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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 and its gas-phase oxidation products could contribute a considerable amount of aerosol through aqueous-phase acid-catalyzed oxidation with hydrogen peroxide (H_2O_2), although the source of H_2O_2 is unclear. The present study revealed a potentially important route to the formation of aqueous oxidants, including H_2O_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 hydroxylmethyl hydroperoxide (HMHP), formaldehyde (HCHO) and methylglyoxal (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–O_3, 70.3±6.3% HMHP, 32.3±5.8% HCHO and 98.6±5.4% MG; and (ii) for MVK–O_3, 68.9±9.7% HMHP, 13.3±5.8% HCHO and 75.4±7.9% MG. A yield of 24.2±3.6% pyruvic acid has been detected for MVK–O_3. HMHP is unstable in the aqueous phase and can transform into H_2O_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 can lead to substantial aerosol formation from the aqueous-phase acid-catalyzed reaction of H_2O_2 with MAC, 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 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). It has been estimated that a global isoprene emission flux of 500–750 $\mathrm{Tg\,yr^{-1}}$ (Guenther et al., 2006), which accounts for ~50% of global VOCs. Contrary to previous assumptions, Claeys et al. (2004a) reported, for the first time, isoprene and its gas-phase oxidation products could contribute to the formation of SOA with an amount of 2 $\mathrm{Tg\,yr^{-1}}$. Subsequent studies of additional SOA production pathways confirmed this conclusion and increased this estimation. Henze et al. (2006) estimated that the amount of SOA produced directly from isoprene is 6.2 $\mathrm{Tg\,yr^{-1}}$, only considering the contribution from OH oxidation. Hoyle et al. (2007) estimated that the amount of SOA from the oxidation products of isoprene is 15 $\mathrm{Tg\,yr^{-1}}$. Matsunaga et al. (2005) estimated a source of SOA from isoprene in the range of 10–120 $\mathrm{Tg\,yr^{-1}}$. Obviously, the amount of isoprene SOA may be larger as more and more laboratory and field evidences are found. This is a substantial contribution to the global biogenic SOA budget (8–40 $\mathrm{Tg\,yr^{-1}}$) (Penner et al., 2001).

The estimations about the amount of isoprene SOA include the amount from both the gas-phase reaction and

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aqueous-phase reaction. Recently, several laboratory studies have revealed that SOA can be formed from isoprene and its gas-phase oxidation products through the acid-catalyzed aqueous-phase reaction in solution (Claeys et al., 2004b; Gelencsér and Varga, 2005; Quivet et al., 2007; Ervens et al., 2008), the reaction in the presence of droplets with a yield of SOA from isoprene about 0.22% (Böge et al., 2006), the process of cloud processing with an amount about 1.6 Tg yr^{-1} (Lim et al., 2005) and the reaction on acidic humid particles (Surratt et al., 2006; Tsigaridis and Kanakidou, 2007). In the studies conducted so far, however, an important question has not been addressed: 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_2O_2) and HO_x (OH and HO_2) 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 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 emissions 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 participate 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^{-1} 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^{-1} for MAC and 41 M atm^{-1} for MVK, Allen et al., 1998; Iraci et al., 1999), choosing 1×10^{-6} cm^{-3} H_2O/cm^3 air (1 g H_2O/cm^3) 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^{-2} M atm^{-1} at this temperature (Allen et al., 1998). If this ratio were combined with the global isoprene emission flux of 625 Tg yr^{-1} (Guenther et al., 2006), the amount of SOA derived from the aqueous-phase reaction of isoprene would be only 0.00025 Tg yr^{-1}, even though isoprene molecules partitioning in the aqueous phase are completely transformed into SOA. Among the gas-phase oxidation products of isoprene, MAC, which is estimated as 160 Tg yr^{-1} in the atmosphere, is an important contributor to SOA (Claeys, et al., 2004b; Surratt et al., 2006). However, even though the total amount of MAC partitioning in the aqueous phase (0.02%, Iraci et al., 1999) were completely transformed into SOA, its burden to SOA could be estimated to be 0.032 Tg yr^{-1}. This value is much lower than the amount of isoprene SOA from aqueous-phase reaction 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. The reasons for higher partitioning into the particle phase may be: (i) the Henry constant could be enhanced significantly by ionic strength effects; (ii) the reactant partitions into non-aqueous moieties of the particles; (iii) in presence of a reaction, the reaction removes the reactant driving more of it from the gas phase into the liquid. Consequently, in the atmosphere, the amount of a compound 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 2–5 μM. 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 generator 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 ~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 ~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-dinitrophenyhydrazine (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 dimer 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°C, 10°C, 25°C and 40°C). In the MAC–O_3 system, four products were identified: formaldehyde (HCHO), methylglyoxal (MG), hydroxylmethyl hydroperoxide (HMHP) and H_2O_2. In addition to these products, pyruvic acid (PYA) was detected in the MVK–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, H_2O_2 and HMHP. The concentration of HMHP decreased with reaction time; the opposite was true for HCHO and H_2O_2. The results were similar for the MVK–O_3 aqueous-phase reaction (Fig. 1b).

