; alternatively, it might be attributed to high-molecular-weight compounds. Of note, the type of oxidant was transformed and the amount of oxidant appeared to be amplified. Moreover, these products were more soluble than the parent reactants, and they were more likely to remain in the aqueous phase.

3.2 Mechanism

On the basis of the present experimental results and the available corresponding gas phase mechanism, we propose a mechanism for the aqueous ozonolysis of isoprene (Fig. 3). In this mechanism, the aqueous phase reaction of ozone with isoprene proceeds via the addition of ozone to one of isoprene's two double bonds to form a molozonide. One double bond in the isoprene molecule is attacked by ozone and the other double bond remains intact when isoprene is excess. This results in the formation of two kinds of molozonides. Next, the molozonide rapidly decomposes, breaking the C–C bond and one of the O–O bonds; this forms a stable aldehyde/ketone plus an energy-rich Criegee biradical. In the case of the 3, 4 attack on the isoprene (pathway *a*), the stable products are MAC and HCHO. The Criegee biradical becomes thermally stabilized and reacts with H_2O to form HMHP for the *a1* pathway and $CH_2=C(CH_3)C(HOO)OH$ for the *a2* pathway. The $CH_2=C(CH_3)C(HOO)OH$ formed via the *a2* pathway is unstable, and it rapidly decomposes into MAC. Alternatively, in the case of the 1, 2 attack on the isoprene (pathway *b*), the stable products are MVK and HCHO. The Criegee biradical becomes thermally stabilized and reacts with H_2O to form HMHP for the *b1* pathway and $CH_2=CHC(CH_3)(HOO)OH$ for the *b2* pathway. The $CH_2=CHC(CH_3)(HOO)OH$ formed in the *b2* pathway is unstable, and it rapidly decomposes into MVK. The expected $CH_2=C(CH_3)C(HOO)OH$ and $CH_2=CHC(CH_3)(HOO)OH$ products were not detected in the experiment, possibly due to their poor stability (Neeb et al., 1997; Sauer et al., 1999). The distribution of pathways *a1* and *a2* (or *b1* and *b2*) cannot be quantified based on the present experimental results. However, it has been suggested that pathway *a2* (or *b2*), which produces a highly substituted intermediate, is dominant compared to pathway *a1* (or *b1*) (Horie and Moortgata, 1991; Atkinson et al., 1995; Hasson et al., 2003).

This mechanism suggests that MVK was produced from the decomposition of the 1, 2 addition complex of isoprene via pathway *a*, and that MAC was produced from the decomposition of the 3, 4 addition complex of isoprene via pathway *b*. Because the combined yield of MAC and MVK approached 100 %, we suggest that the yields of MAC and MVK represent the proportions of pathways *a* and *b*, respectively; i.e., 43 % for pathway *a*, and 57 % for pathway *b*. It was particularly interesting that the observed total molar yield of peroxides was 70 %, despite the expected yield of 100 %. We also previously observed the phenomenon of “missing” peroxides in the aqueous ozonolysis of MAC and MVK (Chen et al., 2008). This gave rise to the question of whether there were any other decomposition pathways for the energy-rich Criegee radicals; e.g., H-migration to form the OH radical (Zhang et al., 2002). Any OH radical that might be produced in the reaction system would be expected to react with isoprene. Huang et al. (2011) reported a much lower combined yield of MAC (11 %) and MVK (24 %) in an aqueous isoprene reaction with OH radicals. However, we observed the combined yield of ~ 100 % for these two C4 carbonyls in the present experiment; this indicated that OH radical formation was negligible. Clearly, further studies are necessary to investigate the identity of “missing” peroxides or other species that may contain reactive oxygen.

