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CONTENTS

Uptake of isoprene, methacrylic acid and methyl methacrylate into aqueous solutions of sulfuric acid and hydrogen peroxide

Ze Liu[1,2], Maofa Ge[1,*], Weigang Wang[1,*]

1. Beijing National Laboratory for Molecular Science (BNLMS), State Key Laboratory for Structural Chemistry of Unstable and Stable Species,
Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. E-mail: liuze@iccas.ac.cn
2. Beijing National Laboratory for Molecular Science (BNLMS), Peking University, Beijing 100871, China

Abstract

Multiphase acid-catalyzed oxidation by hydrogen peroxide has been suggested to be a potential route to secondary organic aerosol formation from isoprene and its gas-phase oxidation products, but the lack of kinetics data significantly limited the evaluation of this process in the atmosphere. Here we report the first measurement of the uptake of isoprene, methacrylic acid and methyl methacrylate into aqueous solutions of sulfuric acid and hydrogen peroxide. Isoprene cannot readily partition into the solution because of its high volatility and low solubility, which hinders its further liquid-phase oxidation. Both methacrylic acid and methyl methacrylate can enter the solutions and be oxidized by hydrogen peroxide, and steady-state uptake was observed with the acidity of solution above 30 wt.% and 70 wt.%, respectively. The steady-state uptake coefficient of methacrylic acid is much larger than that of methyl methacrylate for a solution with same acidity. These observations can be explained by the different reactivity of these two compounds caused by the different electron-withdrawing conjugation between carboxyl and ester groups. The atmospheric lifetimes were estimated based on the calculated steady-state uptake coefficients. These results demonstrate that the multiphase acid-catalyzed oxidation of methacrylic acid plays a role in secondary organic aerosol formation, but for isoprene and methyl methacrylate, this process is not important in the troposphere.

Key words: multiphase acid-catalyzed oxidation; uptake; steady-state uptake coefficient; secondary organic aerosol

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Introduction

Secondary organic aerosol (SOA) accounts for a significant fraction of ambient tropospheric aerosol and receives considerable attention due to its links to climate change and adverse health effects (Pöschl, 2005; Rosenfeld, 2006; Hallquist et al., 2009). SOA scatters and/or absorbs solar and terrestrial radiation directly, and also influences cloud formation indirectly as cloud condensation nuclei. As a result, SOA markedly affects the radiative balance in Earth's atmosphere and plays a central role in climate (IPCC, 2007). SOA also has an important impact on human health and it is now well established that exposure to SOA is associated with damaging effects on the respiratory and cardiovascular systems (Harrison and Yin, 2000; Davidson et al., 2005; Pope and Dockery, 2006). However, there are uncertainties in the true impact of atmospheric aerosols on climate and health because of a lack of information on the kinetics and mechanism of SOA formation.

Field experiments showed a large amount of 2-methyltetrols was formed under high NO$_x$ conditions, which could not be explained by the existing

photooxidation mechanism of isoprene (Claeys et al., 2004a, 2004b). Thus, a new mechanism of multiphase acid-catalyzed oxidation by hydrogen peroxide (H$_2$O$_2$) was proposed by Claeys et al. (2004b) to support the field results. They did a series of experiments by reacting isoprene and its oxidation products with H$_2$O$_2$ in an acidic aqueous solution and found 2-methyltetrols and 2,3-dihydroxymethacrylic acid to be produced. In the troposphere the acidity of aerosols changes drastically, ranging from 60 wt.% to 80 wt.% in the upper troposphere to less than 1 wt.% in the lower troposphere (Cobourn et al., 1980; Ferek et al., 1983; Curtius et al., 2001). H$_2$O$_2$ in ambient air can enter aqueous aerosols and exist with an appreciable concentration due to its high gas-phase concentration and high solubility in water (Hasson and Paulson, 2003). In addition, H$_2$O$_2$ can be produced through aqueous-phase reactions (Anastasio et al., 1994; Valverde-Canossa et al., 2005; Chen et al., 2008). Therefore, it seems to be logical to assume that such reactions may contribute to SOA formation. However, the importance of this process in the atmosphere cannot be evaluated due to the lack of kinetics data. The formation of the 2-methyltetrols through this mechanism was also observed in a subsequent aerosol chamber

* Corresponding author. E-mail: gemaofa@iccas.ac.cn (Maofa Ge); wangwg@iccas.ac.cn (Weigang Wang)

experiment, from which it was also difficult to estimate the importance of the reaction for the real atmosphere (Böge et al., 2006). Thus, it is necessary to study the kinetics of this multiphase acid-catalyzed oxidation.