According to the results described, we speculate that HMHP decomposes in the aqueous solution, yielding HCHO and H_2O_2. The yields of HCHO and H_2O_2 from the decomposition can be derived from the linear regression in Fig. 2, and the values of ΔHCHO/ΔHMHP and $\Delta H_2O_2/\Delta$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 H_2O_2. The half-life of HMHP in the solution, $\tau_{\mathrm{HMHP},1/2}$, was calculated. At neutral pH, $\tau_{\mathrm{HMHP},1/2}$ is in the order of several tens of minutes but, under slightly acidic conditions (i.e. pH≤5.4), $\tau_{\mathrm{HMHP},1/2}$ is at least 100 min. Hence, the HCHO and H_2O_2 observed were produced not only by direct generation but also by decomposition of HMHP. The real primary yields of HCHO and H_2O_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°C, pH=3.0. Correspondingly, the yields of HCHO and H_2O_2 did not increase against the reaction time. Under these conditions, H_2O_2 had a negligible yield (0.29±2.0%), indicating that the ozonolysis reaction cannot produce H_2O_2 directly. Thus, H_2O_2 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°C, pH=3.0. The experimental results indicate that HMHP was decomposed partially during the 24-h period for the derivatization of HCHO–DNPH, although no distinct decrease in HMHP was observed during the 95-min ozonolysis reaction period (Fig. 3). However, during the derivatization period, the proportions of the decomposition of HMHP in different samples collected at the different