3.3 A comparison between aqueous and gas phase reactions

3.3.1 Carbonyls and peroxides

Based on the experimental data, we could deduce the percentages of the two aqueous isoprene molozonides in the reaction; that is, the 1,2 addition complex of isoprene (PO1; pathway *b*) comprised 57 %, and the 3,4 addition complex of isoprene (PO2; pathway *a*) comprised 43 % of the reaction (Fig. 3). Of note, the ratio of PO1 to PO2 values was consistent with that reported in the gas phase ozonolysis of isoprene. For example, Aschmann and Atkinson (1994) reported an experimental PO1 : PO2 ratio of 60 : 40, and Zhang et al. (2002) provided computational evidence that this ratio was 59 : 41. Thus, we might conclude that the product distribution in the first step of ozone addition to isoprene was independent of water. This was supported by several studies that pointed out that the solvent effect was virtually identical on both reactants and products (Gligorovski and Herrmann, 2004; Monod et al., 2005).

For the gas phase ozonolysis of isoprene, many experimental studies have reported yields of MAC and MVK in the ranges of 30–45 % and 10–20 %, respectively (Kamens et al., 1982; Niki et al., 1983; Grosjean et al., 1993; Aschmann and Atkinson, 1994; Sauer et al., 1999). This indicated that not all the Criegee radicals might generate MAC or MVK. This could be explained by the fact that Criegee radicals participate in several competitive reactions, including stabilization to form carbonyls, isomerization to form dioxirane and organic acids, and H-migration to form an OH radical. However, in the present study of the aqueous isoprene–O_3 reaction, we unexpectedly reported a ~ 100 % combined yield of MAC and MVK. Sauer et al. (1999) pointed out that the stabilized Criegee radical reacted with water to generate carbonyls. Our result indicated that condensed water was highly capable of stabilizing the energy-rich Criegee biradical. In our previous studies on the aqueous ozonolysis of MAC, MVK (Chen et al., 2008), alpha-pinene, and beta-pinene (Zhang et al., 2009), we suggested that water played a dual role in the aqueous reactions; that is, the water acted as both a reactant and a sink for the energy of intermediate products. To our knowledge, there is currently no other report on the yields of MAC and MVK formed in aqueous isoprene ozonolysis.

It is worth mentioning that Paulson et al. (1992) reported different yields of MAC and MVK (67 ± 9 % and 26 ± 6 %, respectively) for the gas phase isoprene–O_3 reaction, based on a box model. Their combined yield of MAC and MVK also approached 100 %, but the distribution contrasted with that found in the present study of the aqueous phase reaction. Their model appeared to include some uncertainties. For example, the proposed high OH radical yield may have led to the high MAC and MVK yields derived from the model (Aschmann and Atkinson, 1994); in fact, the distribution of six radicals produced by the OH addition to isoprene could significantly affect the ratio between MAC and MVK.

Like the carbonyl products, we found that the peroxides (H_2O_2 and HMHP) were produced with an unexpectedly high yield (∼ 68 %) in the aqueous isoprene ozonolysis. We suggest that this high peroxide yield might also be attributed to the condensed water effect. Of note, our observed peroxide yield differed dramatically from that previously reported for the gas phase and aqueous ozonolysis of isoprene. For the gas phase isoprene ozonolysis, Becker et al. (1990) detected only 0.1 % and 0.04 % H_2O_2 under humid and dry conditions, respectively. Neeb et al. (1997) reported a HMHP yield of up to 30 % in a high humidity reaction (∼ 75 % RH). Sauer et al. (1999) reported a 14 % yield of H_2O_2 under the same humid experimental conditions, and only ∼ 1 % peroxide yield in dry conditions. The 30 % HMHP yield reported by Neeb et al. (1997) was much higher than the yield we found in the aqueous phase reaction. We speculate that the high HMHP yield may have resulted from the reaction of the Criegee radical $[CH_2OO]^*$ with water clusters $(H_2O)n$ ($n = 2, \ldots, 4$). Computational evidence has suggested that, under high humid conditions (e.g., ∼ 75 % in Neeb et al., 1997), water clusters would be derived (primarily $(H_2O)_2$), and the rate constant of the Criegee radical reaction with water clusters $(H_2O)_2$ would be ~100 times higher than that of Criegee radicals reacting with unimolecular water (Ryzhkov and Ariya, 2006). For the isoprene ozonolysis in water, Gäb et al. (1995) observed 11 % HMHP and 13 % other peroxides. Compared to the results from Gäb et al., we found a similar HMHP yield (15 %), but a much larger H_2O_2 yield (53 %). This gap may have occurred due to the different experimental conditions between the two studies. Gäb et al. carried out the reactions at an isoprene concentration that was ~10–20 times that used in our study. Moreover, some experimental details were different, like the methods of detecting peroxides.

