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# Aqueous-phase ozonolysis of methacrolein and methyl vinyl ketone: a potentially important source of atmospheric aqueous oxidants

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## Abstract

Recent studies indicate that isoprene could contribute a considerable amount of aerosol through aqueous-phase acid-catalyzed oxidation with hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), although the source of  $\text{H}_2\text{O}_2$  is unclear. The present study revealed a potentially important route to the formation of aqueous oxidants, including  $\text{H}_2\text{O}_2$ , from the aqueous-phase ozonolysis of methacrolein (MAC) and methyl vinyl ketone (MVK). Laboratory simulation was used to perform the atmospheric aqueous-phase ozonolysis at different pHs and temperatures. Unexpectedly high molar yields of the products, including hydroxymethyl hydroperoxide (HMHP), formaldehyde (HCHO) and methylglyoxyl (MG), of both of these reaction systems have been seen. Moreover, these yields are almost independent of pH and temperature and are as follows: (i) for MAC- $\text{O}_3$ ,  $70.3 \pm 6.3\%$  HMHP,  $32.3 \pm 5.8\%$  HCHO and  $98.6 \pm 5.4\%$  MG; and (ii) for MVK- $\text{O}_3$ ,  $68.9 \pm 9.7\%$  HMHP,  $13.3 \pm 5.8\%$  HCHO and  $75.4 \pm 7.9\%$  MG. A yield of  $24.2 \pm 3.6\%$  pyruvic acid has been detected for MVK- $\text{O}_3$ . HMHP is unstable in the aqueous phase and can transform into  $\text{H}_2\text{O}_2$  and HCHO with a yield of 100%. We suggest that the aqueous-phase ozonolysis of MAC and MVK can contribute a considerable amount of oxidants in a direct and indirect mode to the aqueous phase and that these compounds might be the main source of aqueous-phase oxidants. The formation of oxidants in the aqueous-phase ozonolysis of MAC and MVK effectively confirms the formation of aerosols from the aqueous-phase acid-catalyzed reaction of  $\text{H}_2\text{O}_2$  with isoprene, even if there are no other sources of oxidants.

## 1 Introduction

An increasing amount of attention has been paid to organic aerosols because of their significant climate effect and because they have an important role in key atmospheric processes (Gelencsér and Varga, 2005) (e.g. acting as cloud condensation nuclei, Navakov and Penner, 1993, and scattering and absorbing solar radiation, Andreae

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and Crutzen, 1997). Photooxidation products of monoterpenes, which are important biogenic volatile organic compounds (VOCs) emitted mainly by terrestrial vegetation, contribute to the secondary organic aerosol (SOA) budget (Kavouras et al., 1998; Kavouras and Stephanou, 2002). Recently, the potentially increasing importance of isoprene regarding SOAs has been realized (Wiedinmyer et al., 2006). Contrary to previous assumptions, compelling recent evidence indicates that isoprene, which has a greater emission than do monoterpenes, and its gas-phase oxidation products also contribute to the formation of SOA (Claeys et al., 2004a; Böge et al., 2006; Kroll et al., 2006). It has been estimated that a global isoprene emission flux of 500–750 Tg yr<sup>-1</sup> (Guenther et al., 2006), which accounts for ~50% of global VOCs, results in an SOA source strength from aqueous-phase reactions of 2–5 Tg yr<sup>-1</sup> (Claeys et al., 2004a, b; Gelencsér and Varga, 2005; Lim et al., 2005; Tsigaridis and Kanakidou, 2007). This is a substantial contribution to the global biogenic SOA budget (8–40 Tg yr<sup>-1</sup>) (Penner et al., 2001).

Recently, several laboratory studies have revealed that SOA can be formed through acid-catalyzed aqueous-phase oxidation of isoprene and its gas-phase oxidation product (Claeys et al., 2004b; Böge et al., 2006; Kroll et al., 2006). In the studies conducted so far, however, an important question has been neglected: what is the source of aqueous oxidants that cause the formation of SOA from isoprene and its gas-phase oxidation products? Therefore, we suggest that much better insights into the source of aqueous oxidants are vital for a better understanding of the mechanisms by which isoprene and its gas-phase oxidation products yield SOA.

It has been assumed that the major aqueous-phase oxidants – namely, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and HO<sub>x</sub> (OH and HO<sub>2</sub>) radicals – come mainly from the gas phase. However, with increased knowledge of aqueous-phase reactions, it has been found that many such reactions can also produce oxidants and, sometimes, aqueous-phase oxidants are produced mainly from aqueous-phase reactions (Anastasio et al., 1994; Finlayson-Pitts and Pitts, 2000; Valverde-Canossa et al., 2005). Smog chamber experiments have revealed that humid conditions are more favorable for the production

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of peroxides than are the dry conditions in the gas-phase ozonolysis of alkenes (Gäb et al., 1995; Neeb et al., 1997; Sauer et al., 1999). Accordingly, the aqueous-phase ozonolysis of alkenes might also produce a considerable yield of peroxides because of the abundance of water molecules (Gäb et al., 1995). Taking into account the huge number of biogenic alkenes, it is logical to presume that the aqueous-phase ozonolysis of alkenes might contribute a considerable amount of oxidants to the aqueous phase, even if only a small number of alkenes participates in aqueous-phase reactions.

