



Understanding the aqueous phase ozonolysis of isoprene: distinct product distribution and mechanism from the gas phase reaction

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Received: 16 February 2012 – Published in Atmos. Chem. Phys. Discuss.: 1 March 2012

Revised: 18 July 2012 – Accepted: 30 July 2012 – Published: 7 August 2012

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, those were (1) carbonyls: $56.7 \pm 3.7\%$ formaldehyde, $42.8 \pm 2.5\%$ methacrolein (MAC), and $57.7 \pm 3.4\%$ methyl vinyl ketone (MVK); (2) peroxides: $53.4 \pm 4.1\%$ hydrogen peroxide (H_2O_2) and $15.1 \pm 3.1\%$ hydroxymethyl 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 $94.8 \pm 4.1\%$. This implied that most of the products in the reaction system were detected. 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 suggest that these unexpected high yields of carbonyls and peroxides are related to the greater capability of condensed water, compared to water vapor, to sta-

bilize 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.

1 Introduction

Carbonyl and peroxide compounds are important trace components in the atmosphere. In recent years, these two compounds are paid more and more attention, because they form components or precursors of secondary organic aerosol (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, 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 it seems that only the reactions occurring on the surface are important for psVOCs (Chen et al., 2008; Huang et al., 2011). Moreover, when biogenic VOCs, like isoprene and terpenes, are emitted from plant cells into the air through the wet surfaces of leaves, they first encounter 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 aim 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; Liu et al., 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 suggests 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 imply that the aqueous reaction of psVOCs merits a separate study that could more precisely evaluate the contributions of gas and aqueous phases to product yields.

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

2 Experimental

A stock solution was prepared with isoprene (Fluka, 99.5 %) diluted in acetonitrile to a final concentration of 2 mM. Acetonitrile was used to assist isoprene to dissolve and disperse in water. 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 O₃ solution with 5 ml isoprene stock solution in a 515-ml quartz aqueous reactor in darkness at different initial pHs (7.0, 5.4, and 3.0), and temperatures (4 °C, 10 °C, and 25 °C). H₂SO₄ was used to adjust the pHs. In the reactor, the concentration of isoprene was $\sim 20 \mu\text{M}$ and the concentration of ozone was 2 to 10 μM . 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 O₂ ($\geq 99.999\%$, 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). Before mixing with isoprene solution, the aqueous ozone concentration was determined by

indigo disulphonate spectrophotometry. 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-dinitrophenylhydrazine (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 based on their Henry's law constants (Sander, 1999). 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.

There is 1 % acetonitrile in the reaction system. We also did experiments in absence of acetonitrile to determine if acetonitrile could affect the products formation and the kinetics. 1- μL pure isoprene (equivalent to 20 μM isoprene in 500 ml solution) was injected directly into the 500-ml ozone solution in the reactor by a syringe and a sealed Teflon stopple, and immediately the reactor (a quartz bottle) was shaken upside down for 2 min. The subsequent experimental steps were the same as those in the reaction system in the presence of acetonitrile. The experiments were performed at one pH (pH=7) and two temperatures (4 °C and 10 °C).

The rate constants for the aqueous ozonolysis of isoprene, methacrolein (MAC) and methyl vinyl ketone (MVK) ($k_{\text{ISO}} = 4.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$; $k_{\text{MAC}} = 2.4 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$; and $k_{\text{MVK}} = 4.4 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, 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 $\sim 20 \mu\text{M}$ 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.