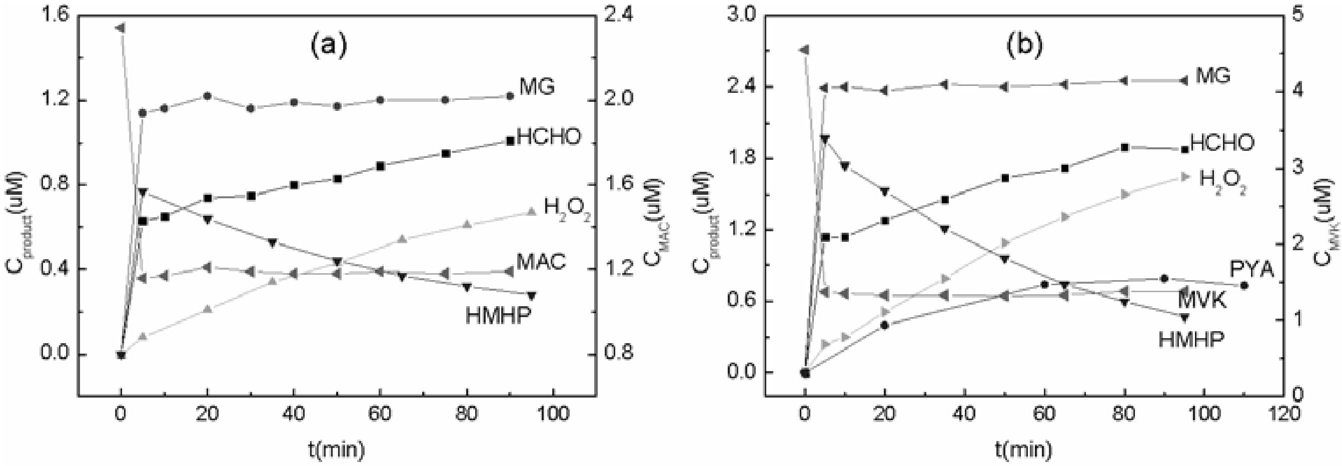

Fig. 1. Temporal concentration profiles of reactant and products in the aqueous-phase ozonolysis of **(a)** MAC and **(b)** MVK (25°C, pH=7.0).

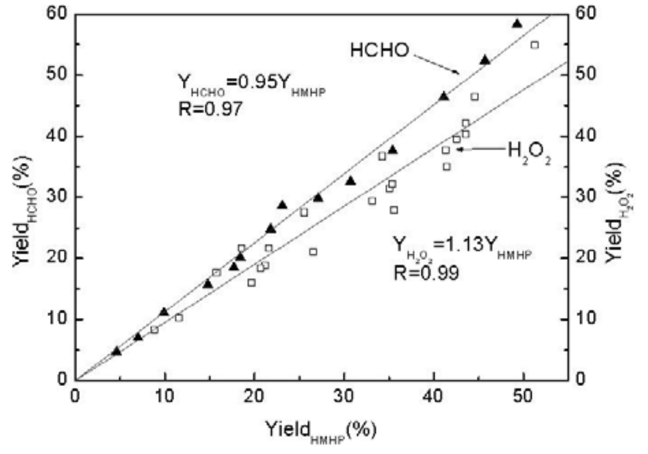

Fig. 2. Regression of the transformation ratios of ΔHCHO/ΔHMHP and $\Delta H_2O_2/\Delta$HMHP.

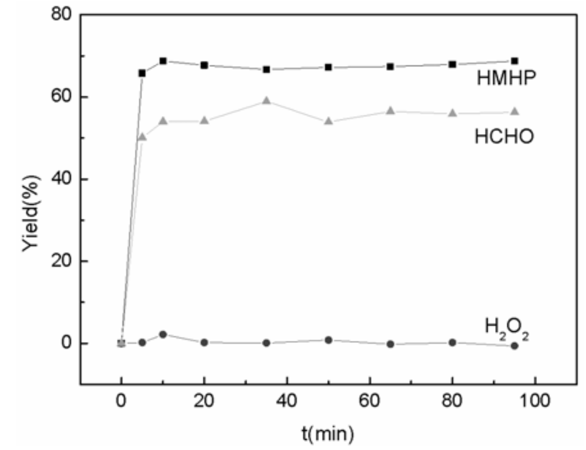

Fig. 3. Temporal yield profiles of HMHP, HCHO and H_2O_2 in MAC–O_3 aqueous-phase reactions under the conditions t=4°C, pH=3.0.

ozonolysis reaction times should be the same because of the same derivatization conditions (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°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_3 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°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_3 and 95.4±9.7% for MVK–O_3.

Such high yields of peroxides and second-generation carbonyls are unexpected. In particular, the total yield of peroxides is ~70% for both MAC–O_3 and MVK–O_3 aqueous-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

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

		MAC–O_3			MVK–O_3		
t (°C)	pH	HCHO[a]	MG	HMHP	HCHO[a]	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[b]			99.6±6.3			95.4±9.7[c]	

[a] The real primary yield of HCHO was calculated by subtracting the yield of HMHP from the yield of HCHO when HMHP had decomposed totally.

