

Laboratory simulation for the aqueous OH-oxidation of methyl vinyl ketone and methacrolein: significance to the in-cloud SOA production

X. Zhang, Z. M. Chen, and Y. Zhao

State Key Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing 100871, China

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Abstract. Increasing evidence suggests that secondary organic aerosol (SOA) is formed through aqueous phase reactions in atmospheric clouds. In the present study, the aqueous oxidation of methyl vinyl ketone (MVK) and methacrolein (MACR) via OH radical were investigated, with an emphasis on the composition and variation of small-molecular-weight organic products. In addition, high-molecular-weight compounds (HMWs) were found, interpreted as the ion abundance and time evolution. Our results provide, for the first time to our knowledge, experimental evidence that aqueous OH-oxidation of MVK contributes to SOA formation. Further, a mechanism primarily involving radical processes was proposed to gain a basic understanding of these two reactions. Based on the assumed mechanism, a kinetic model was developed for comparison with the experimental results. The model reproduced the observed profiles of first-generation intermediates, but failed to simulate the kinetics of most organic acids mainly due to the lack of chemical kinetics parameters for HMWs. A sensitivity analysis was performed in terms of the effect of stoichiometric coefficients for precursors on oxalic acid yields and the result indicates that additional pathways involving HMWs chemistry might play an important role in the formation of oxalic acid. We suggest that further study is needed for better understanding the behavior of multi-functional products and their contribution to the oxalic acid formation.

1 Introduction

Atmospheric processes involving suspended water droplets in clouds play an important role in the production and removal of ambient fine particles (Blando and Turpin, 2000). Recently, interest in the potential formation of secondary organic aerosols (SOA) from cloud processing is growing. The hypothesis for the in-cloud SOA production is that the oxidation of reactive species in the interstitial space of clouds generates water soluble species. They dissolve into cloud droplets and undergo further oxidation, creating low-volatility compounds. These compounds remain at least in part in the particle phase after droplet evaporation, leading to SOA (Kanakidou et al., 2005). This hypothesis has been supported by a number of laboratory studies, the results of which roughly followed two tracks. The first is the low-volatility organic acid formation (Carlton et al., 2006, 2007, 2009; Altieri et al., 2008), which also provides an additional source of particle-phase oxalate observed in cloud-influenced air masses (Sorooshian et al., 2007). The second active track is the oligomer and humic-like substances (HULIS) production from the photooxidation of a series of low-molecular-weight species, including pyruvic acid (Altieri et al., 2006; Guzman et al., 2006), glyoxal (Carlton et al., 2007; Volkamer et al., 2009), methylglyoxal (Altieri et al., 2008), and glycolaldehyde (Perri et al., 2009). In light of the laboratory evidence, recent models predicted a substantial increase of SOA production when aqueous SOA formation pathways were incorporated (Lim et al., 2005; Chen et al., 2007; Carlton et al., 2007; Ervens et al., 2008). However, the mechanism with respect to the aqueous chemistry has not been completely understood and SOA precursors included in current models that represent cloud processing are limited.



Correspondence to: Z. M. Chen
(zmchen@pku.edu.cn)

Methacrolein (MACR) and methyl vinyl ketone (MVK), as two major first-generation products in the oxidation of isoprene, are of great interest due to their large global abundance (Montzka et al., 1993; Griffin et al., 1999; Simpson et al., 1999) and high reactivity (Gierczak et al., 1997; Chen et al., 2008b). The atmospheric transformation of these two carbonyls has received considerable studies, mainly including determining their gas-phase reaction products (Tuazon and Atkinson, 1989, 1990; Aschmann et al., 1996; Orlando et al., 1999), measuring aerosol growth from their photooxidation (Kroll et al., 2006; Ng et al., 2006), elucidating reaction pathways in terms of SOA formation (Kroll et al., 2005; Surratt et al., 2006; Szmigielski et al. 2007), and investigating their uptake kinetics onto particles (Nozière et al., 2006; Chen et al., 2008a; Zhao et al., 2010). Chamber experiments have demonstrated that MACR is an important intermediate in SOA formation whereas MVK was found to produce no SOA (Kroll et al., 2006; Surratt et al., 2006). However, the detailed mechanism of SOA formation from these two species via their aqueous oxidation remains uncertain. Tropospheric lifetimes (τ_{OH}) of MACR and MVK are estimated to be 6–10 h (Atkinson and Arey, 2003), thus enabling them to have great concentrations at higher altitudes (Henze et al., 2006) or encounter a cloud formation process in the air above boreal forests. Indeed, both of them have been observed in cloud droplets with high concentrations (i.e. $< \text{DL} \sim 0.5 \mu\text{M}$ for MACR and $0.02 \sim 0.2 \mu\text{M}$ for MVK, van Pinxteren et al., 2005), highlighting the importance of their aqueous photochemistry in SOA formation. To our knowledge, Claeys et al. (2004) put forth a possible route to SOA formation from aqueous-phase acid-catalyzed oxidation of MACR by hydrogen peroxide. Liu et al. (2009) studied the photooxidation of MACR in the aqueous phase under simulated cloud droplet conditions. They proposed that the radical chemistry could explain the products observed from OH-oxidation of MACR. El Haddad et al. (2009) investigated the fate of MACR in cloud evapo-condensation cycles, estimating that SOA yield ranged from 2 to 12%. Nozière et al. (2010) reported that sulfate salts could play important roles on the transformation of MACR/MVK to organosulfates in wet aerosols, when exposed to light. Up to date, the aqueous oxidation of MVK via OH radicals has not been experimentally studied.

Here we simulate experimentally the aqueous OH-initiated oxidation of MACR and MVK at pH and temperature values typical of atmospheric clouds. Small products were well characterized and evidence of high-molecular-weight compounds (HMWs) formation was presented. The product analysis provides useful information for elucidating the mechanism underlying aqueous reactions of MACR/MVK with OH radical. Based on the proposed mechanism, a detailed kinetic model was developed to better understand the in-cloud chemistry of these two carbonyls.