In summary, the isoprene ozonides may encounter more water molecules in condensed water than in dry/humid air. This favored the stabilization of the Criegee radicals that formed from the decomposition of ozonides. In turn, this promoted the formation of abundant peroxide and carbonyl products. Therefore, the first-generation products, including peroxides and carbonyls, were produced with high yields in the aqueous isoprene ozonolysis system compared to the gas phase reaction.

3.3.2 Organic acids

To our knowledge, with the ozonolysis of alkenes in the presence of water, organic acid, particularly formic acid, is considered to be another important product that accompanies the carbonyl products (Horie et al., 1994; Neeb et al., 1997; Sauer et al., 1999). These products arise from the reaction of Criegee radicals and water molecules through two pathways, the P1 for carbonyl formation and the P2 for organic acid formation (Sauer et al., 1999), as follows:

$$R_1R_2COO + H_2O \rightarrow R_1R_2C(OH)OOH \rightarrow R_1R_2C(O) + H_2O_2 \quad (P1)$$

$$R_1HCOO + H_2O \rightarrow R_1HC(OH)OOH \rightarrow R_1C(O)OH + H_2O \quad (P2)$$

Here, R_1 and R_2 represent hydrogen, alkyl, or alkenyl groups. However, our result showed that no organic acid was observed in the aqueous ozonolysis of isoprene.

Although Reacts. (P1) and (P2) occur simultaneously in the aqueous reaction, similar to the gas phase reaction, the condensed water may inhibit the decomposition of $R_1HC(OH)OOH$ (α-hydroxy hydroperoxide) into water and organic acid. Instead, more H_2O_2 and aldehyde might be produced, like MAC and HCHO, via React. (P1). This explanation was supported by a theoretical investigation of the reaction between water and CH_2OO and CH_3CHOO radicals (Crehuet et al., 2001; Anglada et al., 2002). In that study, the results suggested that the water-catalyzed decomposition of α-hydroxy hydroperoxide to H_2O_2 and aldehyde had a lower activation energy than the decomposition to water and organic acid. In addition, in the ozonolysis of 2-methyl-3-buten-2-ol, Carrasco et al. (2007) observed formic acid only under the dry condition; no formic acid formed under the humid condition, but they observed an important increase in carbonyl compounds. They suggested that the P1 pathway mentioned above must be more important in the presence of water. Moreover, they suggested an alternative explanation for the production of formic acid: that it was formed from the decomposition of some primary product in the gas phase ozonolysis of terminal alkenes in the presence of water vapor (Neeb et al., 1997). However, we observed no formic acid produced from the aqueous ozonolysis of either isoprene or MAC/MVK; thus, the pathway was insignificant in this study.

4 Conclusions and implications

We aimed to simulate the aqueous ozonolysis of isoprene, which may potentially be an important surface reaction on atmospheric wet particles and plants. We tested ozonolysis under different pHs (7.0, 5.4 and 3.0) and temperatures (4, 10, and 25 °C), and we determined the chemical stoichiometry of the reaction. The products were well characterized carbonyls, peroxides, and organic acids. The molar yields of various products were independent of the investigated pHs and temperatures; these yields were: $56.7 \pm 6.7\,\%$ HCHO, $42.8 \pm 2.5\,\%$ MAC, $57.7 \pm 3.4\,\%$ MVK, $53.4 \pm 4.1\,\%$ H_2O_2, $15.1 \pm 3.1\,\%$ HMHP, and undetected organic acids ($< 1\,\%$ estimated by the detection limit). The total carbon yield was estimated to be 95 ± 4 % on the basis of the observed products and consumed isoprene. This implied that most of the products in the reaction were detected. Our results suggested that condensed water could greatly enhance the yields of first-generation carbonyls and peroxides, but it reduced the organic acid yield to an undetectable level. Finally, we proposed a reaction mechanism that fit the experiment results.