[b] Total C = $(\mathrm{Yield}_{\mathrm{HCHO}} + \mathrm{Yield}_{\mathrm{HMHP}} + \mathrm{Yield}_{\mathrm{MG}} \times 3 + \mathrm{Yield}_{\mathrm{PYA}} \times 3)/4$.

[c] The yield of PYA (24.2±3.6%) has been added to the measurement of carbon balance of the MVK–O_3 aqueous reaction system.

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. $\mathrm{R}_{\mathrm{MAC/O3}}$=0.98 ($n$=21) and $R_{\mathrm{MVK/O3}}$=0.99 (n=24)) (Fig. 4). The proportions of ΔMAC/ΔO_3 and ΔMVK/ΔO_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).

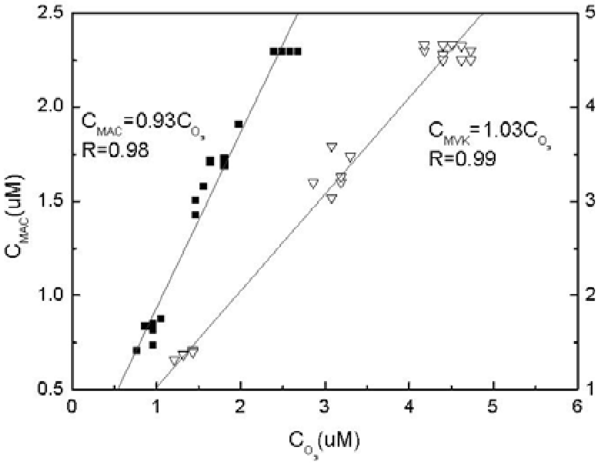

Fig. 4. The linear regression of the reactant ratios of MAC/O_3 and MVK/O_3.

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 $[CH_2OO]^*$ and $[CH_3C(OO)CHO]^*$ for MAC–O_3, and $[CH_2OO]^*$ and $[CH_3COCHOO]^*$ for MVK–O_3. Then, $[CH_2OO]^*$ is collisionally stabilized and reacts with H_2O to form HMHP (Gäb et al., 1985). HMHP is