2 Experimental

2.1 Reagents and materials

The solutions were prepared using MACR (Alfa Aesar, 95+%); MVK (Avocado, 95+%); H_2O_2 (Sigma, 50% water solution); and H_2SO_4 (Beijing Chemical Plant, 98%) diluted in ultrapure water (Milli-Q). The initial concentrations of MACR, MVK, and H_2O_2 in the reactor were 0.2, 0.2, and 2 mM, respectively, in HPLC-UV and IC analysis. These values, which were \sim two orders of magnitude higher than those in atmospheric cloud droplets, were used to better characterize the possible products formed. The initial concentrations of reactants are ten times higher in HPLC-MS analysis for better characterizing the high molecular weight ions formed. The source and purity of each authentic standard for verifying possible products are: formaldehyde (Riedel-delaen, 36.5% solution), glyoxal (Sigma, 40% solution), methylglyoxal (Avocado, 40% solution), formic acid (Alfa Aesar, 97%), acetic acid (Alfa Aesar, 99.9985%), pyruvic acid (Avocado, 98%), oxalic acid (Alfa Aesar, anhydrous, 98%), and malonic acid (Alfa Aesar, 99.5+%).

2.2 Apparatus

The experiment was carried out in a 2.1 L quartz reactor. The OH radical source is the photolysis of hydrogen peroxide. The irradiation was performed by a Xenon arc lamp (300W, Perkin Elmer), which was mounted above the reactor. Temperature was controlled by circulating water in the jacket surrounding the reactor. The volume of the aqueous solution was 2 L. A 0.1 L gas space was left over the liquid level. Because of the existence of the top gas space, the upper limits for the loss of aqueous MACR and MVK were estimated to be $\sim 0.07\%$ and $\sim 0.01\%$, respectively, based on their Henry constants (i.e. 6.5 M atm^{-1} for MACR and 41 M atm^{-1} for MVK at 298 K) (Iraci et al., 1999). Therefore, the interference of gas-phase reactions can be eliminated.

2.3 Procedures

The aqueous reactions were carried out as close as possible to the conditions of atmospheric cloud droplets, namely, $T = 283 \text{ K}$ and $\text{pH} = 4$ (van Pinxteren et al., 2005, electronic supplementary material). Before the irradiation, reagents were introduced into the reactor and the aqueous mixture was magnetically stirred for 15 min. Reactants and products were pumped out of the reactor and analyzed periodically over the course of an experiment.

2.4 Control experiments

To verify that the observed products resulted from the aqueous OH-oxidation, five control experiments were conducted: (1) H_2O_2 (11 μM) + MACR (4.6 μM); (2) H_2O_2 (2 mM) + MVK (0.2 mM); (3) H_2O_2 (2 mM) + UV; (4) MACR

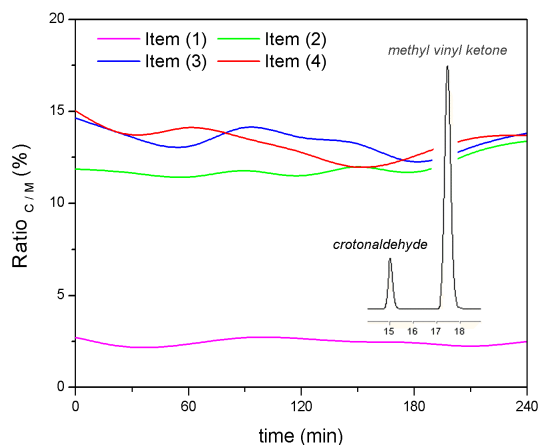


Fig. 1. Transformation of MVK in water solution. Item (1): 0.2 mM MVK in acetonitrile (pH=7); Item (2): 0.2 mM MVK in ultrapure water (pH=7); Item (3): 0.2 mM MVK + 2 mM H₂O₂ in ultrapure water (pH=7); and Item (4): 0.2 mM MVK + 2 mM H₂O₂ in ultrapure water (pH=4). (The inset figure is the HPLC-UV spectra of MVK dissolved in ultrapure water).

(0.2 mM) + UV; and (5) MVK (0.2 mM) + UV. In our previous study, we have confirmed that H₂O₂ has no significant effect on the transformation of MACR in darkness under our experimental condition (Zhang et al., 2009), likewise the fate of MVK, see items (3) and (4) in Fig. 1. The continuous photolysis of H₂O₂, which was extensively studied before, generates OH radicals directly. Figure S1 in the supplementary material shows that the model reproduces the time evolution of 2 mM H₂O₂ solution under photolysis. Note that the degradation rate of H₂O₂ is slightly lower than those together with MACR/MVK, indicating the competition for OH radicals between MACR/MVK and H₂O₂. As for the UV-irradiation case, the decay of MACR/MVK due to the photolysis is far slower than that by OH-oxidation, see Fig. S2 in the supplementary material, so MACR/MVK was consumed primarily by means of OH radicals not by direct photolysis.

To verify the stability of known products in hydrogen peroxide, two mixed standards were prepared: (1) formaldehyde (0.1 mM) + methylglyoxal (0.1 mM) + glyoxal (0.1 mM) + H₂O₂ (2 mM) + H₂SO₄ (0.05 mM); and (2) formic acid (0.1 mM) + acetic acid (0.1 mM) + pyruvic acid (0.1 mM) + oxalic acid (0.1 mM) + H₂O₂ (2 mM) + H₂SO₄ (0.05 mM). Samples were kept in 283 K in darkness until analysis by HPLC-UV or IC. The results show that the effect of H₂O₂ on the stability of carbonyls is insignificant, see Fig. S3 in the supplementary material. However, rapid pyruvic acid loss occurs within 10 min and in the meantime, acetic acid concentration substantially increases, as shown in Fig. S4 in the supplementary material. The rapid transformation of pyruvic acid to acetic acid in H₂O₂ solution, which is consistent with previous studies (Carlton et al., 2006), can explain the unexpected loss of pyruvic acid over the course of OH oxidation.