Isoprene, with a global emission of 500–750 Tg/yr, is the most representative biogenic volatile organic compound (Guenther et al., 2006). Because of its two double bonds, isoprene is highly reactive and is readily oxidized in the atmosphere by OH, NO_3 and O_3. In recent years, many field (Claeys et al., 2004a; Edney et al., 2005; Kleindienst et al., 2007) and laboratory (Kroll et al., 2005, 2006; Kleindienst et al., 2006; Ng et al., 2008) studies have indicated that isoprene oxidation may indeed contribute to the formation of SOA in the atmosphere. Even if the yield is minor, the overall contribution of isoprene to SOA could be large owing to the large global source strength. Methacrylic acid is a gas-phase product from the ozonolysis of isoprene (Jacob and Wofsy, 1998; Chien et al., 1998; Williams et al., 2001; Orzechowska and Paulson, 2005), and the mixing ratios are of the order of 100 pptv (Suzuki, 1997). Methyl methacrylate is widely used in polymer and resin production, and the sources of its emission are numerous such as manufacturing of plastics, aircraft and electronic components (Graedel, 1978). In this work we studied the uptake kinetics of isoprene, methacrylic acid and methyl methacrylate into aqueous solutions of sulfuric acid (H_2SO_4) and H_2O_2. The steady-state uptake coefficients were determined for the first time, and the atmospheric implication was discussed.

1 Materials and methods

1.1 Chemicals

Isoprene (95%, Alfa Aesar), methacrylic acid (95%, Alfa Aesar), methyl methacrylate (95%, Alfa Aesar), H_2SO_4 (> 96 wt.%, Beijing Chemical Reagents Company) and H_2O_2 (30 wt.% aqueous solution, Beijing Chemical Reagents Company) were used as purchased. The reactant gases were prepared individually. Isoprene was injected into an evacuated 15 L glass flask to 7.6 Torr and pressurized with pure helium to 2 atm. For methacrylic acid or methyl methacrylate, the vapor was entrained by a small helium flow and introduced into the main flow. The aqueous solutions of H_2SO_4 and H_2O_2 were prepared by mixing ultrapure water (with resistivity of 18 MΩ·cm) with H_2SO_4 and H_2O_2. The solution was replaced after each experiment.

1.2 Apparatus

All the uptake measurements were performed by using a rotated wetted wall reactor (RWWR) coupled to a single-photon ionization time of flight mass spectrometer (SPI-TOFMS). This equipment had been built and used in our previous work (Liu et al., 2010, 2011), here is a brief description. The RWWR consisted of a horizontal glass flow reactor and a rotating inner cylinder (length L = 30 cm, inner radius R = 1.25 cm). A small volume of solution (ca. 3.5 mL, corresponding to a film thickness of

ca. 0.15 mm) was placed in the inner cylinder, which was rotated at 10–15 r/min to maintain an even liquid film on the wall. A glass stirring bar rested on the bottom of the inner cylinder to make sure that the solution was mixed and spread sufficiently. A mixture of helium and water vapor in equilibrium with the solution was used as carrier gas so that the change of solution composition could be avoided during one experimental period of time. Reactant gas was introduced into the main flow at a small flow rate (ten percent or less of the carrier gas) through a movable injector. The movable injector centered in the RWWR allowed for the variation of the contact distance between reactant gas and solution. Typically, the total pressure was 15–65 Torr and the temperature was 298 K. In this work, the measurements were operated under approximate laminar flow conditions.