The unexpected high yield of carbonyl and peroxide compounds produced in the aqueous isoprene ozonolysis may potentially affect isoprene SOA formation and oxidant transformation in the atmosphere. The carbonyls, MAC and MVK, are considered to be an important precursor of aqueous SOA (Chen et al., 2008; El Haddad et al., 2009; Zhang et al., 2010; Liu et al., 2012). Of note, HCHO was detected in high yield as a first-generation product. Apart from this direct product, the further oxidation of MAC and MVK and the decomposition of HMHP could also produce HCHO (e.g., Chen et al., 2008). In aqueous solution, HCHO could combine with bisulfite to form stable hydroxymethanesulfonic acid, and this would prevent the oxidation of S(IV) into S(VI). This mechanism could conserve the oxidants, particularly H_2O_2, which can produce OH radicals in photolysis and in the Fenton reaction. This could potentially result in wet particles with high oxidative capacity.

Furthermore, both H_2O_2 and HMHP act as important aqueous oxidants in addition to serving as a source of hydroxyl (OH) and alkoxyl (RO) radicals. Herrmann et al. (2005) pointed out that, except for the uptake of OH radicals into the aqueous phase (which accounts for 20.6 %), aqueous OH sources are highly related to H_2O_2 reactions (which account for 58.8 %), including the Fenton reaction with Fe^{2+} and its photolysis. Here, we suggested that the aqueous ozonolysis of isoprene could significantly contribute to the presence of aqueous H_2O_2. Recently, Hullar and Anastasio (2011) found that the OH-initiated oxidation of organic compounds in aqueous solutions could, in turn, produce H_2O_2. Therefore, the aqueous isoprene reaction with ozone appears to initiate a cycle of H_2O_2-OH radical that potentially enhances the formation of SOA. In addition, peroxide can oxidize S(IV) into S(IV); this increases the aqueous phase acidity, which

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supports the formation of SOA from isoprene oxidation (Surratt et al., 2007). However, the relative importance of these two processes, i.e., the oxidation of S(IV) by H_2O_2 and the stabilization of S(IV) by HCHO, requires further evaluation.

In summary, aqueous isoprene ozonolysis consumes ozone, but generates highly-soluble peroxides, which results in a transformation of oxidants in both kind and phase, and may even amplify the oxidants. Assuming this result might be applicable to all unsaturated VOCs, it can be speculated that the aqueous ozonolysis of unsaturated VOCs would represent a significant source of aqueous phase oxidants, and furthermore, VOCs may potentially contribute significantly to aqueous SOA in the atmosphere. This mechanism might give an implication for partly explaining the "missing" OH radical source over the tropical rain forest that was revealed by Lelieveld et al. (2008).

Globally, plants represent the source of most VOCs in the atmosphere, but their emission depends on many physical and chemical factors. Biogenic unsaturated VOCs, like isoprene and terpenes, must undergo an aqueous ozonolysis on the surface of plants, within a thin film of moisture, and then produce carbonyls and peroxides, and furthermore, SOA. Clearly, the extent of this reaction would differ in clean and polluted regions, because ozonolysis depends on the ambient concentration of O_3. This reaction may affect the O_3 and SO_2 depositions onto plants. In the future, the chemistry that occurs at the vegetation–atmosphere interface should be considered for a better understanding of VOC emission and SOA formation.

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Table 1. Molar yields (%) of products in the aqueous ozonolysis of isoprene under different conditions.