Methacrolein (MAC) and methyl vinyl ketone (MVK), as the major constituents of first-generation carbonyl products in the oxidation of isoprene, account for a combined molar yield of >50% in the conversion of isoprene (Montzka et al., 1993; Li et al., 1997; Griffin et al., 1999; Simpson et al., 1999; Atkinson and Arey, 2003). Besides the secondary source from the oxidation of isoprene, MAC and MVK might also be directly emitted by anthropogenic sources (Biesenthal and Shepson, 1997). Hence, it can be estimated that there is >320 Tg yr<sup>-1</sup> of MAC and MVK present in the atmosphere. Moreover, the tropospheric lifetimes of MAC and MVK are estimated to be 6–10 h (Gierczak et al., 1997). Therefore, it can be presumed that MAC and MVK participate in and profoundly impact atmospheric chemistry with their huge quantities and high reactivity. However, the significance of their aqueous-phase reactions in the atmosphere requires evaluation.

Iraci et al. (1999) estimated that only 0.02% of the total amount of MAC and 0.1% of the total amount of MVK enter the aqueous phase under a condition of gas–aqueous partition equilibrium at 298 K, based on the Henry constants of the compounds (i.e. 6.5 M atm<sup>-1</sup> for MAC and 41 M atm<sup>-1</sup> for MVK, Allen et al., 1998; Iraci et al., 1999), choosing 1 × 10<sup>-6</sup> cm<sup>-3</sup> H<sub>2</sub>O/cm<sup>3</sup> air (1 g H<sub>2</sub>O/cm<sup>3</sup>) as a generous estimate of cloud liquid water content (Pruppacher and Klett, 1997). According to this arithmetic, it can be estimated that only 0.00004% of the total isoprene present will reside in the aqueous phase at 298 K, based on its Henry constant of 1.3 × 10<sup>-2</sup> M atm<sup>-1</sup> at this temperature (Allen et al., 1998). If this ratio were combined with the global isoprene emission flux of 625 Tg yr<sup>-1</sup> (Guenther et al., 2006), the amount of SOA derived from

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the aqueous-phase reaction of isoprene would be only  $0.00025 \text{ Tg yr}^{-1}$ , even though isoprene molecules partitioning in the aqueous phase are completely transformed into SOA. Obviously, this value is much lower than that estimated from the field measurements and laboratory studies mentioned earlier. This indicates that the Henry constant might not be the crucial factor in determining the amount of a compound that participates in aqueous-phase reactions in the atmosphere, where water is suspended in the form of small particles. Consequently, the amount of isoprene that participates in the aqueous-phase reaction should be much larger than the equilibrium amount calculated from the simple gas-aqueous equilibrium determined by its Henry constant. Similarly, it can be estimated that a huge amount of MAC and MVK participates in the aqueous-phase reaction. Therefore, it is extremely important to study aqueous-phase reactions of MAC and MVK.

In the present study, an experimental investigation of the ozonolysis of MAC and MVK in the aqueous phase was carried out to determine the source of oxidants in the aqueous-phase reaction of isoprene and other alkenes. The major products, including second-generation carbonyls, peroxides and organic acids, were identified and quantified, and their yields were determined. In addition, reaction mechanisms were proposed on the basis of experimental results. Finally, the atmospheric implications regarding the source of oxidants in the atmospheric aqueous phase are discussed.

## 2 Experimental

The solutions were prepared using MVK (Avocado, 95+%) and MAC (Sigma, 95+%) diluted in ultrapure water (Mili-Q). The concentrations of MAC and MVK used were  $2\text{--}5 \mu\text{M}$ . As blank experiments, the mixtures of water with MAC or MVK were tested before the final series of aqueous-phase reactions were carried out, and no peroxides, other carbonyl compounds or organic acids were detected. These reactant solutions were adjusted to different pHs in pH-conditional experiments.

The experimental apparatus comprised an ozone generator, an ozone solution gen-

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erator and an aqueous reactor, each of which was made of quartz glass. Ozone solution was prepared by bubbling ozone through a 2.6-l water solution at a flow rate of 60 ml/min.  $O_3$  was generated by UV irradiation of  $O_2$ , and the concentration of gas-phase  $O_3$  was  $\sim 280$  ppm at 298 K. The concentration of the  $O_3$  solution did not increase after 120 min, and was in the order of several micromolar.

The aqueous-phase experiments were performed by mixing 450 ml of  $O_3$  solution with 50 ml of organic reactant solution in the aqueous reactor. The reaction solution was shaken thoroughly and placed in a thermostat in darkness. A 15-ml gas space was left over the liquid level so that the reaction solution could be mixed. Because of the existence of the top gas space, the upper limits for the loss of aqueous ozone, MAC and MVK were estimated to be  $\sim 7.1\%$ ,  $0.02\%$  and  $0.006\%$ , respectively, at 298 K, based on their Henry constants. Therefore, the contribution of the gas-phase reaction was mostly eliminated and, thus, the reaction could be regarded as an aqueous-phase reaction. Additionally, a small amount of  $H_2O_2$  ( $< 10\%$  of the  $H_2O_2$  produced from the reactions) was found in the ozone solution before the organic reactant was added. Several possible mechanisms exist for aqueous  $H_2O_2$  formation from  $O_3$  and involve species such as HO,  $HO_2$  and  $O_2^-$  acting as intermediates (Heikes et al., 1982; Chameides and Davies, 1984). The  $H_2O_2$  formed in the  $O_3$  solution was measured in each experiment and was considered in the data analysis.