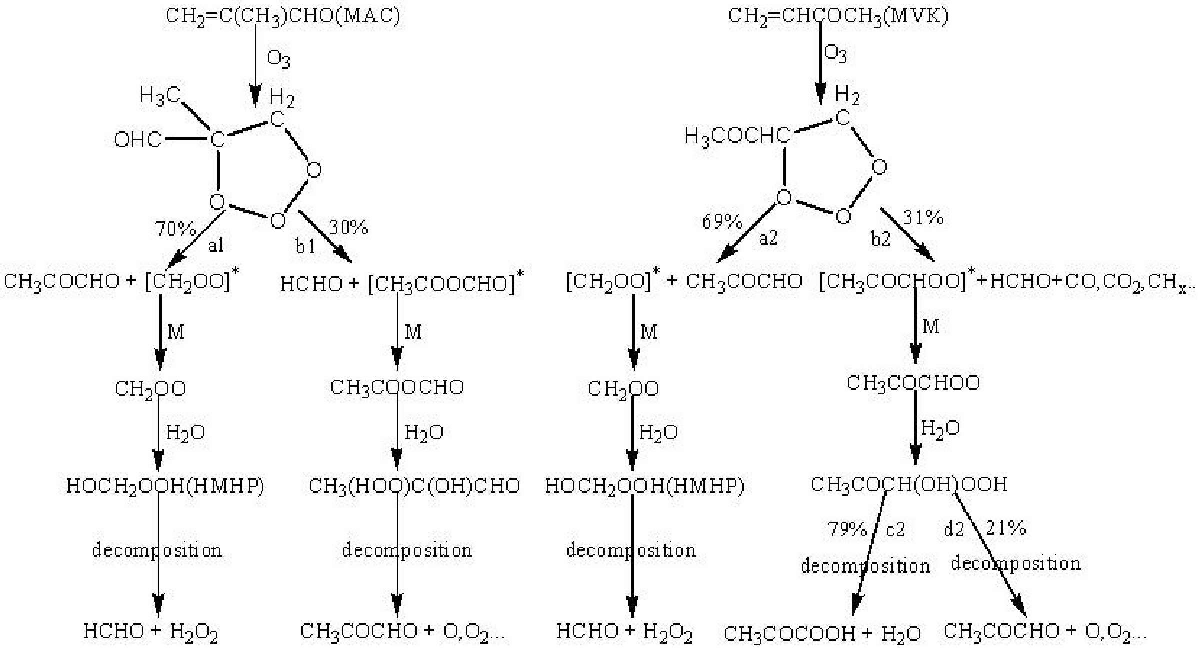

Fig. 5. Mechanisms of the ozonolysis of MAC and MVK in the aqueous phase.

unstable and decomposes rapidly into H_2O_2 and HCHO under a condition of pH>3. $[CH_3C(OO)CHO]^*$ formed in the MAC–O_3 reaction system reacts with H_2O after stabilization to form $CH_3(HOO)C(OH)CHO$, which is much more unstable than is HMHP and decomposes rapidly into MG. However, H_2O_2 cannot form during the decomposition of $CH_3(HOO)C(OH)CHO$ 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 to support this assumption. $CH_3(HOO)C(OH)CHO$ 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 $[CH_3COCHOO]^*$ formed in the MVK–O_3 reaction system, which is followed by the formation of $CH_3COCH(OH)OOH$. Unlike $CH_3(HOO)C(OH)CHO$, there is a hydrogen atom on the carbon atom that bonds with the –OOH group in $CH_3COCH(OH)OOH$, and thus the decomposition of $CH_3COCH(OH)OOH$ has two pathways, forming PYA and MG (Sauer et al., 1999; Aplincourt and Anglada, 2003). $CH_3COCH(OH)OOH$ 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 $CH_3COCH(OH)OOH$. Crehuet et al. (2001) confirmed that the water-assisted HMHP decomposition produced a lower activation barrier for the formation of HCHO + H_2O_2 than that in the formation of HCOOH+H_2O. This is consistent with the results of our study. In fact, Neeb et al. (1997) concluded that HMHP decomposed to yield HCOOH+H_2O almost exclusively, in agreement with the unimolecular process reported by Crehuet et al. (2001).

According to our experimental results, the formation of $[CH_2OO]^*$ dominated both of the aqueous MAC–O_3 and MVK–O_3 systems (Fig. 5). In the MVK–O_3 reaction system, the value of b2 was larger than the yield of HCHO, possibly because some other compounds were formed from the decomposition of molozonide. In summary, because of 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 products. Consequently, high yields of both peroxides and second-generation carbonyls were produced in both the MAC–O_3 and MVK–O_3 aqueous-phase reaction systems. The chemical stoichiometry of the aqueous ozonolysis of MAC and MVK can be presented as Reactions (1–3):

$$\mathrm{MAC} + \mathrm{O_3} \rightarrow 0.99\mathrm{MG} + 0.70\mathrm{HMHP} + 0.32\mathrm{HCHO} \quad (1)$$

$$\begin{aligned}\mathrm{MVK} + \mathrm{O_3} \rightarrow\ & 0.75\mathrm{MG} + 0.24\mathrm{PYA} + 0.69\mathrm{HMHP} \\ & + 0.13\mathrm{HCHO} + 0.18\mathrm{C_1}\ \mathrm{unknown}\end{aligned} \quad (2)$$

$$\mathrm{HMHP} \rightarrow \mathrm{HCHO} + \mathrm{H_2O_2} \quad (3)$$

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 aqueous-phase reaction includes not only the reaction in the bulk of droplets but also the reaction on the surface of droplets. Moreover, nanometer-size water clusters, $(H_2O)_n$, which are ubiquitous in the atmosphere, are considered to potentially participate in the atmospheric chemistry (Ryzhkov et al., 2006; Sennikov et al., 2005). Therefore, 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, i.e., bulk reaction), both O_3 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_3 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. These scenarios may enlarge the aqueous-phase reaction scope than that considered usually in previous multiphase chemical models. Then, what is the percentage for each of the three reaction scenarios? This needs further laboratory and modeling studies. However, we strongly recommend the reaction on the surface of droplets including scenario 2 and scenario 3 is significant 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.