2.5 Product analysis

In the present study, the carbonyl compounds were analyzed by determining their derivatives of 2, 4-dinitrophenylhydrazine (DNPH) using high-performance liquid chromatography (HPLC) instrument (Agilent 1100, USA) equipped with an ultraviolet detector. The peroxides were determined on the basis of fluorescent analysis by HPLC instrument (Agilent 1100, USA) with post-column derivation, involving the hemin-catalyzed oxidation of peroxides to a fluorescent derivative using hydroxyphenylacetic acid (Hua et al., 2008). The organic acids were analyzed using ion chromatography (DIONEX 2650, USA) equipped with an ED50 conductivity detector. An AS11 column (4 mm) with an AG11-HC (4×50 mM) guard column and an Anion Trap column (ATC-3, 9×24 mm, for 4 mM) were used for anion detection. The sampling volume was 100 mL, and the eluting solution was 0.4–6 mM NaOH (gradient) with a flow rate of 1.2 mL/min. The detection limits of carbonyl compounds in ultrapure water solution can be found in our previous work (Wang et al., 2009); the detection limit of hydrogen peroxide in ultrapure water solution is 0.02 μM; the detection limits of formic, acetic, pyruvic, oxalic, and malonic acid in the ultrapure water solution are 0.08, 0.1, 0.5, 0.04, and 0.4 μM, respectively. In addition, a HP 1100 LC-MS Trap SL System (Agilent, USA) consisting of a series 1100 HPLC and an ion trap mass spectrometer equipped with electro-spray interface (ESI) was used to determine the HMWs. The chromatographic isocratic separations were performed on a LC column (Agilent ZORBAX SB-C18, 2.1×150 mm, 5 μm) at 26 °C, the mobile-phase was methanol/water mixture (40/60, v/v) at a flow rate of 0.25 mL/min. The electro-spray ionization was performed in the positive/negative ion mode under optimum conditions as follows: capillary voltage 3500 V, nebulizer pressure 35.0 psi, dry gas flow rate 8.0 L min⁻¹ and dry gas temperature 330 °C. Full scan mode was used to acquire the MS spectra of the HMWs with a scan range of m/z from 35 to 300.

2.6 Modeling methodology

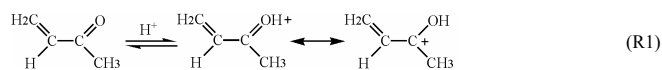
A box model was performed using the aqueous OH-oxidation mechanism elucidated in Section 3.3. This specific mechanism, which is on the basis of CAPRAM 3.0 developed by Herrmann et al. (2000) and updated by Herrmann et al. (2005), includes 64 aqueous reactions involving MACR/MVK and their small products, in addition to 2 photolysis reaction, as listed in Table S1 that can be found in the supplementary material. The initial MACR/MVK, H₂O₂ and O₂ concentrations input were 0.2, 2, and 0.36 mM, respectively, representing those used in the experiments. The simulation was carried out on a 10-min basis and preceded for 7 h. Modeled OH radical concentrations over the course of experiments were on average 1.5×10⁻¹² – 2.0×10⁻¹² M

(Fig. S5 of the supplementary material), which were comparable with Tan et al. (2009).

3 Results and discussion

3.1 Transformation of MVK

As shown in Fig. 1, two peaks were found in the liquid chromatogram of MVK-DNPH derivative, indicating that in addition to MVK, another carbonyl coexisted in the experiment elute. This unknown carbonyl has been identified as crotonaldehyde, an isomeric compound of MVK (Wang et al., 2009). In order to avoid the analytical artifacts, four sets of solutions were prepared in darkness: (1) 0.2 mM MVK in acetonitrile (pH=7); (2) 0.2 mM MVK in ultrapure water (pH=7); (3) 0.2 mM MVK + 2 mM H₂O₂ in ultrapure water (pH=7); and (4) 0.2 mM MVK + 2 mM H₂O₂ in ultrapure water (pH=4). The temporal profile of solution (1), see Fig. 1, shows that the amount of MVK that transformed to crotonaldehyde in acetonitrile is to be minus, indicating that the observed transformation did not result from the analytical procedure. On the other hand, approximately one seventh of MVK dissolved in water turned into crotonaldehyde regardless of whether H₂O₂ or sulfuric acid was added, suggesting the potentially important role of water in inducing this transformation. Based on the generic hydration that has been studied previously (Nozière et al., 2006), the hydrolysis of MVK is proposed as follows (R1).



The subsequent formed carbonium ion is an important intermediate, through which the skeletal rearrangement are known to occur under certain conditions. Mechanisms for rearrangements of aliphatic ketones with sulfuric acid catalysis mainly involve the shift of conjugate acid hydroxyl group to an adjacent carbon atom (Barton et al., 1952), the shift of the carbonyl oxygen to an adjacent carbon atom (Zook et al., 1955), and the alkyl group shift (Rothrock and Fry, 1958). Application of the above mechanisms to MVK transformation leads to the prediction that the methyl group would exchange with a hydrogen atom of the vinyl group. However, it is impossible to exclude other pathways resulting in the rearrangement of MVK in the absence of catalysis. Further study is needed to elucidate mechanisms for the transformation of MVK to crotonaldehyde.