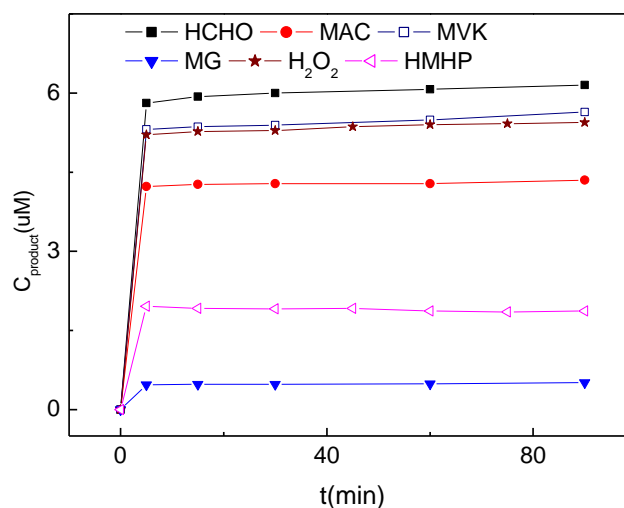


Fig. 1. The temporal profiles of the products in the aqueous isoprene ozonolysis. $T = 4 \text{ }^\circ\text{C}$, $\text{pH} = 7.0$, initial concentration ratio of isoprene versus O_3 , $C_{\text{ISO}}:C_{\text{O}_3} = 2:1$.

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 $\sim 0.05 \mu\text{M}$. We have done a series of experiments with an initial concentration ratio of $C_{\text{ISO}}:C_{\text{O}_3}$ from 2:1 to 20:1. As an example, Fig. 1 shows the temporal profiles of the products at $T = 4 \text{ }^\circ\text{C}$, $\text{pH} = 7.0$, and an initial concentration ratio of $C_{\text{ISO}}:C_{\text{O}_3} = 2:1$. It was clear that, once the isoprene and ozone solutions were mixed, a number of products formed rapidly, and then reached a plateau. A minor amount of methylglyoxal (MG) was observed when the concentration of isoprene was below or close to the concentration of ozone; in contrast, no MG was observed when the isoprene was in large excess to ozone ($C_{\text{ISO}}:C_{\text{O}_3} > 10:1$), this indicated that MG was not a first generation product. 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.

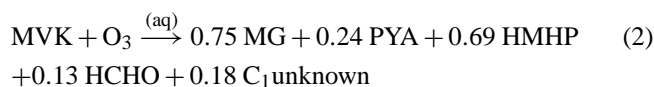
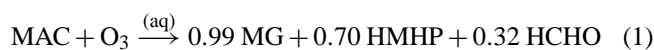
Next, we derived the stoichiometric ratio between isoprene and ozone in an aqueous reaction. We need to know the amount of consumed isoprene and the amount of ozone consumed by isoprene. We knew that, in the reaction system, ozone would be consumed by isoprene and by its first-generation products, those are MAC and MVK. The equations of MAC and MVK react with ozone were already

Table 1. Molar yields (% mean $\pm 2\sigma$) of products in the aqueous ozonolysis of isoprene under different conditions.

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

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

known as follows (Chen et al., 2008):



Where PYA represents pyruvic acid. The uncertainties of the product yields can be found in our previous work (Chen et al., 2008). The aqueous ozonolysis of MAC and MVK could produce MG with yields of 99 % and 75 %, as shown in Eq. (1) and (2) respectively. Combining these two yields and the observed MG, we can estimate the amount of O_3 consumed by MAC and MVK. In the cases with a minor amount of MG formation in the aqueous ozonolysis of isoprene, if we want to know the amount of ozone consumed by isoprene, we need to eliminate the ozone consumed by MAC and MVK. Given the rate constants of MAC– O_3 and MVK– O_3 in the aqueous phase mentioned previously (Pedersen and Sehested, 2001), one mol 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. So we can get the amount of ozone consumed by isoprene by subtracting the ozone consumed by MAC and MVK from the total consumed ozone. In the cases with undetectable MG, we thought ozone was fully consumed by isoprene. 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 $^{\circ}\text{C}$, 10 $^{\circ}\text{C}$, and 25 $^{\circ}\text{C}$). X-axis represented the amount of consumed O_3 ($\Delta C_{\text{C},\text{O}_3}$) by isoprene in the reaction. Y-axis represented the determined total amount of produced