The variation of reactant gas concentration during uptake was monitored by SPI-TOFMS. The reactant gas was ionized by a 118 nm vacuum ultraviolet (VUV) laser, which is a soft ionization technique with single-photon energy of 10.5 eV. The VUV laser was generated by focusing the third harmonic (355 nm, ca. 30 mJ per pulse) of a Nd:YAG laser in a tripling cell that contained about a 250 Torr argon/xenon (10/1) gas mixture. To separate the VUV laser beam from the 355 nm fundamental beam, a magnesium fluoride prism (apex angle = 6°) was inserted in the laser beams. In this case, one is quite sure that the mass signal was generated by ionization purely through the VUV laser radiation with gentle power (ca. 1 μJ per pulse, pulse duration ≈ 5 nsec). For each of the three reactant gases, only the molecular ion peak was observed. The intensity of the molecular ion peak was recorded to investigate the uptake kinetics.

1.3 Calculation of steady-state uptake coefficients

To quantify the uptake kinetics, the steady-state uptake coefficient (γ_{ss}), defined as the probability that the gas-phase molecule will be taken up irreversibly by the liquid (Howard, 1979), was calculated when an irreversible component was observed in the uptake experiment. The calculation method was described as follows:

As an uptake experiment began, the movable injector was placed at its maximum position downstream. In that situation the solution was unexposed, and the unperturbed concentration of reactant gas could be obtained as the original signal, S_0. Then the injector was pulled upstream to expose the solution to the reactant gas. The steady-state uptake was indicated by a constant offset between the original signal and the steady-state uptake signal with time, S. The observed first-order rate constant for removal of the reactant gas from the gas phase, k_{obs} (sec^{-1}), was calculated from Eq. (1):

$$\ln(\frac{S}{S_0}) = -k_{obs}\frac{L}{v_{ave}} \tag{1}$$

where, L (cm) is the contact distance of the reactant gas and the solution, and v_{ave} (cm/sec) is the average gas flow velocity of the reactant gas. k_{obs} was determined more accurately by placing the injector at various positions in the

reactor to change the contact distance. The rate constant for removal of the reactant gas, k (sec^{-1}), can be determined by correcting k_{obs} for diffusion (Murphy and Fahey, 1987; Hanson et al., 1992; Gershenzon et al., 1995):

$$\frac{1}{k} = \frac{1}{k_{obs}} - \frac{1}{k_{diff}} \qquad (2)$$

$$k_{diff} = \frac{3.66 D_i}{R^2} \qquad (3)$$

where, R (cm) is the inner radius of the rotating cylinder, D_i (cm^2/sec) is the diffusion coefficient which can be calculated from the Huller-Schettler-Gidding method (Fuller et al., 1966), and k_{diff} is the diffusion-limited rate (sec^{-1}). Finally, γ_{ss} can be determined from

$$\gamma_{ss} = \frac{4kV}{\omega A} \qquad (4)$$

where, ω (m/sec) is the mean molecular speed of the reactant gas, V (cm^3) is the volume of the reaction zone, and A (cm^2) is the geometric area of the exposed solution.

2 Results

For all three compounds, the uptake into both H_2SO_4 solutions and H_2SO_4/H_2O_2 mixed solutions was studied to make sure that the steady-state uptake were caused by multiphase acid-catalyzed oxidation. Each compound exhibited different uptake behavior from the other two, which is described here respectively.