Both the reactants and the major products were determined in the experiments. Carbonyl compounds were analyzed by determining their derivatives of 2,4-dinitrophenylhydrazine (DNPH) with high-performance liquid chromatography (HPLC) (Agilent 1100, USA). Peroxides were analyzed online using post-column derivatization method by HPLC, in which hydroxyphenylacetic acid was oxidized to a fluorescent dimmer by peroxides and catalyzed by hemin; this method was described in detail in our previous work (Xu and Chen, 2005). Organic acids were analyzed using ion chromatography with an  $ED_{50}$  conductivity detector (DIONEX 2650, USA). The concentration of ozone in the aqueous phase was determined by indigo disulphonate spectrophotometry.

### 3 Results and discussion

The ozonolysis of MAC and MVK in the aqueous phase was studied at different pHs (pH=7.0, 5.4 and 3.0) and temperatures ( $t=4^{\circ}\text{C}$ ,  $10^{\circ}\text{C}$ ,  $25^{\circ}\text{C}$  and  $40^{\circ}\text{C}$ ). In the MAC– $\text{O}_3$  system, four products were identified: formaldehyde (HCHO), methylglyoxyl (MG), hydroxymethyl hydroperoxide (HMHP) and  $\text{H}_2\text{O}_2$ . In addition to these products, pyruvic acid (PYA) was detected in the MVK– $\text{O}_3$  system. The molar yields of these products were determined relative to the conversion of MAC or MVK.

A typical pattern of kinetics curves for the ozonolysis of MAC is shown in Fig. 1a. It can be seen that the ozonolysis time was  $<5$  min. The concentration of MAC decreased quickly within 5 min and then remained constant, indicating that ozone was completely consumed within this time, which was confirmed by ozone analysis. The concentration of MG was unchanged after 5 min, but the phenomena were different for HCHO,  $\text{H}_2\text{O}_2$  and HMHP. The concentration of HMHP decreased with reaction time; the opposite was true for HCHO and  $\text{H}_2\text{O}_2$ . The results were similar for the MVK– $\text{O}_3$  aqueous-phase reaction (Fig. 1b).

According to the results described, we speculate that HMHP decomposes in the aqueous solution, yielding HCHO and  $\text{H}_2\text{O}_2$ . The yields of HCHO and  $\text{H}_2\text{O}_2$  from the decomposition can be derived from the linear regression in Fig. 2, and the values of  $\Delta\text{HCHO}/\Delta\text{HMHP}$  and  $\Delta\text{H}_2\text{O}_2/\Delta\text{HMHP}$  are 0.95 and 1.13, respectively. These values indicate that HMHP formed in the aqueous-phase ozonolysis of MAC and MVK decomposes at a rapid rate exclusively into HCHO and  $\text{H}_2\text{O}_2$ . The half-life of HMHP in the solution,  $\tau_{\text{HMHP},1/2}$ , was calculated. At neutral pH,  $\tau_{\text{HMHP},1/2}$  is in the order of several decade minutes but, under slightly acidic conditions (i.e.  $\text{pH}\leq 5.4$ ),  $\tau_{\text{HMHP},1/2}$  is at least 100 min. Hence, the HCHO and  $\text{H}_2\text{O}_2$  observed were produced not only by direct generation but also by decomposition of HMHP. The real primary yields of HCHO and  $\text{H}_2\text{O}_2$  in the reaction systems were obtained based on further experimental results.

As illustrated in Fig. 3, HMHP was stable and its yield was unchanged during the experimental period under the conditions  $t=4^{\circ}\text{C}$ ,  $\text{pH}=3.0$ . Correspondingly, the yields

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of HCHO and H<sub>2</sub>O<sub>2</sub> did not increase against the reaction time. Under these conditions, H<sub>2</sub>O<sub>2</sub> had a negligible yield (0.29±2.0%), indicating that the ozonolysis reaction cannot produce H<sub>2</sub>O<sub>2</sub> directly. Thus, the concentration of H<sub>2</sub>O<sub>2</sub> detected in the reaction was derived from the decomposition of HMHP. However, the case is different for HCHO, which has two sources – direct formation and decomposition of HMHP – even under the conditions  $t=4^{\circ}\text{C}$ , pH=3.0. The experimental results indicate that HMHP was decomposed partially during the 24-h period for the derivation of HCHO–DNPH, although no distinct decrease in HMHP was observed during the 95-min ozonolysis reaction period (Fig. 3). However, during the derivation period, the proportions of the decomposition of HMHP in different samples collected at the different ozonolysis reaction times should be the same because of the same derivation condition (pH=2.0) of HCHO. Therefore, the calculated yields of HCHO are the same in the samples (Fig. 3). Consequently, the yield of HCHO obtained under the conditions  $t=4^{\circ}\text{C}$ , pH=3.0 is still not its real primary yield in the aqueous-phase ozonolysis of MAC because of the limitation of the offline analytical method used for HCHO. The yield of HCHO obtained under these conditions should actually be higher than the real primary yield. According to the analysis described, the real primary yield of HCHO should be equal to the difference between the yield of HCHO when HMHP has decomposed totally and the real primary yield of HMHP. This is similar to the values of the MVK–O<sub>3</sub> system.