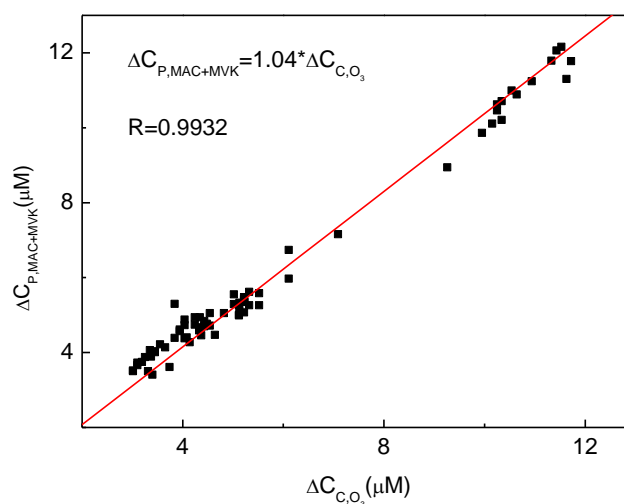


Fig. 2. The linear regression of the proportion of the formed product concentration ($C_{\text{P,MAC+MVK}}$) versus the consumed ozone concentration ($\Delta C_{\text{C},\text{O}_3}$). $n=72$.

MAC+MVK ($C_{\text{P,MAC+MVK}}$) in the reaction. On the basis of Eqs. (1), (2) and the calculation method mentioned above, the minor amount of MG formed in the reaction system was converted to MAC and MVK. 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 ($\Delta C_{\text{C},\text{O}_3}$) or isoprene ($\Delta C_{\text{C},\text{ISO}}$) was related to the produced concentration of MAC + MVK ($C_{\text{P,MAC+MVK}}$) as follows: $\Delta C_{\text{C},\text{O}_3} \geq \Delta C_{\text{C},\text{ISO}} \geq \Delta C_{\text{P,MAC+MVK}}$. Combining the result shown in Fig. 2 ($\Delta C_{\text{P,MAC+MVK}}:\Delta C_{\text{C},\text{O}_3} = 1.04$, approaching 1, within experimental error, that is 2 standard deviation, 2σ), we assumed that $\Delta C_{\text{C},\text{O}_3} = \Delta C_{\text{C},\text{ISO}}$, that is, the aqueous ozonolysis of isoprene would proceed at a stoichiometric O_3 : isoprene ratio of 1:1.

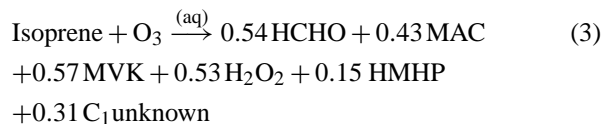
Considering the stoichiometric ratio of 1 : 1 between isoprene and ozone, the ozone consumed by isoprene ($\Delta C_{C,O_3}$) can be used to represent the amount of isoprene that participated in the reaction, when isoprene is in excess, and MG is limited to a low concentration that can be considered 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 ($T = 4^\circ\text{C}$, 10°C , and 25°C) are summarized in Table 1. It was clear that the molar yields of peroxides and carbonyl compounds were nearly independent of the investigated pH and temperature conditions for the aqueous isoprene ozonolysis. The carbon yield ($94.8 \pm 4.1\%$) approached 100% for the investigated reaction system; this implied that most of the products were detected. We calculated the mean and standard deviation of the yields based on the 8 repeated experiments at each pH and temperature.

For the aqueous ozonolysis of isoprene in the absence of acetonitrile, the experimental results give the molar yields as follows: HCHO ($60.1 \pm 2.0\%$ at 4°C ; $56.2 \pm 3.2\%$ at 10°C), MAC ($48.1 \pm 1.5\%$ at 4°C ; $50.8 \pm 4.3\%$ at 10°C), MVK ($58.1 \pm 1.7\%$ at 4°C ; $60.2 \pm 1.0\%$ at 10°C), HMHP ($18.2 \pm 2.7\%$ at 4°C ; $16.8 \pm 2.8\%$ at 10°C), and hydrogen peroxide ($59.1 \pm 2.0\%$ at 4°C ; $60.0 \pm 2.7\%$ at 10°C). No organic acids were observed. These yields are near to those obtained in the corresponding reactions performed in the presence of acetonitrile. The relative deviation of the corresponding yields obtained from these two types of experiments is $\leq 10\%$. In addition, Gab et al. (1995) had found that acetonitrile would not affect the product distribution in the aqueous ozonolysis of alkenes, only slowed the ozonolysis rate. The acetonitrile concentration presented in their work was higher than that in our work. In summary, we suggest that 1% acetonitrile used in the present study has little effect on the products formation. Because using acetonitrile stock solution of isoprene is more constant, reliable and easier to implement than using a syringe in each experiment, all the experiments discussed in the present study were performed using acetonitrile stock solution of isoprene.