3.2 Identification of low-molecular-weight products

Products identified chromatographically in the OH-oxidation of MACR are formaldehyde (FA), methylglyoxal (MG), formic acid (FOA), acetic acid (AA), pyruvic acid (PA), and oxalic acid (OA). These observations are generally consistent with Liu et al. (2009), in which FA, MG, PA, and OA

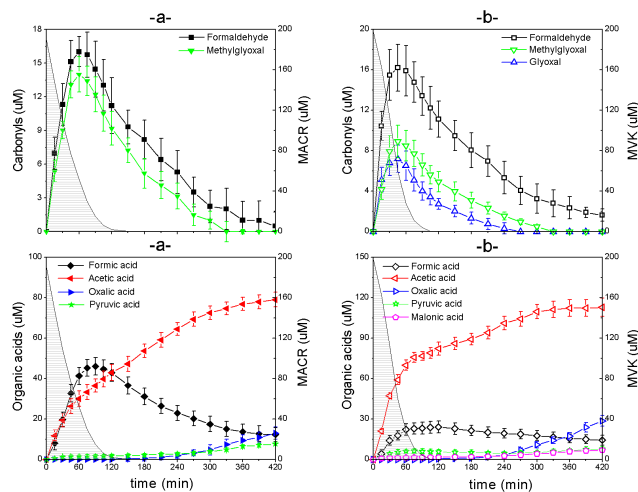


Fig. 2. Temporal concentration profiles of reactants and products in the aqueous OH-oxidation of (a) MACR, and (b) MVK (283 K, pH=4.0).

were identified as well. In addition to these products, glyoxal (GL) and malonic acid (MA) are detected in the MVK–OH reaction system. It is not surprising for the oxalic acid formation in view of previous laboratory and model results, which confirmed that the aqueous phase oxidation of pyruvic acid, glyoxal, and methylglyoxal produced oxalic acid (Lim et al., 2005; Carlton et al., 2007; Altieri et al., 2008). The detection of malonic acid is less expected, although this observation is in agreement with a recent study. Perri et al. (2009) reported that malonic acid was a product of the OH-oxidation of glycolaldehyde, which can be derived from the MVK–OH reaction mechanism proposed in Sect. 3.4. A pattern of kinetic curves for the aqueous oxidation of MACR via OH radical at pH 4 and 283 K is shown in Fig. 2a. Once the irradiation begins, MACR concentration decreases and various products form immediately. Based on the shape of growth curves, all the products can be classified into two different groups. One group includes formaldehyde, methylglyoxal and formic acid. Their concentrations are observed to decrease rapidly once MACR is depleted. On the contrary, concentrations of acetic acid, pyruvic acid, and oxalic acid continue to increase or reach a plateau even after MACR disappearance, indicating that reactions other than the initial MACR oxidation can give these compounds as well. Similar results for the MVK–OH reaction are shown in Fig. 2b.

3.3 Evidence for HMWs formation

In addition to the small products, we also observed some compounds that are of a higher molecular weight than reactants. These compounds were not detected in a standard mixture including MACR, MVK, FA, GL, MG, FOA, AA, PA, OA, and MA, suggesting they are not artifacts during analytical procedures. The HPLC-MS spectra for selected

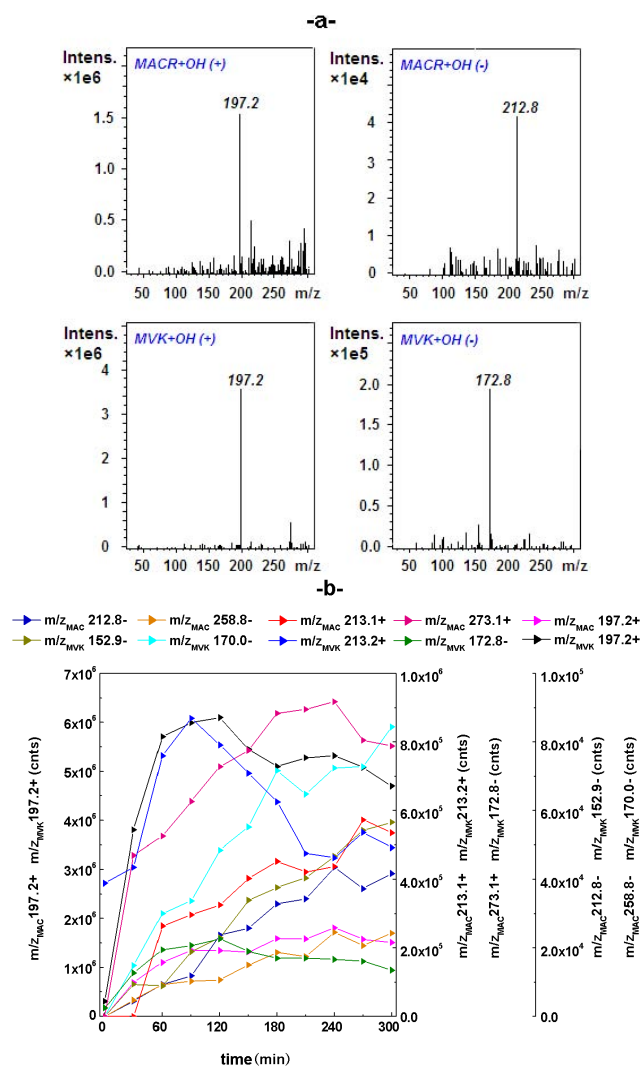


Fig. 3. Characteristics of high-molecular-weight ions (HMWs): **(a)** Selected HPLC-MS spectra of HMWs (The retention time of HMWs formed from MACR-OH reactions in positive and negative mode is ~ 3 – 5 and ~ 2 – 4 min, respectively. The retention time of HMWs formed from MVK-OH reactions in positive and negative mode is ~ 3 – 5 and ~ 2 – 4 min, respectively.); **(b)** Evolution of selected HMWs from MACR/MVK-OH reactions.

high-molecular-weight ions in both positive and negative modes are shown in Fig. 3a. Most ions are distributed in the m/z range of 150–300. The time series of dominating HMWs are shown in Fig. 3b. The concentrations of HMWs increase rapidly in the beginning, and then, reach a plateau or decrease after 4 h reactions, indicating that they are sensitive to the photooxidation. This study provides evidence that the aqueous MACR/MVK oxidation produces HMWs. It should be noted the initial MACR/MVK concentration of 2 mM used in the HPLC-MS analysis is much higher than that can be expected in cloud droplets. Tan et al. (2009) have revealed a strong dependence of the oligomer formation on the ini-

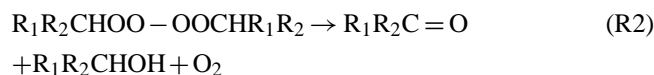
tial precursor concentration in the aqueous OH-oxidation of glyoxal. The glyoxal HMW production from the MVK-OH reaction, in which glyoxal is formed with a high yield as reported in our experiments, might need to consider this concentration effect.