The experimental results under different conditions are summarized in Table 1. The yields of peroxides and second-generation carbonyls are almost independent of pH and temperature in the aqueous ozonolysis of MAC and MVK. The organic acids were also determined at pH=7.0 and  $t=25^{\circ}\text{C}$ . PYA was detected as the only organic acid in the ozonolysis of MVK in the aqueous phase, with a yield of 24.2±3.6%, and no organic acids were detected in the ozonolysis of MAC in the aqueous phase. Both of these reaction systems have a fine carbon balance approaching 100%: 99.6±6.3% for MAC–O<sub>3</sub> and 95.4±9.7% for MVK–O<sub>3</sub>.

Such high yields of peroxides and second-generation carbonyls are unexpected. In particular, the total yield of peroxides is ~70% for both MAC–O<sub>3</sub> and MVK–O<sub>3</sub> aqueous-

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phase reaction systems, and this value is much higher than those previously reported for the aqueous ozonolysis of alkenes. Gäb et al. (1995) determined the yields of alkyl and hydroxyalkyl hydroperoxides in the ozonolysis of ethene, isoprene and three other alkenes under two conditions: in dry air and in water. The ozonolysis in water produced almost exclusively 1-hydroxyalkyl hydroperoxides, in 10–30% yields, whereas the dry gas-phase ozonolysis produced few peroxides (<1%), unless there were methyl substituents in the double bonds, in which case a yield of up to 5% of methyl hydroperoxide was produced. It is difficult to compare the results of the present study with those of Gäb et al. (1995) because the reaction conditions were different. Gäb et al. (1995) carried out their reactions at concentrations ~20–40 times those in the present study. Moreover, the MAC and MVK we studied were different from the alkenes that they studied. However, the yields of peroxides in aqueous-phase reactions were much higher than those in the gas-phase reaction for both their study and the present study. Therefore, we conclude that water molecules can significantly contribute to the increased yield of peroxides in the ozonolysis of C=C-containing compounds via the pathway of generating 1-hydroxyalkyl hydroperoxides (namely, HMHP) for vinyl compounds.

The stoichiometric proportions of the ozonolysis of MAC and MVK in the aqueous phase were obtained using a linear regression method based on the experimental results, with strong linear relationships (i.e.  $R_{MAC/O_3}=0.98$  ( $n=21$ ) and  $R_{MVK/O_3}=0.99$  ( $n=24$ )) (Fig. 4). The proportions of  $\Delta MAC/\Delta O_3$  and  $\Delta MVK/\Delta O_3$  were obtained as 0.93 and 1.03, respectively, which indicates that the aqueous ozonolysis of MAC and MVK proceeds at a stoichiometric proportion of 1:1.

We propose possible mechanisms for the ozonolysis of MAC and MVK in the aqueous phase based on the experimental results discussed (Fig. 5).

The aqueous-phase reaction of ozone with alkenes is, through analogy with the gas phase, believed to proceed via the addition of ozone to the double bond to form a molozonide, which decomposes rapidly into a carbonyl compound and a corresponding Criegee radical (Hatakeyama and Akimoto, 1994). There are two possible pathways for the formation of molozonide following the addition of  $O_3$  to MAC or MVK, yielding

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[CH<sub>2</sub>OO]\* and [CH<sub>3</sub>C(OO)CHO]\* for MAC–O<sub>3</sub>, and [CH<sub>2</sub>OO]\* and [CH<sub>3</sub>COCHOO]\* for MVK–O<sub>3</sub>. Then, [CH<sub>2</sub>OO]\* is collisionally stabilized and reacts with H<sub>2</sub>O to form HMHP (Gäb et al., 1985). HMHP is unstable and decomposes rapidly into H<sub>2</sub>O<sub>2</sub> and HCHO under a condition of pH>3. [CH<sub>3</sub>C(OO)CHO]\* formed in the MAC–O<sub>3</sub> reaction system reacts with H<sub>2</sub>O after stabilization to form CH<sub>3</sub>(HOO)C(OH)CHO, which is much more unstable than is HMHP and decomposes rapidly into MG. However, H<sub>2</sub>O<sub>2</sub> cannot form during the decomposition of CH<sub>3</sub>(HOO)C(OH)CHO because, unlike in HMHP, it is difficult for its α-OH to react with the –OOH group because of a bigger steric effect caused by the carbonyl group in this molecule. Further study is needed for this assumption. CH<sub>3</sub>(HOO)C(OH)CHO was not detected in the experiment owing to its poor stability in the aqueous phase (Neeb et al., 1997; Sauer et al., 1999). The case is similar to the [CH<sub>3</sub>COCHOO]\* formed in the MVK–O<sub>3</sub> reaction system, which is followed by the formation of CH<sub>3</sub>COCH(OH)OOH. Unlike CH<sub>3</sub>(HOO)C(OH)CHO, there is a hydrogen atom on the carbon atom that bonds with the –OOH group in CH<sub>3</sub>COCH(OH)OOH, and thus the decomposition of CH<sub>3</sub>COCH(OH)OOH has two pathways, forming PYA and MG (Sauer et al., 1999; Aplincourt and Anglada, 2003). CH<sub>3</sub>COCH(OH)OOH was not detected in the experiment because of its poor stability. However, there is also a hydrogen atom on the carbon atom that bonds with the –OOH group in HMHP but no acid is formed, which seems to be inconsistent with the formation of PYA from CH<sub>3</sub>COCH(OH)OOH. Crehuet et al. (2001) confirmed that the water-assisted HMHP decomposition produced a lower activation barrier for the formation of HCHO + H<sub>2</sub>O<sub>2</sub> than that in the formation of HCOOH + H<sub>2</sub>O. This is consistent with the results of our study. In fact, Neeb et al. (1997) concluded that HMHP decomposed to yield HCOOH + H<sub>2</sub>O almost exclusively, in agreement with the unimolecular process reported by Crehuet et al. (2001).