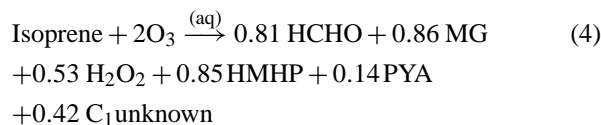
In summary, the experimental results showed that the aqueous ozonolysis of isoprene proceeded at a stoichiometric ratio of 1:1; furthermore, in the aqueous isoprene ozonolysis, the consumption of one mol of ozone produced 0.68 mol of peroxides (H_2O_2 : 0.53; HMHP: 0.15), 1.6 mol of carbonyl compounds (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, in the earth's atmosphere where ozone is in excess compared to isoprene, one mol of isoprene can consume 2 mol of ozone, and produce 1.38 mol of peroxides, 1.67 mol of carbonyl 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 :



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



The uncertainties of the product yields shown in Eq. (3) can be found in Table 1 in the present study. A minor amount of carbon was not accounted for in these equations (Eqs. (3) and (4)). The chemical identity of the missing carbon is not known. Here, we tentatively assign a stoichiometry factor (0.42) which would be the appropriate molar factor if the unknown compounds were in fact C_1 compounds. The type of oxidant was transformed from ozone to peroxides. Moreover, these oxidant products (peroxides) were more soluble than the parents (O_3 and isoprene), and they were more likely to stay in the aqueous phase.

3.2 Mechanism

On the basis of the present experimental results and the available corresponding gas phase mechanism shown in Fig. 3a (Aschmann and Atkinson, 1994; Zhang et al., 2002; Aplincourt and Anglada, 2003a and b; and references therein), we propose a mechanism for the aqueous ozonolysis of isoprene (Fig. 3b). 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 $\text{CH}_2 = \text{C}(\text{CH}_3)\text{CH}(\text{OOH})\text{OH}$ for the *a2* pathway. The $\text{CH}_2 = \text{C}(\text{CH}_3)\text{CH}(\text{OOH})\text{OH}$ 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 $\text{CH}_2 = \text{CHC}(\text{CH}_3)(\text{OOH})\text{OH}$