2.1 Isoprene

Acid-catalyzed reactions with H_2O_2 can proceed for compounds that contain a C=C double bond and/or an aldehyde function. Isoprene, which has two C=C double bonds, should be highly reactive. However, no uptake behavior was observed in the uptake measurements over the acidity range of 0 wt.% to 80 wt.%. Figure 1 shows the signal intensity of isoprene during the uptake experiments into 80 wt.% H_2SO_4 solution (Fig. 1a) and 80 wt.%+1 wt.% H_2O_2 solution (Fig. 1b). After the first 90 sec, the injector was pulled toward the upstream and the isoprene was exposed to solution. The exposure was stopped at the 290 sec point by pushing the injector back. The signal intensity stayed constant, demonstrating that the uptake did not occur when isoprene was exposed to the solutions.
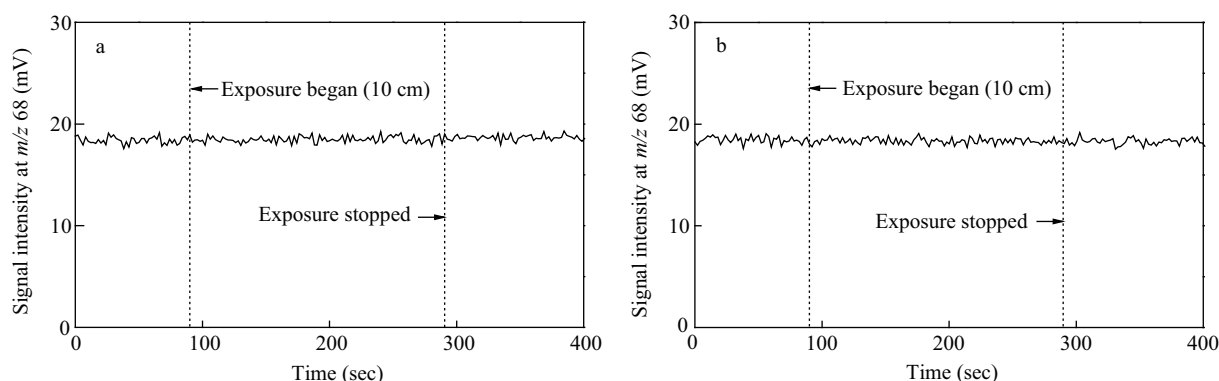
2.2 Methacrylic acid

The uptake of methacrylic acid was very different from that of isoprene. Only reversible uptake was observed for the H_2SO_4 solution over the acidity range of 0 wt.% to 80 wt.%. Figure 2a depicts the experimental profile of methacrylic acid into 60 wt.% H_2SO_4 solution. The signal dropped instantly upon exposure and then returned to its original level as the solution was saturated. Pushing the injector back produced an opposite change in signal, corresponding to desorption of methacrylic acid. The similarity in shape and total area of the adsorption and desorption curves means that methacrylic acid partitioned reversibly into the solution.

The uptake of methacrylic acid into H_2SO_4/H_2O_2 mixed solution was reversible for the acidity of 20 wt.%, but had both reversible and steady-state components for the acidity of 30 wt.%–80 wt.%. Figure 2b shows the typical partially irreversible uptake curve into 60 wt.% H_2SO_4+1 wt.% H_2O_2 solution. Methacrylic acid was found to be taken up and released at a later time, but in addition, a constant offset in the signal was observed. This is due to the occurrence of a chemical reaction, transforming some of the dissolved methacrylic acid molecules to products irreversibly.

To estimate the uptake kinetics, the steady-state uptake coefficient (γ_{ss}) was calculated when the irreversible component was observed. Figure 3 shows the loss of methacrylic acid as a function of injector position. The variation of $\ln(S/S_0)$ was found to decrease linearly versus the contact distance of methacrylic acid and the solution. As all decays followed first-order kinetics, we obtained the decay rates k_{obs} from the slopes using a linear regression method. The steady-state uptake coefficients calculated are summarized in Table 1.

2.3 Methyl methacrylate

The uptake of methyl methacrylate into H_2SO_4 solution was found to be reversible, which was similar to that of methacrylic acid. However, the time that the signal needed to return its original level was much shorter than that of methylacrylic acid. For the H_2SO_4/H_2O_2 mixed solutions, reversible uptake was observed up to the acidity of 60 wt.%. The steady-state component appeared with acidity of 70 wt.% and 80 wt.%, and the steady-state uptake
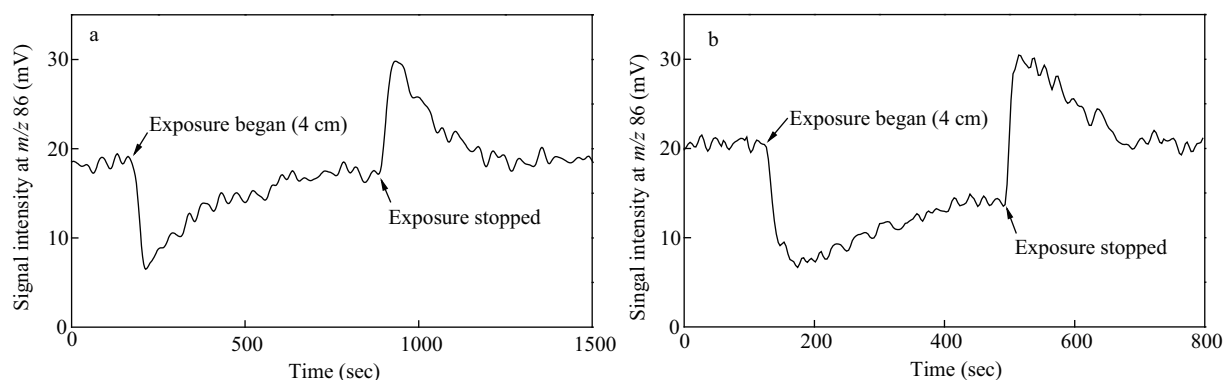