In the atmospheric aqueous phase, MAC and MVK may be oxidized potentially by O_3, OH radicals, and NO_3 radicals. On the basis of the rate constants and concentration levels of these oxidants, their relative importance in the oxidation of MAC and MVK can be compared with the lifetimes, as shown in Table 2.

From the lifetimes in the bulk of droplets estimated in Table 2, it seems that in the daytime, the OH radicals would dominate the oxidation of MAC and MVK, and in the nighttime when the OH concentration is very low, the O_3 would dominate or compete with NO_3 radicals. As can be seen from the abovementioned data, however, up to date, there are not enough studies for the aqueous-phase rate constants for the oxidation of MAC and MVK (Lilie and Henglein, 1970; Kumar et al., 1990; Pedersen and Sehested, 2001). Obviously, more studies for the accurate aqueous-phase rate constants are needed to evaluate the relative importance of the three kinds of oxidants in the oxidation of MAC and MVK in the atmospheric aqueous phase.

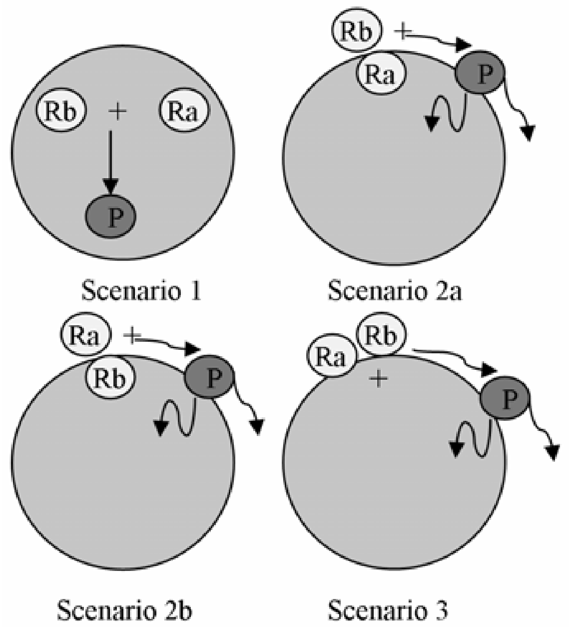

Fig. 6. Different reaction scenarios for the aqueous-phase reaction. Ra, reactant a; Rb, reactant b; P, product.

The aqueous-phase reaction includes not only the reaction in the bulk of droplets but also the reaction on the surface of droplets, as shown in Fig. 6, and especially, the latter may be more important and more ubiquitous than the former in the atmosphere. The surface reaction rate depends upon the reaction rate constant and surface concentration of reactants. The surface concentration of reactants can be estimated according to the surface accommodation coefficients (α_s), when the desorption process could be negligible at the stage of initial adsorption or when the surface reaction rate is much larger than the desorption rate. α_s is defined as the probability that the molecules undergoes neither scattering nor immediate chemical reaction upon collision with the particle but is accommodated in the sorption layer of the particle ($0 \leq \alpha_s \leq 1$) (Pöschl et al., 2007; Ammann and Pöschl, 2007). Based on the aqueous-phase reaction rate constants and the surface accommodation coefficients (α_s) of oxidants, the lifetimes of MAC and MVK reaction with oxidants on the surface of droplets may be estimated as following.

The uptake rate of the absorbate OX (r_a=d{OX}/dt; here OX indicates an oxidant) by droplets can be given in Eq. (4):

$$r_a = \frac{d\{OX\}}{dt} = \alpha_s Z \tag{4}$$

$$Z = \frac{1}{4}\bar{c} A_s [OX] \tag{5}$$

Table 2. Comparison of atmospheric lifetimes of MAC and MVK reaction with different oxidants on the surface and in the bulk of droplets.