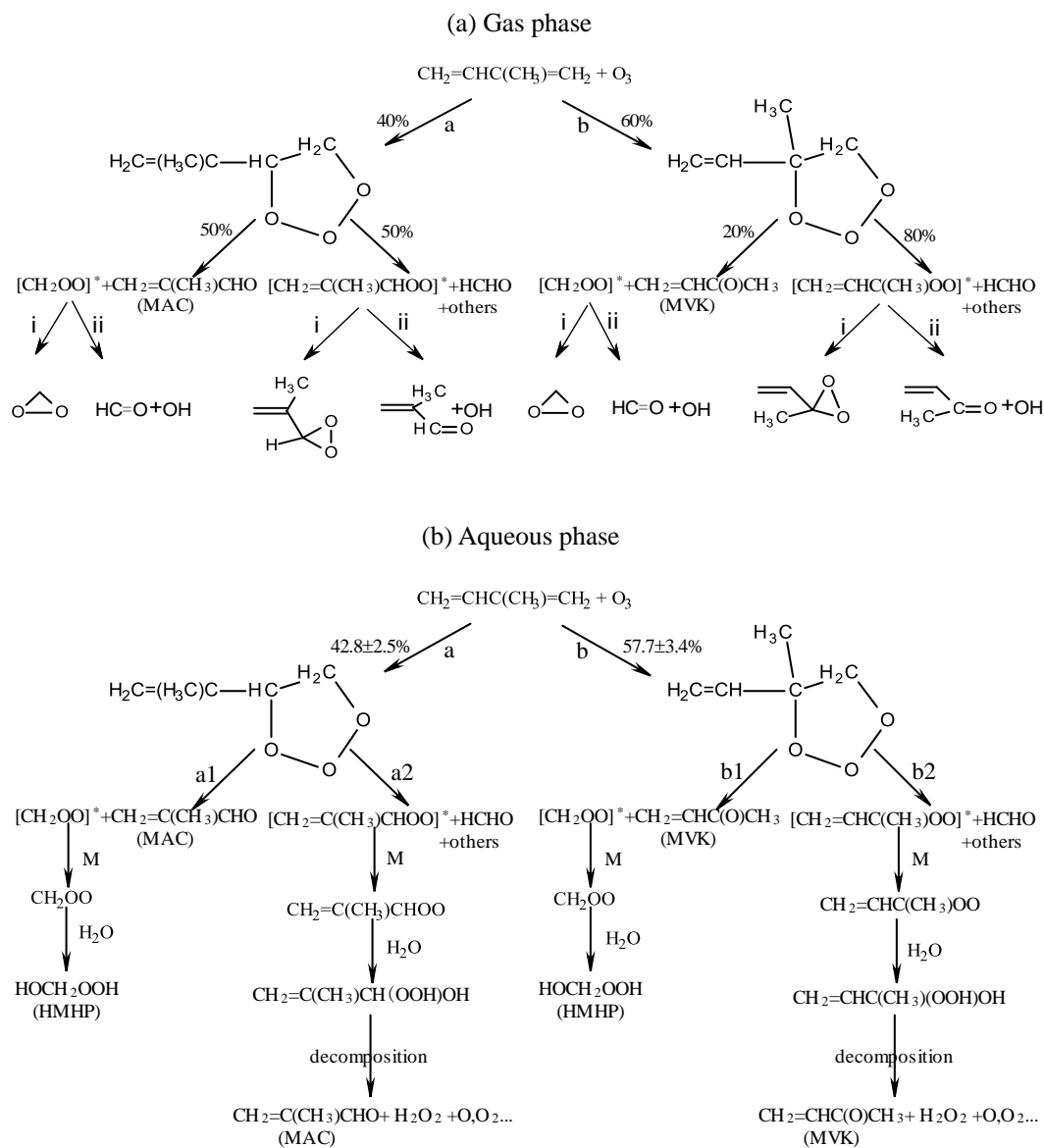


Fig. 3. Mechanisms of ozonolysis of isoprene in (a) the gas phase and (b) aqueous phase. In (a), pathway i: isomerization; pathway ii: decomposition, stabilization and bimolecular reaction.

for the *b2* pathway. The $\text{CH}_2 = \text{CHC}(\text{CH}_3)(\text{OOH})\text{OH}$ formed in the *b2* pathway is unstable, and it rapidly decomposes into MVK. The expected $\text{CH}_2 = \text{C}(\text{CH}_3)\text{CH}(\text{OOH})\text{OH}$ and $\text{CH}_2 = \text{CHC}(\text{CH}_3)(\text{OOH})\text{OH}$ 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, in the gas phase, 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 Moortgat, 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 *b*, and that MAC was produced from the decomposition of the 3, 4 addition complex of isoprene via pathway *a*. Because the combined yield of MAC and MVK approached 100%, we suggest that the yields of MAC and MVK, which were determined in this study, represent the proportions of pathways *a* and *b*, respectively; i.e., $42.8 \pm 2.5\%$ for pathway *a*, and $57.7 \pm 3.4\%$ for pathway *b*. In addition, every sub-pathway would produce either H_2O_2 or HMHP. H_2O_2 was produced by pathways *a2* + *b2*, and HMHP was produced by pathways *a1* + *b1*. Thus the total amount of peroxides ($\text{H}_2\text{O}_2 + \text{HMHP}$) represents all the

Table 2. Molar yields (%) of MAC, MVK and peroxides in the ozonolysis of isoprene under different conditions.