Fig. 1 Signal intensity profiles of isoprene during the uptake measurements into 80 wt.% H_2SO_4 solution (a) and 80 wt.% H_2SO_4+1 wt.% H_2O_2 solution (b).

Fig. 2 Uptake profiles of methacrylic acid. (a) Reversible uptake into 60 wt.% H_2SO_4 solution; (b) Combined reversible and irreversible uptake into 60 wt.% H_2SO_4+1 wt.% H_2O_2 solution.

Table 1   Summarization of the experimental conditions and steady-state uptake coefficients of methylacrylic acid

H_2SO_4 (wt.%)	H_2O_2 (wt.%)	Pressure (Torr)	Flow rate (STP cm^3/min)	γ^a ($\times 10^{-4}$)
30	1	64.3	330	0.415 ± 0.024
40	1	61.0	330	1.056 ± 0.028
50	1	56.0	330	1.130 ± 0.111
60	1	53.2	330	2.805 ± 0.042
70	1	19.6	330	6.162 ± 0.120
80	1	16.3	330	28.52 ± 1.980

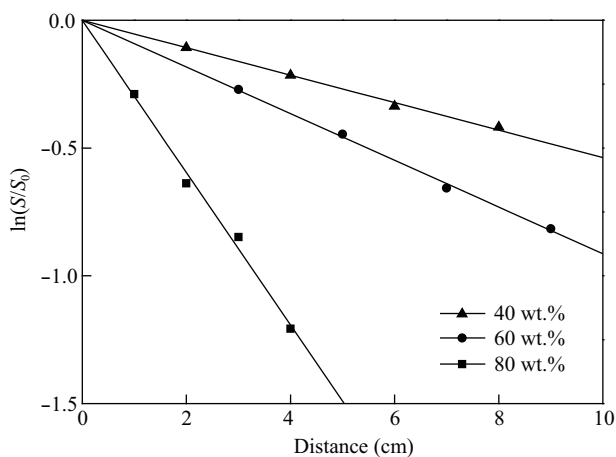[a] Each value is the average of three measurements, and the error corresponds to one standard deviation (σ).

Fig. 3 Methacrylic acid signal loss as a function of exposed distance for H_2SO_4/H_2O_2 mixed solution with acidity of 40 wt.%, 60 wt.%, and 80 wt.%.

coefficient was calculated to be $(0.103 ± 0.007) \times 10^{-4}$ and $(1.266 ± 0.067) \times 10^{-4}$, respectively. This means that methyl methacrylate can partition into the solution and then react with H_2O_2, but the reaction rate is much slower than the reaction rate of methacrylic acid.

3 Discussion

The uptake of gas by solution is a complex interaction that can be divided into a series of processes, including gas-phase diffusion, adsorption/desorption at the surface, reaction at the surface, solvation, liquid-phase diffusion and reaction in the bulk liquid (Davidovits et al., 2006). The uptake was governed by some or all of these processes. In this work, reaction at the surface and liquid-phase

diffusion is not considered because the solution in the RWWR was mixed sufficiently and continually. So in sum, the uptake is influenced mainly by four processes: gas-phase diffusion, adsorption/desorption, solvation and reaction.