t(°)	pH	HCHO	MAC	MVK	H_2O_2	HMHP
4	3.0	58.0 ± 2.9	42.9 ± 2.5	57.9 ± 2.7	49.6 ± 4.1	17.3 ± 2.0
	5.4	59.2 ± 1.2	44.2 ± 2.3	59.1 ± 3.2	51.9 ± 1.7	18.2 ± 2.3
	7.0	59.4 ± 3.0	44.7 ± 0.6	58.4 ± 1.8	54.9 ± 3.4	16.5 ± 2.1
10	3.0	54.9 ± 1.5	41.6 ± 0.7	57.7 ± 2.8	54.3 ± 2.5	14.2 ± 2.0
	5.4	56.5 ± 3.4	42.3 ± 0.8	55.9 ± 2.6	54.3 ± 2.0	14.3 ± 1.4
	7.0	59.2 ± 2.6	44.4 ± 1.7	57.7 ± 2.7	56.6 ± 2.7	13.3 ± 1.8
25	3.0	53.6 ± 2.0	40.8 ± 1.5	57.5 ± 2.9	54.5 ± 3.9	14.2 ± 2.2
	5.4	54.8 ± 3.7	42.0 ± 2.3	57.9 ± 3.4	52.6 ± 2.2	14.7 ± 1.2
	7.0	54.8 ± 1.8	42.1 ± 1.6	57.2 ± 1.8	52.0 ± 1.6	13.2 ± 0.5
Mean		56.7 ± 3.7	42.8 ± 2.5	57.7 ± 3.4	53.4 ± 4.1	15.1 ± 3.1
Total C				94.8 ± 4.1		

Note: Total C = $(\text{Yield}_{\text{HCHO}} + \text{Yield}_{\text{MAC}} \times 4 + \text{Yield}_{\text{MVK}} \times 4 + \text{Yield}_{\text{HMHP}})/5$.

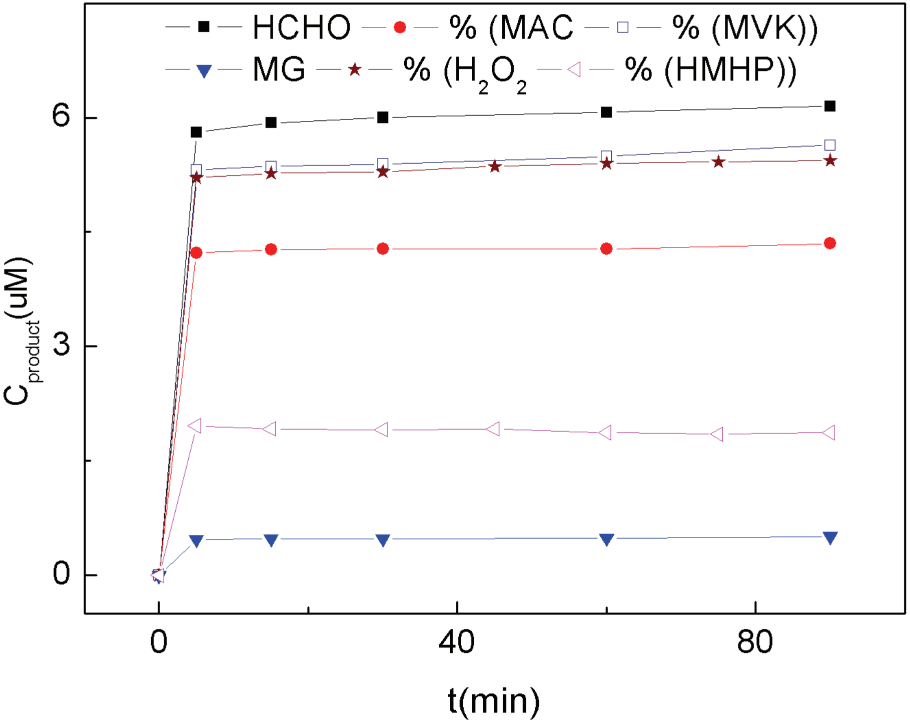

Fig. 1. The temporal profiles of the products in the aqueous isoprene ozonolysis. $T = 4\,^{\circ}\mathrm{C}$, pH = 7.0, initial concentration ratio of isoprene versus O_3, C_{ISO}: $C_{O_3} = 2:1$.