Y _{MAC}	Y _{MVK}	Y _{HMHP}	Y _{H₂O₂}	Y _{other ROOH}	Gaseous	Aqueous	reference
41	18				(E)		Kamens et al. (1982)
33	13				(E)		Niki et al. (1983)
67 ± 9	26 ± 6				dry (M)		Paulson et al. (1992)
44 ± 2	17 ± 1				dry (E)		Grosjean et al. (1993)
38.7 ± 3.0	15.9 ± 1.3				dry (E)		Aschmann and Atkinson (1994)
21	12				dry (T)		Zhang et al. (2002)
			0.036		dry (E)		Becker et al. (1990)
		<1			dry (E)		Neeb et al. (1997)
		0.5 ± 0.1	0.7 ± 0.3	5.0 ± 0.1	dry (E)		Gäb et al. (1995)
34.7 ± 0.6	14.3 ± 0.6		1		dry (E)		Sauer et al. (1999)
39.7 ± 1.2	19.7 ± 0.6		14		75 % RH at 295 K (E)		Sauer et al. (1999)
			0.1		63 % RH at 297 K (E)		Becker et al. (1990)
		30			75 % RH at 293 K (E)		Neeb et al. (1997)
		11.1 ± 0.9	~0.1	13.1 ± 0.8		√(E)	Gäb et al. (1995)
42.8 ± 2.5	57.7 ± 3.4	15.1 ± 3.1	53.4 ± 4.1			√(E)	This work

Note: Dry indicates that the experiments were done under dry conditions (RH < 5 %); √ indicates that the experiments were done in water; M, model study; T, theoretical study; E, experimental study.

pathways, and thus, the yield of H₂O₂ + HMHP was supposed to be 100 %. However, the observed total molar yield of peroxides was 70 %. 30 % molar yield of peroxides was missing. We also previously observed the phenomenon of “missing” peroxides in the aqueous ozonolysis of MAC and MVK (Chen et al., 2008). This gives rise to the question of whether there are 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. We have known that the combined molar yield (CY) of MAC and MVK was 35 % in aqueous isoprene–OH reaction and ~100 % in the aqueous ozonolysis of isoprene (the present study) respectively. The consumed amount of isoprene by OH radical should be estimated. If assuming that 5 % of isoprene was consumed by OH radical and 95 % by O₃, we would expect a CY with 96.8 % (obtained by 5 % × 35 % + 95 % × 100 %), which was less than the observed 100 % molar yield in the experiment. That is, the experimental result indicated that the isoprene–OH reaction was minor (<5 %) in our experiments. Clearly, further studies are necessary to investigate the identity of “missing” peroxides or other species that may contain reactive oxygen.

In the present work, we obtained the yield of each product (peroxides and carbonyls), resulting in a total carbon yield of approaching 100 % in the aqueous ozonolysis of isoprene. As a comparison, the total carbon yield of peroxides and carbonyls in the gas phase reaction is much less than 100 %. We conclude that there is a large difference of the common product distribution between the gas phase and aqueous phase, implying that the mechanism must be different. From Fig. 3,

it can be seen that the main difference between aqueous and gas phase mechanisms arises from the subsequent reaction of the energy-rich Criegee biradical (marked with *). In the aqueous phase, the energy-rich Criegee biradicals are stabilized and then reacts via bimolecular reactions with H₂O, while in the gas phase they can undergo decomposition, isomerization, stabilization and bimolecular reactions. Consequently, the products have fewer species and higher yields in the aqueous phase than in the gas phase. Our experimental results suggest that the condensed water is highly capable of stabilizing the energy-rich Criegee biradical.

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 57.7 ± 3.4 %, and the 3, 4 addition complex of isoprene (PO2; pathway *a*) comprised 42.8 ± 2.5 % of the reaction (Fig. 3b.). 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 on both reactants and products was energetically identical (Gligorovski and Herrmann, 2004; Monod et al., 2005).