	MAC			MVK		
	O_3	OH	NO_3	O_3	OH	NO_3
$[OX]_g(cm^{-3})$ [a]	7×10^{11}	1.6×10^{6}	5×10^{8}	7×10^{11}	1.6×10^{6}	5×10^{8}
$H(M\ atm^{-1})$ [b] 298 K	1.14×10^{-2}	25	0.6	1.14×10^{-2}	25	0.6
$[OX]_{a,e}(M)$ [c]	3.2×10^{-11}	1.6×10^{-12}	1.2×10^{-11}	3.2×10^{-11}	1.6×10^{-12}	1.2×10^{-11}
α_s [d]	1	1	1	1	1	1
Molecularweight	48	17	62	48	17	62
$k(M^{-1}\ s^{-1})$	2.1×10^{4} [e]	5.8×10^{9} [f]	10^3–10^6 [g]	4.4×10^{4} [e]	8.5×10^{9} [h]	10^3–10^6 [g]
$\tau_{bulk}(h)$	36	0.03	23–23 000	19	0.02	23–23 000
τ_{surf} ratio [i]	1	1.1	38–38 000	1	1.4	70–70 000

[a] where $[O_3]_g$, the 24 h daytime and nighttime average concentration of O_3 in the troposphere; $[OH]_g$, the 12 h daytime average concentration of OH radicals in the troposphere; $[NO_3]_g$, the 12 h nighttime average concentration of $[NO_3]$ radicals in the troposphere.

[b] Ervens et al. (2003);

[c] $[OX]_{a,e}$ aqueous-phase concentrations of oxidants at the gas-aqueous equilibrium;

[d] Although bulk accommodation coefficients (α_b) are available (Ervens et al., 2003), 0.05 for OH, 0.05 for O_3 and 0.004 for NO_3, there are no measurements of surface accommodation coefficients (α_s) for these oxidants, they are likely to be very close to 1 (M. Ammann, private communication, 2008);

[e] Pedersen and Sehested (2001);

[f] In analogy with CH_3CH=CHCHO, (Lilie and Henglein, 1970);

[g] estimated from other organic compounds, Herrmann et al. (2005);

[h] Lilie and Henglein (1970);

[i] τ_{surf} ratio is estimated by the surface concentrations of oxidants and their aqueous-phase reaction rate constants with MAC and MVK. The surface concentration estimates from adsorption flux determined by α_s, without considering desorption.

$$\overline{c}=\sqrt{\frac{8RT}{\pi M_{OX}}} \tag{6}$$

where Z is the rate of collisions between the gaseous molecules and droplet surface, α_s is the surface accommodation coefficient of oxidant, $\overline{c}$ is the mean molecular velocity of the gas molecules, A_s is the effective surface area of droplets, R is the gas constant, T is the temperature and M_{OX} is the molecular weight of the oxidant. {OX} indicates the concentration of oxidant on the surface of droplets, whereas [OX] indicates the gas-phase concentration of oxidant.

We can obtain:

$$r_a=\frac{d\{OX\}}{dt}\propto\alpha_s\frac{[OX]}{\sqrt{M_{OX}}} \tag{7}$$

at the beginning the surface concentration of oxidant were zero, then the concentration at time t is

$$\{OX\}\propto\frac{[OX]}{\sqrt{M_{OX}}}t \tag{8}$$

By combining the aqueous-phase rate constants in Table 2 with Eq. (8), the ratio of the lifetimes of MAC and MVK reaction with different oxidants on the surface of droplets can be estimated as:

$$\tau_{MAC-O3}:\tau_{MAC-OH}:\tau_{MAC-NO3}=\frac{1}{\{O_3\}k_{MAC-O3}}:\frac{1}{\{OH\}k_{MAC-OH}}:\frac{1}{\{NO_3\}k_{MAC-NO3}} \tag{9}$$

$$\tau_{MVK-O3}:\tau_{MVK-OH}:\tau_{MVK-NO3}=\frac{1}{\{O_3\}k_{MVK-O3}}:\frac{1}{\{OH\}k_{MVK-OH}}:\frac{1}{\{NO_3\}k_{MVK-NO3}} \tag{10}$$