3.4 Mechanisms

Mechanisms specific to the aqueous OH-initiated oxidation of reactive species mainly include acid catalyzed chemical processes and radical chemistry. Altieri et al. (2008) proposed an acid catalyzed esterification pathway to explain the oligomer formation from reactions of methylglyoxal with OH. Liu et al. (2009) proposed that the radical chemistry contribute to the products from the OH-oxidation of MACR. More recently, the radical reaction mechanism has been employed to explain the organosulfates formation from aqueous reactions of sulfate radicals and organic compounds in the presence of light (Nozière et al., 2010; Perri et al., 2010). In this study, we suggest that the observed small products primarily result from free radical processes, see schemes in Figs. 4 and 5.

3.4.1 MACR-OH

The first step of MACR-OH reaction invariably includes terminal and central OH addition, and the aldehydic hydrogen atom abstraction by OH. The electrophilic addition of OH produces two carbon-centered hydroxyl-containing radicals, followed by a sequence of rapid reaction with dissolved O_2 . The peroxy radicals (RO_2) react primarily with NO, HO_2 , NO_3 , and other RO_2 in the atmosphere (Finlayson-Pitts and Pitts, 2000), while the self-reaction of RO_2 become dominant in the aqueous phase. In principle, one expects a tetroxide structure ($ROOOOR$)* to be formed, which would decompose by four pathways, see Reaction (R2). This process has been extensively studied by von Sonntag and Schuchman (1997). The R_1R_2CHO radical formed via the second channel of Reaction (R2) is an important intermediate, and its dominating fate in the aqueous phase is the scission of C–C bond, producing the observed formaldehyde, methylglyoxal, acetic acid, together with some free radicals. These radicals could be the origin of formic acid. Oxalic acid and pyruvic acid are mainly from the further oxidation of first generation products.



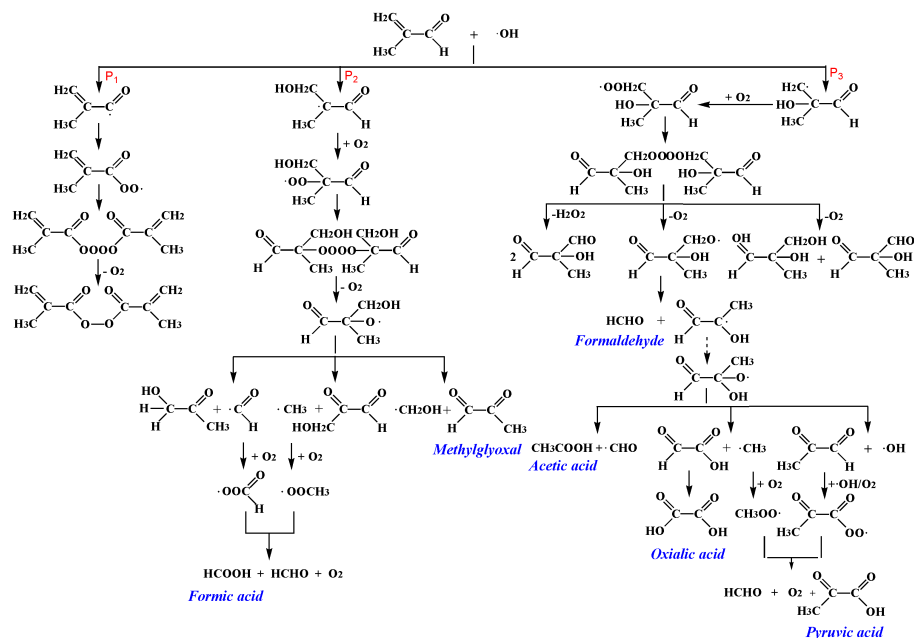


Fig. 4. Scheme for the tentatively proposed reaction pathways leading to the observed products from the MACR–OH reaction.

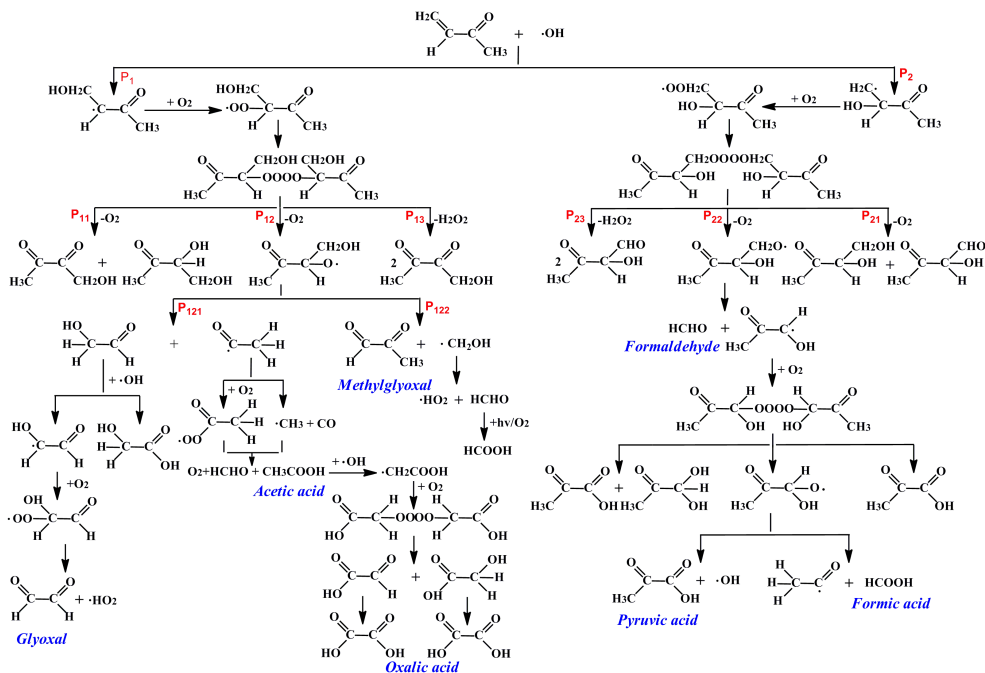


Fig. 5. Scheme for the tentatively proposed reaction pathways leading to the observed products from the MVK–OH reaction.