Table 2 gives a comparison of the molar yields of major products in the gas phase and aqueous phase ozonolysis of

isoprene. In gas phase, many experimental studies have reported yields of MAC and MVK in the ranges of 30–45 % and 10–20 % respectively, whatever the relative humidity between 0 % and 75 %. This indicates that not all the corresponding 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 (MAC and MVK), isomerization to form dioxirane and organic acids, and H-migration to form an OH radical (Fig. 3a). It is worth mentioning that Paulson et al. (1992) reported different yields of MAC and MVK ($67 \pm 9\%$ and $26 \pm 6\%$, respectively) for the gas phase isoprene- O_3 reaction, based on a box model. Their combined yield of MAC and MVK approached 100 %. Their model appeared to include some uncertainties. For example, the proposed OH radical yield (68 %), which is higher than the value (25 %–50 %) obtained in other experimental studies (Atkinson et al., 1992; Donahue et al., 1998; International Union of Pure and Applied Chemistry 2005 recommendation; Malkin et al., 2010), may have led to the high MAC and MVK yields derived from the model (Aschmann and Atkinson, 1994). In the present study of the aqueous isoprene- O_3 reaction, we unexpectedly reported a $\sim 100\%$ combined yield of MAC and MVK. To our knowledge, there is currently no other report on the yields of MAC and MVK formed in aqueous isoprene ozonolysis. Our results indicate that condensed water is highly capable of stabilizing the energy-rich Criegee biradical, and reacts with the resulting radical to generate stable carbonyls. 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 suggest that water plays a dual role in the aqueous reactions; that is, the water acts as both a reactant and a sink for the energy of intermediate radicals.

Like the carbonyl products, we found that the peroxides (H_2O_2 and HMHP) were produced with high yields (68 %) in the aqueous isoprene ozonolysis. Our observed peroxide yield differed from that previously reported for the gas phase and aqueous ozonolysis of isoprene (Table 2). Under dry conditions, reported HMHP yield was less than 1 % in the gas phase ozonolysis of isoprene (Gäb et al., 1995; Neeb et al., 1997), while under high humid conditions ($\sim 75\%$ RH), a HMHP yield of up to 30 % was reported by Neeb et al. (1997). Then in the aqueous ozonolysis of isoprene, Gäb et al. (1995) observed $11 \pm 0.9\%$ HMHP, and here, we observed a $15.1 \pm 3.1\%$ yield of HMHP. We speculate that the high HMHP yield under humid or aqueous conditions may have resulted from the reaction of the Criegee radical $[CH_2OO]^*$ with water clusters $(H_2O)_n$ ($n = 2, \dots, 4$). Computational evidence has suggested that, water clusters can be formed (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 with unimolecule water (Ryzhkov and Ariya, 2006). Under dry conditions, Becker et al. (1990) reported a 0.036 % yield of

H_2O_2 and Sauer et al. (1999) reported a 1 % yield of H_2O_2 . Under humid conditions, Becker et al. (1990) reported a 0.1 % yield of H_2O_2 and Sauer et al. (1999) reported a 14 % yield of H_2O_2 . In the aqueous phase, Gäb et al. (1995) reported less than 0.1 % H_2O_2 but $13.1 \pm 0.8\%$ 1-hydroxyalkyl hydroperoxides, and we observed $53.4 \pm 4.1\%$ H_2O_2 . Despite the huge difference between the results of these experiments, we found that the yield of H_2O_2 increased with the water content increased. The increased H_2O_2 may be due to water assisted decomposition of the α -hydroxy hydroperoxides, $CH_2=C(CH_3)CH(OOH)OH$ and $CH_2=CHC(CH_3)(OOH)OH$, which we cannot determine by now; the products would be H_2O_2 plus MAC and MVK (Aplincourt and Anglada, 2003b).