According to our experimental results, the formation of [CH<sub>2</sub>OO]\* dominated both of the aqueous MAC–O<sub>3</sub> and MVK–O<sub>3</sub> systems (Fig. 5). In the MVK–O<sub>3</sub> reaction system, the value of b<sub>2</sub> was larger than the yield of HCHO, possibly because some other compounds were formed from the decomposition of molozonide. In summary, because of

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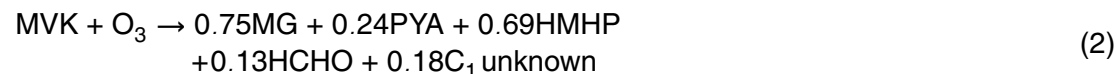
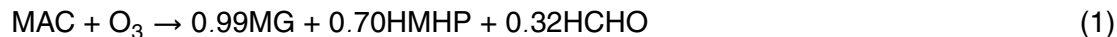
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the existence of huge amounts of water molecules, the Criegee radicals formed from the decomposition of ozonides in the aqueous ozonolysis of MAC and MVK were inclined to stabilize and then form peroxides and corresponding carbonyl compounds, rather than directly decompose into other matters. Consequently, high yields of both peroxides and second-generation carbonyls were produced in both the MAC–O<sub>3</sub> and MVK–O<sub>3</sub> aqueous-phase reaction systems. The chemical stoichiometry of the aqueous ozonolysis of MAC and MVK can be presented as Reactions (1–3):



In summary, when one molecule of ozone is consumed in the aqueous-phase ozonolysis of MAC and MVK, 0.7 molecules of peroxide and 1.6–2.0 molecules of carbonyl compound are produced. Therefore, in these processes, the type of oxidant is changed and the amount of oxidant is amplified.

## 4 Atmospheric implications

The generalized aqueous-phase ozonolysis of MAC and MVK in the atmosphere can be categorized into three chemical scenarios (Fig. 6): (i) in scenario 1 (the complete aqueous-phase reaction), both O<sub>3</sub> and MAC (or MVK) stay and react in the aqueous phase; (ii) in scenario 2a and scenario 2b (the interfacial reaction), one reactant stays in the aqueous phase and reacts, via collision, with another reactant from the gas phase; and (iii) in scenario 3 (the interfacial reaction), neither O<sub>3</sub> nor MAC (or MVK) stays in the aqueous phase but both can contact the aqueous phase simultaneously from the gas phase and react at the instant of contact. However, we are unsure whether scenario

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3 should be included in the category of the aqueous-phase reaction, but it is strongly recommended for a rapid reaction such as the ozonolysis of MAC and MVK. If so, the Henry constants mentioned previously would no longer be a key factor restricting the aqueous-phase reaction. Of course, this hypothesis should be further evaluated. In summary, the participation of the water molecules in the reaction is the key point for all three scenarios of the aqueous-phase reactions. Scenario 2 and scenario 3 cannot be carried out in laboratory simulations because, to our knowledge, it is difficult to distinguish between gas-phase and aqueous-phase reactions. Although only scenario 1 of aqueous reactions was performed in the present study, we suggest that the results can be extended to the whole aqueous-phase ozonolysis of MAC and MVK, including scenario 2 and scenario 3.

Under simulated atmospheric conditions, including different temperatures and pHs, the present laboratory study revealed that the ozonolysis of MAC and MVK in the aqueous phase can produce unexpectedly high yields of HMHP, MG and HCHO, and HMHP can transform rapidly into  $\text{H}_2\text{O}_2$  and HCHO with a yield of 100% because of its instability. In particular, these newly produced compounds are much more soluble than their precursors and are strongly inclined to stay in the aqueous phase ( $H_{\text{HMHP}}=5.0\times 10^5 \text{ Matm}^{-1}$ ,  $H_{\text{H}_2\text{O}_2}=1.0\times 10^5 \text{ Matm}^{-1}$  at 295 K;  $H_{\text{MG}}=3.7\times 10^4 \text{ Matm}^{-1}$  at 295 K;  $H_{\text{HCHO}}=6.3\times 10^3 \text{ Matm}^{-1}$  at 298 K) (Pandis and Seinfeld, 1989; Zhou and Lee, 1992; Lee and Zhou, 1993). However, the significance of a reaction in the atmosphere depends not only on the yield of its products but also on its reaction rate. The ozonolysis rate constants of MAC and MVK in the aqueous phase are extremely high ( $2.4 (\pm 0.1)\times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  and  $4.4 (\pm 0.2)\times 10^4 \text{ M}^{-1} \text{ s}$ , respectively, Pederson and Sehested, 2001), so the rate bottleneck for these reactions is the amount of these two species participating in aqueous-phase reactions.