3.4.2 MVK–OH

In analogy to MACR, OH attacks MVK at the central and terminal carbon atoms of the double bond (reaction pathways denoted P1 and P2) to form two carbon-centered hydroxyl-containing radicals, which are then oxidized by O_2 to pro-

duce RO_2 radicals. As discussed earlier, in a water cage, the self-reaction of RO_2 radicals occurs, giving a tetroxide structure, which will decompose via four pathways, see Reaction (R2). Here we focus on the RO radical formation channel, namely, P12 and P22.

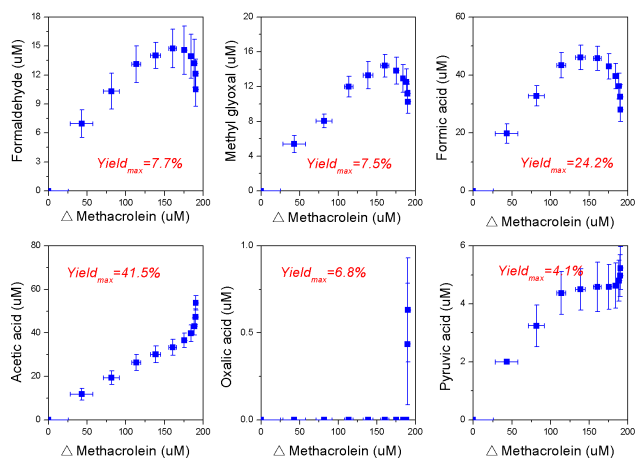
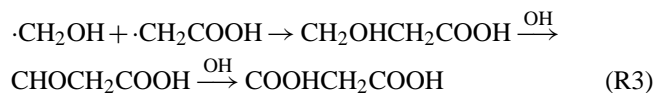


Fig. 6. Yields of low-molecular-weight products from the OH-oxidation of MACR.

For pathway P12, two types of RO radical decomposition are proposed, creating glycolaldehyde (P121) and methylglyoxal (P122), respectively. Glycolaldehyde contains a hydroxyl group adjacent which the abstraction of H atom by OH radical is more likely to occur, followed by a rapid O₂ addition. The resulting RO₂ radical, undergoing the elimination of HO₂, yields glyoxal. The oxidation of glycolaldehyde also leads to glycolic acid. As mentioned earlier, malonic acid formation from the OH-oxidation of glycolaldehyde has been reported, thus providing support that the observed malonic acid in our MVK–OH reaction system is reasonable. We assume that the combination of free radicals can probably give an explanation (Reaction R3). Accompanying glycolaldehyde, CH₃CO radical is produced, and its further oxidation leads to acetic acid and subsequently, oxalic acid. As for methylglyoxal, its degradation initiates via the abstraction of aldehydic H-atom by OH radical, producing pyruvic acid. Lim et al. (2005) proposed that a part of methylglyoxal contributed to the oxalic acid formation via glyoxylic acid, while the current mechanism did not include this route. Pathway P22 mainly results in formaldehyde, formic acid, and pyruvic acid, via similar pathways as P12.



3.5 Product yields

A series of experiments for the aqueous OH-oxidation of MACR/MVK were carried out at two controlled pH values (pH=4.0 and 7.0). It turns out that the acidity has no significant effect on the molar yields of small products. Here the molar yield is defined as the ratio of the production molar amount of a product versus the consumption molar amount of a reactant (MACR/MVK). As shown in Fig. 6, the primary

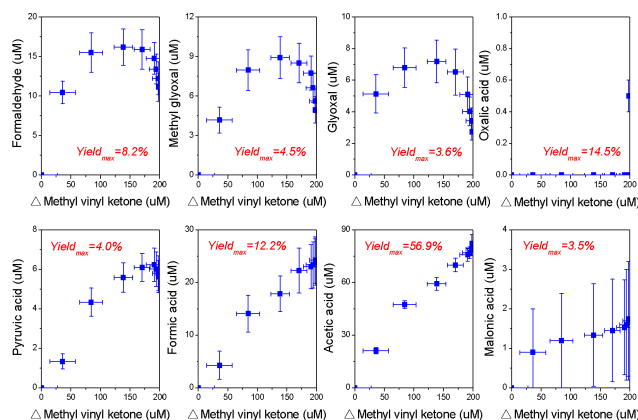


Fig. 7. Yields of low-molecular-weight products from the OH-oxidation of MVK.

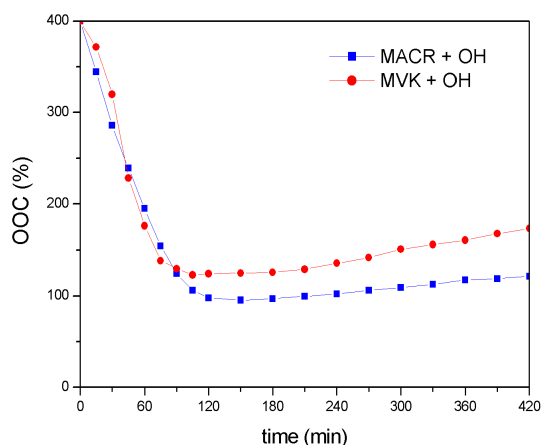


Fig. 8. Total organic carbon balance from the OH-oxidation of MACR and MVK.

intermediates are formaldehyde, formic acid and methylglyoxal, while oxalic acid is apparently produced later because its concentration starts to accumulate after MACR is consumed. Acetic acid and pyruvic acid can be regarded as both first and secondary-generation products, since their concentrations are continuously increasing. The yields of formaldehyde, methylglyoxal and acetic acid after 0.2 mM MACR was fully consumed are comparable with results in Liu et al. (2009). When calculating molar yields for the MVK oxidation, we have taken into account the fraction of MVK that transformed to crotonaldehyde, see Fig. 7.