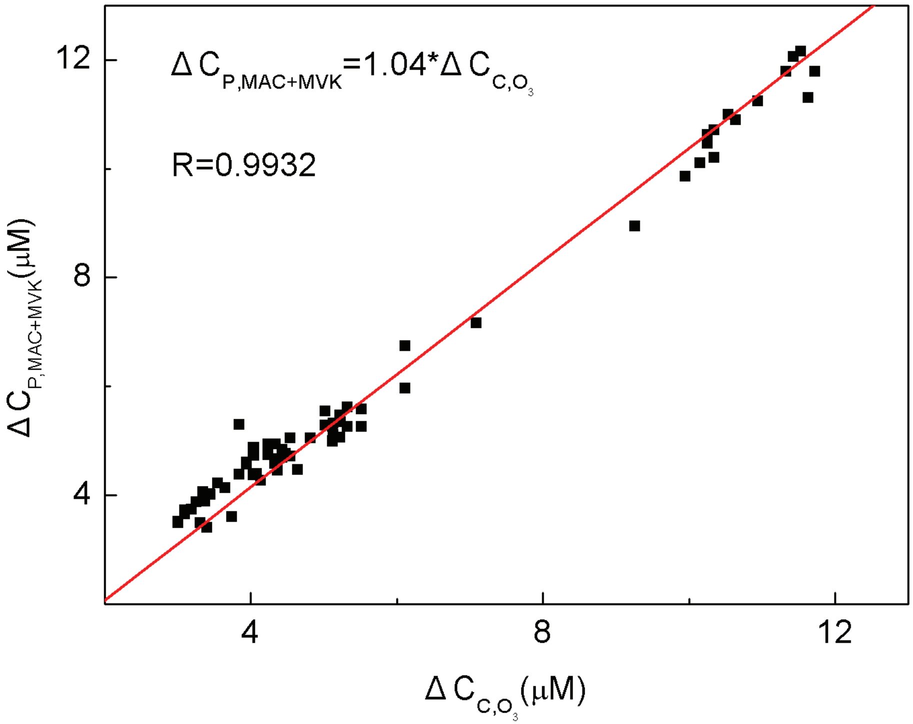

Fig. 2. The linear regression of the proportion of the formed product concentration ($C_{P,MAC+MVK}$) versus the consumed ozone concentartion ($\Delta C_{C,O_3}$). $n = 72$.

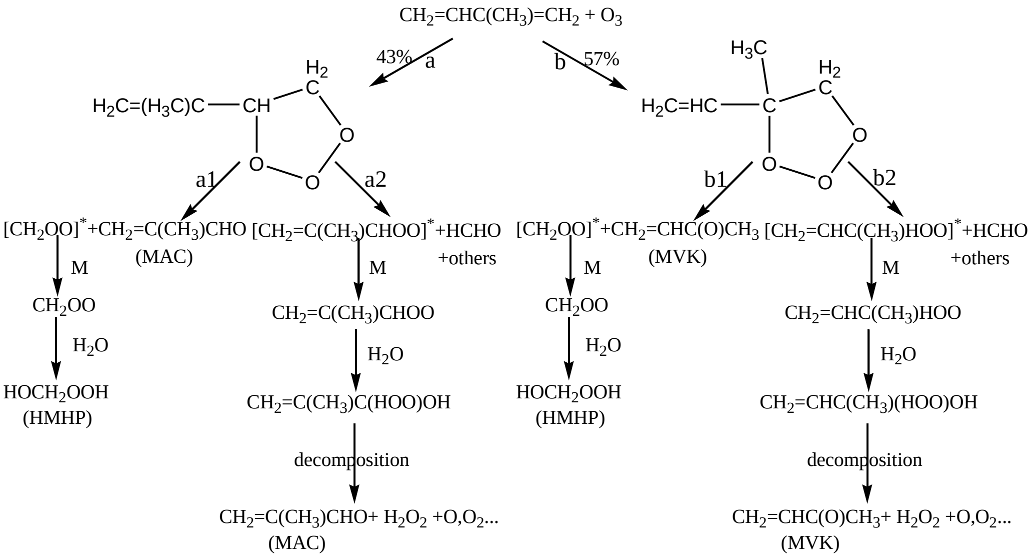

Fig. 3. Mechanism of the aqueous ozonolysis of isoprene.

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