To the best of our knowledge, there have been no reports regarding the amount of MAC and MVK participating in aqueous-phase reactions, although it can be roughly estimated. According to the estimate by Claeys et al. (2004a), the oxidation of isoprene and its gas-phase oxidation products contributes 2-methyltetrols and 2,3-

dihydroxymethacrylic acid, which are two important components of SOA in the atmosphere, with a combined yield of ~0.2%. This is achieved by aqueous-phase acid-catalyzed oxidation with H<sub>2</sub>O<sub>2</sub>: a perfect analog to atmospheric sulfate formation (Claeys et al, 2004b; Böge et al., 2006). Obviously, this yield should be controlled by two factors: (i) the amount of isoprene and its gas-phase oxidation products participating in aqueous-phase reactions; and (ii) the yield of 2-methyltetrols and 2,3-dihydroxymethacrylic acid produced by the aqueous-phase oxidation of isoprene and its gas-phase oxidation products.

Like the aqueous-phase oxidation of sulfite [S(IV)] (Seinfeld and Pandis, 1998), and compared with oxidation by H<sub>2</sub>O<sub>2</sub>, oxidation by O<sub>3</sub> might be the predominant pathway for the aqueous-phase oxidation of isoprene and its gas-phase oxidation products under a weak acidic condition (i.e. pH<sub>≥</sub>5). Moreover, this pH condition is typical in the atmospheric aqueous-phase over the tropical rain forest zone where there is abundant vegetation and little anthropogenic activity. Consequently, in this region, oxidation by H<sub>2</sub>O<sub>2</sub> could be a minor reaction pathway for isoprene and its gas-phase oxidation products, and thus the yield of 2-methyltetrols and 2,3-dihydroxymethacrylic acid might be low in atmospheric aqueous-phase reactions. Hence, it can be estimated that a considerable amount of isoprene and its gas-phase oxidation products reacts with oxidants on the surface or in the bulk of the aqueous phase. This is similar to the situation with MAC and MVK. Therefore, it is reasonable to conclude that a considerable amount of MAC and MVK can participate in aqueous-phase reactions in the atmosphere.

According to this analysis, the aqueous-phase ozonolysis of MAC and MVK produces a huge amount of peroxide and, thus, provides a direct source of oxidants to the atmospheric aqueous phase. Moreover, these reactions can also contribute a huge amount of MG and HCHO. These two carbonyl compounds might contribute a considerable amount of HOx (OH and HO<sub>2</sub>) radicals and H<sub>2</sub>O<sub>2</sub> by photolysis (Atkinson and Arey, 2003). Furthermore, HCHO can complex with S(IV) in the aqueous phase to produce hydroxymethanesulfonate (Seinfeld and Pandis, 1998), resulting in the reduction of peroxide consumption by S(IV). Therefore, the formation of MG and HCHO in the

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aqueous phase can be regarded as an indirect source of aqueous oxidants.

In conclusion, the aqueous-phase ozonolysis of MAC and MVK might be an important source of atmospheric aqueous oxidants. If this conjecture were extended to the aqueous-phase ozonolysis of isoprene and terpenes, which are major components of biogenic VOCs, one could speculate that the aqueous-phase ozonolysis of isoprene, terpenes and their oxidation products could be a significant, or even the main, source of atmospheric aqueous oxidants. These aqueous oxidants, especially the peroxides, produced by the aqueous-phase reaction itself effectively confirm the formation of SOA from isoprene and its gas-phase products via the mechanisms proposed by Claeys et al. (2004b), even if there are no other sources of aqueous oxidants. Moreover, the present study also provides convictive theoretical evidence for the field measurement. Based on their field measurement, Valverde-Canossa et al. (2005) suggested that organic peroxides, which were observed only in cloud samples, contributed to the total peroxides, from 14% during daytime to 80% during nighttime, and that the cloud ozonolysis reaction of alkenes was the main source of H<sub>2</sub>O<sub>2</sub> during nighttime and of hydroxyalkyl hydroperoxides throughout the day. Therefore, the oxidants from aqueous-phase reactions might have a major role in aqueous-phase chemistry, especially in the formation of secondary aerosols (SAs), including sulfates and SOAs, via aqueous-phase reactions.

Further detailed laboratory and field experiments must be performed to determine the kinetic, phase-partitioning and other properties of the aqueous-phase reactions that would enable both a better understanding of the source of aqueous oxidants and judgment of the overall significance of aqueous-phase chemistry in the formation of SAs.

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**Table 1.** Yields (%) of products in the aqueous ozonolysis of MAC and MVK under different conditions.

		MAC–O <sub>3</sub>			MVK–O <sub>3</sub>		
<i>t</i> (°C)	pH	HCHO <sup>a</sup>	MG	HMHP	HCHO <sup>a</sup>	MG	HMHP
4	3.0	34.9±3.0	96.1±2.4	67.6±3.2	14.4±1.2	73.7±1.1	67.8±2.2
	5.4	32.6±2.6	97.2±3.0	69.9±2.0	13.1±1.9	76.1±1.9	69.1±2.8
	7.0	33.8±2.5	97.4±2.6	68.7±5.5	10.0±2.9	74.9±1.8	72.2±3.2
10	3.0	33.2±5.5	99.1±2.0	69.3±2.9	12.9±2.1	74.2±1.0	69.3±3.0
	5.4	30.0±1.9	97.4±3.2	72.5±5.4	14.7±5.1	76.2±1.0	67.5±2.7
	7.0	30.1±2.3	96.5±2.8	72.4±6.3	12.2±2.3	75.7±0.8	70.0±2.8
25	3.0	31.9±3.6	98.6±5.4	70.6±4.5	18.3±1.7	74.3±2.7	63.9±4.8
	5.4	31.4±4.7	98.9±4.8	71.1±3.2	15.5±3.0	74.2±2.1	66.7±4.1
	7.0	30.6±3.7	102.2±5.4	71.9±3.7	13.4±4.9	75.4±1.7	68.8±2.4
40	3.0	30.9±5.0	100.2±5.0	71.6±5.0	11.6±4.8	74.6±8.5	70.6±9.5
	5.4	34.1±5.8	99.5±4.5	68.4±6.2	12.3±5.8	77.4±7.1	69.9±9.7
	7.0	32.7±3.6	100.0±3.5	69.8±4.2	11.5±4.7	78.2±7.9	70.7±7.0
Mean		32.3±5.8	98.6±5.4	70.3±6.3	13.3±5.8	75.4±7.9	68.9±9.7
Total C <sup>b</sup>			99.6±6.3			95.4±9.7 <sup>c</sup>	