Based on the calculated molar yields, the observed organic carbon (OOC, defined as the sum of dissolved organic carbon molar yields) was estimated here, taking the observed carbonyls and organic acids as the only products present in these two reaction systems (R4). As shown in Fig. 8, the amount of OOC at longer irradiation time is much lower than the initial value, indicating that a significant portion of products were not characterized in this study. These

missing products primarily possibly include organic peroxides. Moreover, some compounds, like formic acid, will be completely oxidized into CO_2 and H_2O , which are difficult to measure in the aqueous phase. In Liu et al. (2009), the total carbon yields were also far from being balanced and they suggested that the non qualified oligomers could explain the lack of carbon. OOC values begin to increase at 3 h because a substantial amount of organic acids are created. Since first-generation intermediates are almost consumed, some reaction routes involving multi-functional compounds might lead to their production. As shown in Fig. 3, most HMWs reach a plateau or begin to decrease after ~ 3 h of reaction, shedding light on the possibility that further degradation of HMWs contribute to the organic acid formation.

$$\text{OOC}_{\text{MACR}}(\%) = 4 \times [\text{MACR}_{\text{yield}}] + [\text{FA}_{\text{yield}}] + \quad (\text{R4})$$

$$3 \times [\text{MG}_{\text{yield}}] + [\text{FOA}_{\text{yield}}] + 2 \times [\text{OA}_{\text{yield}}] + 3 \times [\text{PA}_{\text{yield}}]$$

$$\text{OOC}_{\text{MVK}}(\%) = 4 \times [\text{MVK}_{\text{yield}}] + [\text{FA}_{\text{yield}}] +$$

$$2 \times [\text{GL}_{\text{yield}}] + 3 \times [\text{MG}_{\text{yield}}] + [\text{FOA}_{\text{yield}}] + 2 \times [\text{OA}_{\text{yield}}] +$$

$$3 \times [\text{PA}_{\text{yield}}] + 3 \times [\text{MA}_{\text{yield}}]$$

Both MACR–OH and MVK–OH reactions generate dicarboxylic acids, which are recognized as precursors of SOA. The SOA yield, defined as the ratio of the mass concentration of aerosol formed to that of MACR/MVK reacted, increases significantly with the reaction time. The maximum values are 8.8% from MACR–OH and 23.8% from MVK–OH after 7 h reaction, if the partition efficiency of both oxalic and malonic acid was estimated as 100%. It should be noted that the estimated SOA yield in this study cannot be completely applied to atmospheric clouds conditions, for the following three reasons. (i) The observed HMWs were not considered in the calculation. (ii) All dicarboxylic acids react further with OH to form smaller acids (Ervens, et al., 2008), resulting in a decrease of the total SOA mass. (iii) SOA production will be interrupted by evapo-condensation cycles, considering that the lifetime of an individual cloud droplet is only a few minutes. However, these SOA formation pathways might continue during water evaporation (El Haddad, et al., 2009).

3.6 Modeling

Based on the assumed mechanism and a set of known reaction rate constants, we have conducted a kinetic simulation of these two reaction systems. As shown in Figs. 9 and 10, the temporal profiles of first-generation intermediates, namely, formaldehyde, glyoxal, methylglyoxal, and formic acid are predicted with reasonable agreement to the experimental data. But the model failed to simulate the kinetics of acetic, pyruvic and oxalic acid. Note that the measured concentrations of acetic and pyruvic acid were still increasing after 3-h reaction, when first-generation intermediates were

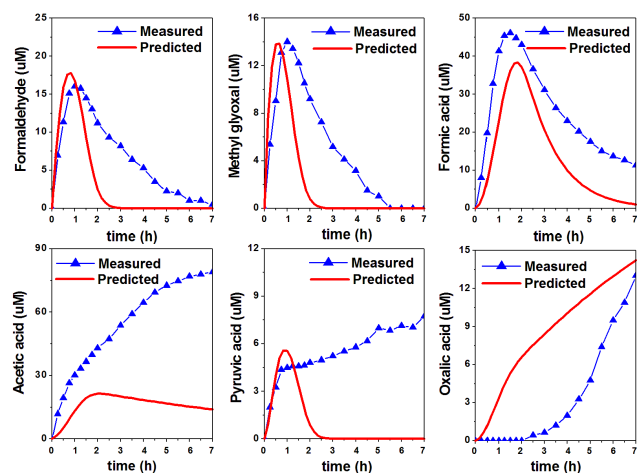


Fig. 9. Measured and predicted concentrations of small products from the MACR–OH reaction.