Noticeably, in the description above, the desorption process on the surface of droplets is not considered. In fact, the surface concentration of a species should be obtained by combining the rates of adsorption and desorption. Obviously, the surface concentration without considering desorption should be higher than that with considering desorption. However, in the presence of a rapid surface reaction, such as the ozonolysis of MAC and MVK, the actual residence time of a reactant on the surface is much shorter than its desorption lifetime. In this case, the surface concentration of reactant may be limited to a low level, but its amount participating in the surface reaction may be considerable. Thus, it is difficult to estimate the accurate surface concentration of reactant, resulting in the difficulty in estimating the accurate lifetime of reactant. Additionally, up to date, there are no measured values of surface accommodation coefficients (α_s), although bulk accommodation coefficients (α_b) are available (Ervens et al., 2003). α_s is the maximum value for α_b (Pöschl et al., 2007), and the values of α_s are likely to be very close to 1 for many atmospheric relevant conditions (M. Ammann, private communication, 2008). In order to obtain the relative lifetimes of MAC and MVK oxidation on the surface of droplets, we choose the values of α_s as 1 for OH, O_3, and NO_3, as shown in Table 2. The lifetime ratio results are shown in Table 2. We think the ratio of the lifetimes of MAC and MVK reaction with different oxidants on the surface of droplets may not be influenced greatly, especially for the case in the presence of rapid surface reaction, even though the desorption process is considered. Of course, this needs further study.

From Table 2, it can be seen, unlike the case in the bulk, that the O_3 oxidation is comparable with the OH oxidation for MAC and MVK on the surface of droplets, whereas the NO_3 oxidation is negligible. Obviously, this conclusion should be further evaluated using the more accurate parameters such as mass accommodation coefficients and aqueous-phase rate constants. Although there is a great uncertainty, we suggest that the O_3 oxidation of MAC and MVK is significant in the atmospheric aqueous phase.

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 H_2O_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 ($H_{\mathrm{HMHP}}=5.0\times10^5\,\mathrm{M\,atm^{-1}}$, $H_{\mathrm{H2O2}}=1.0\times10^5\,\mathrm{M\,atm^{-1}}$ at 295 K; $H_{\mathrm{MG}}=3.7\times10^4\,\mathrm{M\,atm^{-1}}$ at 295 K; $H_{\mathrm{HCHO}}=6.3\times10^3\,\mathrm{M\,atm^{-1}}$ 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 ($2.4\,(\pm0.1)\times10^4\,\mathrm{M^{-1}\,s^{-1}}$ and $4.4\,(\pm0.2)\times10^4\,\mathrm{M^{-1}\,s}$, 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 recent studies, the yield of SOA from isoprene is about 1–3% under different atmospheric conditions, including the gas-phase reaction and aqueous-phase reaction (Henze et al., 2006; Hoyle et al., 2007; Matsunaga et al., 2005; Kroll et al., 2005, 2006). In accordance with the estimation of Böge et al. (2006) and Lim et al. (2006), the yield of SOA from aqueous-phase reaction is about 0.22%. 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 SOA 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_2O_2, oxidation by O_3 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≥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_2O_2 could be a minor reaction pathway for isoprene and its gas-phase oxidation products, and thus the yield of SOA 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_2) radicals and H_2O_2 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 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. These aqueous oxidants, especially the peroxides, produced by the aqueous-phase reaction itself effectively confirm the formation of SOA from MAC 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 supporting laboratory evidence for the field measurement. In this respect, 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_2O_2 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 SOA, 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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