<sup>a</sup> The real primary yield of HCHO was calculated by subtracting the yield of HMHP from the yield of HCHO when HMHP had decomposed totally.

<sup>b</sup> Total C = (Yield<sub>HCHO</sub> + Yield<sub>HMHP</sub> + Yield<sub>MG</sub> × 3 + Yield<sub>PYA</sub> × 3) / 4.

<sup>c</sup> The yield of PYA (24.2±3.6%) has been added to the measurement of carbon balance of the MVK–O<sub>3</sub> aqueous reaction system.

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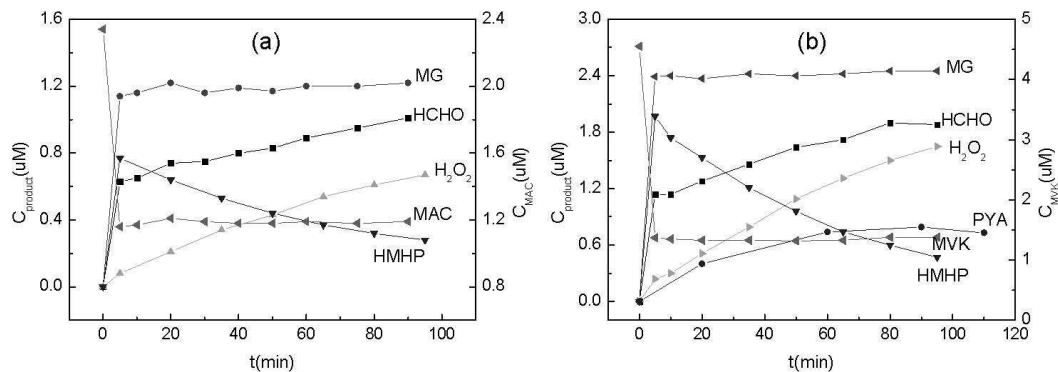
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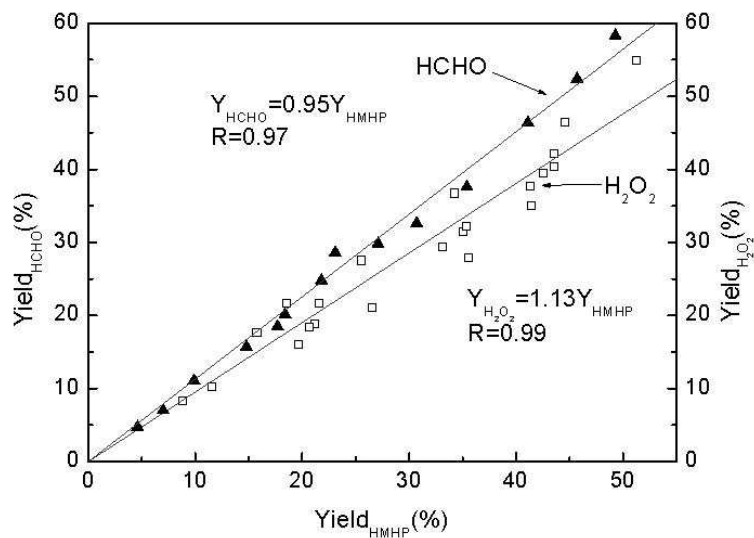


**Fig. 1.** Temporal concentration profiles of reactant and products in the aqueous-phase ozonolysis of **(a)** MAC and **(b)** MVK (25°C, pH=7.0).

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**Fig. 2.** Regression of the transformation ratios of  $\Delta\text{HCHO}/\Delta\text{HMHP}$  and  $\Delta\text{H}_2\text{O}_2/\Delta\text{HMHP}$ .