In summary, the isoprene ozonides may encounter more water molecules in condensed water than in dry/humid air. This favors the stabilization of the Criegee radicals that formed from the decomposition of ozonides. In turn, this promotes 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 acids, particularly formic acid, are 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 Reaction (R1) for carbonyl formation and the Reaction (R2) for organic acid formation (Gäb et al., 1985; Neeb et al., 1997; Dowideit and Sonntag, 1998; Sauer et al., 1999; Hasson et al., 2003; Jonsson et al., 2006), as follows:



Here, R_1 and R_2 represent hydrogen, alkyl, or alkenyl groups. The second part of Reaction (R1) was an equilibrium. The hydroxyhydroperoxide was in equilibrium with the corresponding carbonyl and hydrogen peroxide (Dowideit and Sonntag, 1998). On the opposite, the second part of Reaction (R2) is not an equilibrium, and the unstable hydroperoxides decompose into the corresponding acids. However, our result showed that no organic acid was observed in the aqueous ozonolysis of isoprene. Although Reactions (R1) and (R2) may 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 via Reaction (R2). Instead, more H_2O_2 and carbonyls might be produced, like MAC and HCHO, via Reaction (R1). This

explanation is supported by a theoretical investigation of the reaction between water and CH_2OO and CH_3CHOO biradicals (Crehuet et al., 2001; Anglada et al., 2002). In that study, the results suggest that the pathway of water-catalyzed decomposition of α -hydroxy hydroperoxide to H_2O_2 and aldehyde is the one with a lower activation barrier compared to the pathway of decomposition to water and organic acid. In addition, in the gas phase ozonolysis of 2-methyl-3-buten-2-ol, Carrasco et al. (2007) observed formic acid only under the dry condition; no formic acid was formed under the humid condition, but they observed an important increase in carbonyl compounds. They suggested that the Reaction (R1) 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. However, we observed no formic acid produced from the aqueous ozonolysis of either isoprene or MAC/MVK; thus, Reaction (R2) was insignificant in this study.

4 Conclusions and implications

We aim to simulate the atmospheric aqueous ozonolysis of isoprene, which may potentially be an important surface reaction on atmospheric wet particles and plants. We tested ozonolysis under different relevant pHs (7.0, 5.4 and 3.0) and temperatures (4 °C, 10 °C, and 25 °C), and we determined the chemical stoichiometry of the reaction. The detected products include carbonyls, peroxides, and organic acids. The molar yields of various products were independent of the investigated pHs and temperatures; these yields were: $56.7 \pm 3.7\%$ 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 instrumental detection limit). The total carbon yield was estimated to be $94.8 \pm 4.1\%$ on the basis of the observed products and consumed isoprene. This implied that most of the products in the reaction were detected. Our results suggest that compared to the corresponding gas phase reaction, 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.

Both H_2O_2 and HMHP act as important aqueous oxidants in the atmospheric aqueous phase in addition to serving as a source of hydroxyl (OH) and alkoxy (RO) radicals. In their detailed aqueous phase organic chemistry model CAPRAM 3 for the remote scenario, Herrmann et al. (2005) pointed out that, except for the uptake of OH radicals into the aqueous phase (which accounts for 21.6% of the total aqueous OH radical), aqueous OH sources are highly related to the reactions of H_2O_2 (which account for 58.5%), such as H_2O_2

photolytic decomposition and H_2O_2 Fenton reaction with Fe^{2+} . Here, we suggest 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, which potentially enhances the formation of aqueous SOA considering that H_2O_2 and OH radicals are important aqueous oxidants for organic compounds (Carlton et al., 2006; Zhang et al., 2010; Ervens et al., 2011; Huang et al., 2011; Liu et al., 2012; Tan et al., 2012). In addition, peroxide can oxidize S(IV) into S(VI); this increases the aqueous phase acidity, and thus in favor of SOA formation from isoprene oxidation (Surratt et al., 2007).

In summary, aqueous isoprene ozonolysis consumes ozone, but generates highly-soluble peroxides, which results in a transformation of oxidants in both gas and aqueous phases, 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 to aqueous SOA via both interface and bulk reactions with the aqueous oxidants in the atmosphere.

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 (Hewitt et al., 1990; Altimir et al., 2006). 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.

Acknowledgements. The authors gratefully thank the National Natural Science Foundation of China (grants 21077003 and 40875072) and the State Key Laboratory of Environmental Simulation and Pollution Control (special fund 10Z03ESPCP) for financial support.

Edited by: R. McLaren

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