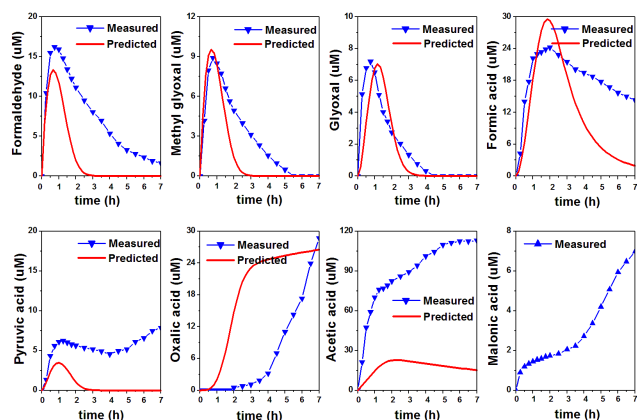


Fig. 10. Measured and predicted concentrations of small products from the MVK–OH reaction.

insufficient to be responsible for their formation. We suggest the decomposition of HMWs probably accounted for the subsequent growth of these organic acids. This hypothesis can be supported by the HPLC–MS analysis of products, see Fig. 3b, showing that HMWs stop growing at longer irradiation time. To the best of our knowledge, Carlton et al. (2007) expanded mechanisms for the aqueous photooxidation of glyoxal by adding simplified reactions of larger multifunctional species and they found these reactions appear to be responsible for most of the oxalic acid production. Thus, detailed mechanisms involving reaction rate constants for specific HMWs are needed to be incorporated in our model for better explaining our observations.

As for oxalic acid, the shape of simulated kinetic curve was not consistent with the observed one, even though the model reproduced its concentrations to more than 85% in both two reactions. The aqueous mechanism in our box model has offered three channels to the oxalic acid

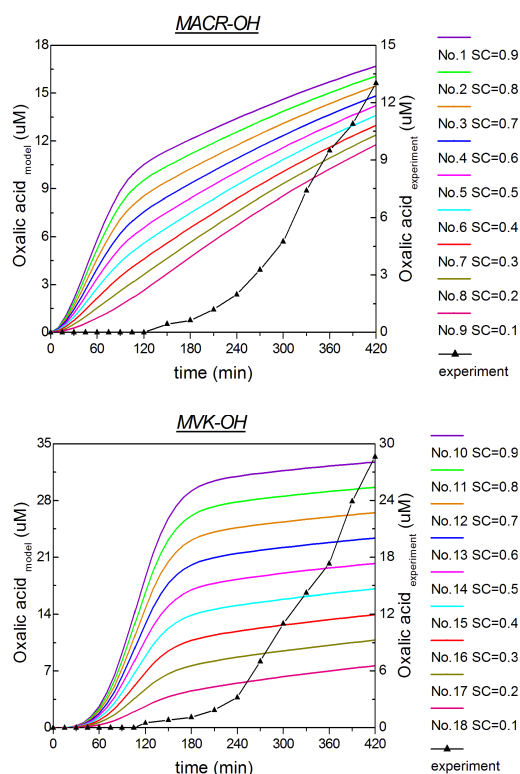


Fig. 11. Evaluation of the effect of stoichiometric coefficients (SC) of glyoxylic acid and glycolaldehyde on the oxalic acid yield (simulation No. 1–9 for MACR–OH and simulation No. 10–18 for MVK–OH).

formation. The first one originates from H-atom abstraction of acetic acid by OH, the second starts with glycolaldehyde via either glycolic acid or glyoxal as an intermediate, and the third begins directly from glyoxylic acid. Since the decomposition rate of acetic acid is slow, the last two channels become the major contributor to oxalic acid. To our knowledge, the stoichiometric coefficients for the formation of glycolaldehyde and glyoxylic acid are not known, thus can be treated as adjustable parameters. A sensitivity analysis was undertaken and 18 simulations (No. 1–9 for MACR–OH and No. 10–18 for MVK–OH) were performed under different stoichiometric coefficients, namely, from 0.1 to 0.9. Figure 11 shows the model responses, represented by oxalic acid concentrations as a function of time. On the one hand, higher stoichiometric coefficients lead to higher oxalic acid yields. On the other hand, the shape of simulated kinetic curves tends to resemble the observed one at lower stoichiometric coefficients. This discrepancy can be ascribed to the competition for OH radicals between oxalic acid precursors and other reactive species. In this manner, in order to better simulate oxalic acid both in shape and dose, we suggest that the three channels in our model were possibly not the dominating oxalic acid formation pathways and other routes, like the

decomposition of HMWs, potentially play an important role in the oxalic acid production. Confirmation of this hypothesis, however, needs corresponding measurement for kinetics of OH-initiated reactions and detailed characterization of HMWs.

4 Conclusions and implications

An experimental study of the aqueous OH-oxidation of MACR and MVK at cloud relevant conditions is reported in this work. We propose that the reaction of MACR/MVK with OH radical is dominated by radical processes giving rise primarily to low-molecular-weight products, including the SOA precursor dicarboxylic acids. Notably, the formation of malonic acid from MVK is unexpected, highlighting the importance of aqueous MVK chemistry in SOA formation. These two reactions also generate HMWs, which contribute SOA upon droplet evaporation. It is interesting to note that MVK will transform, at least in part, to its isomer crotonaldehyde in water phase, increasing the variety of products and complicity of mechanisms in the real atmosphere. Based on the proposed mechanisms, a box model was used to simulate the kinetics of small products. Model predictions which were in good agreement with experimental observations were first-generation intermediates. However, concentrations of organic acids simulated were much lower than those measured at longer irradiation time, indicating that some additional chemistry might be responsible for the continuous production of organic acids. We also made a sensitivity analysis for the yield of oxalic acid and the simulation results suggest the decomposition of HMWs might contribute significantly to its formation.

This work adds to the increasing body of literatures that cloud processing contributes to the SOA formation in the atmosphere. In addition, the chemical pathways proposed in this study are mostly applicable to aqueous particles. Considering the higher concentrations of dissolved particle constituents and longer lifetime of aqueous particles (Ervens and Volkamer, 2010), the aqueous MACR/MVK oxidation should play a more important role in atmospheric chemistry than expected before. The SOA mass yield evaluated in this study is supposed to be less than the amount produced in real clouds because we cannot rule out the possibility that pathways involving HMWs account for a significant fraction of SOA in the aqueous phase. Detailed mechanism is still needed so that they can be incorporated into kinetics models to better predict SOA formation from cloud processing.

Supplementary material related to this article is available online at:
<http://www.atmos-chem-phys.net/10/9551/2010/acp-10-9551-2010-supplement.pdf>.

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