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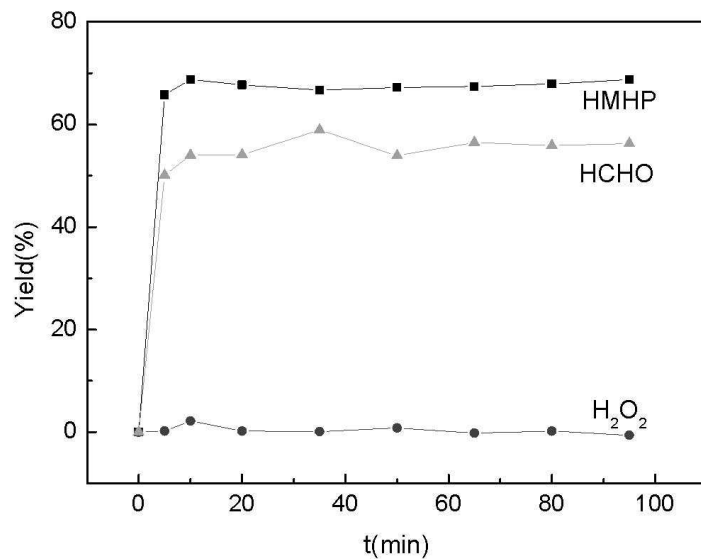
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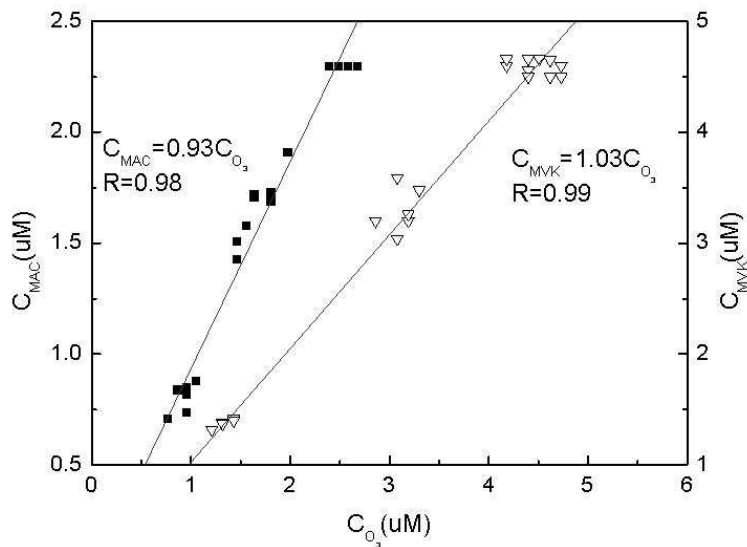


**Fig. 3.** Temporal yield profiles of HMHP, HCHO and H<sub>2</sub>O<sub>2</sub> in MAC–O<sub>3</sub> aqueous-phase reactions under the conditions  $t=4^{\circ}\text{C}$ ,  $\text{pH}=3.0$ .

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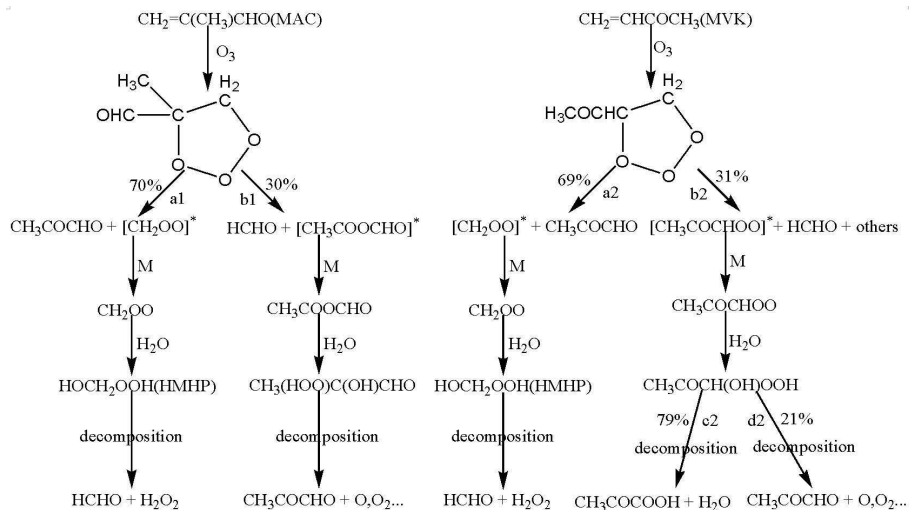
**Fig. 4.** The linear regression of the reactant ratios of MAC/ $O_3$  and MVK/ $O_3$ .

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**Fig. 5.** Mechanisms of the ozonolysis of MAC and MVK in the aqueous phase.

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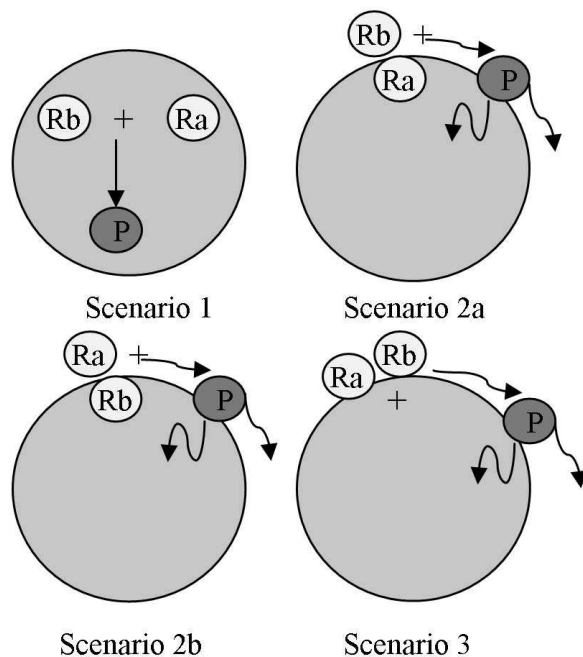
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**Fig. 6.** Different reaction scenarios for the aqueous-phase reaction. Ra, reactant a; Rb, reactant b; P, product.

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