For these three compounds, no irreversible uptake was observed during the uptake measurements into H_2SO_4 solution, thus the reaction process can be ignored here. Gas-phase diffusion cannot be the factor leading to the different uptake behaviors of these compounds because of the similar experimental conditions. Thus, the uptake was determined by adsorption/desorption and solvation processes, that is, by the volatility and solubility of these compounds. Table 2 lists the vapor pressure and Henry's law constant data in water of these three compounds at 298 K.

Its high volatility and low solubility hindered the up-take of isoprene into the solution, so a constant signal intensity was observed during the uptake measurements. The partitioning of isoprene into the aqueous phase was considered to be enhanced under acidic conditions due to the effects of hydration (Claeys et al., 2004b), but this was not observed below the acidity of 80 wt.% in our work. Limbeck et al. (2003) found that the formation of polymers occurred during the heterogeneous reaction of isoprene with H_2SO_4, but in that study the isoprene was forced to go through an acid impregnated filter and interacted with H_2SO_4. Liggio et al. (2007) found isoprene can be taken up and polymerize in acidic sulfate aerosols, but the acidity of aerosols was very high (pH = −1.45). In addition, the uptake of isoprene was depressed and even not observed with increasing relative humidity. This is in agreement with our experimental results.

Table 2   Vapor pressure and Henry's law constant data of isoprene, methacrylic acid and methyl methacrylate

	Vapor pressure (torr)^a	Henry's law constant (M/atm)
Isoprene	550[a]	0.013[b]
Methacrylic acid	0.99[a]	2600[c]
Methyl methacrylate	38.5[a]	3.125[a]

[a] The data were acquired from WebWISER: http://webwiser.nlm.nih.gov/.
[b] Mackay and Shiu, 1981.
[c] Khan et al., 1992.

According to the data in Table 2, methacrylic acid should be taken up readily into solution. This hypothesis is proved by our results. The signal of methacrylic acid dropped sharply to the one-third of the original level when the exposure first started. After that, it took about 700 sec to return back to its original value due to the fact that the extremely high solubility led to a long time to reach equilibrium. Methyl methacrylate, which has moderate volatility and solubility, can partition into H_2SO_4 solution, but the time needed to reach equilibrium is much shorter than that of methacrylic acid.

For the H_2SO_4/H_2O_2 mixed solution, these compounds with C=C double bonds can be oxidized in the liquid phase once they enter the solution, so the reaction may play a role in determining the uptake process. Because the acid-catalyzed oxidation is irreversible, steady-state uptake should be observed if the reaction is not too slow. Due to its high volatility and low solubility, isoprene can hardly touch the liquid surface or enter the solution. So isoprene was not oxidized by H_2O_2 in the solution although it has been proved that isoprene can indeed be oxidized by H_2O_2 in the liquid phase (Claeys et al., 2004b). Thus, an unchanging real-time signal is observed in Fig. 1b.

A steady-state component was observed during the uptake measurements of methacrylic acid and methyl methacrylate, and the steady-state uptake coefficients were calculated after correcting for gas-phase diffusion. The steady-state uptake of methacrylic acid appears for solutions with acidity above 30 wt.%, while the steady-state uptake of methyl methacrylate appears with acidity above 70 wt.%. In addition, the steady-state uptake coefficient of methacrylic acid is one magnitude larger than that of methyl methacrylate for the solution with same acidity. Actually, the steady-state uptake coefficient was determined by the reaction because the reaction was slower than absorption or solvation. Some molecules absorbed or dissolved were depleted through the reaction while others were released back into the gas phase. That is why partially irreversible uptake can be observed. Thus, these differences of steady-state uptake coefficients can be explained by the different reactivity of methacrylic acid and methyl methacrylate. It is well known that the C=C double bond can be oxidized by H_2O_2 in acidic solution. In this case, epoxidation occurs first followed by an acidic hydrolysis to form diols (March, 1992). Due to the fact that hydrolysis of epoxy compounds is very fast (Paulot et al., 2009; Minerath et al., 2009; Wang et al., 2012), epoxidation is the rate-limiting step, which is determined by the electron density of the C=C double bond. The electron-withdrawing conjugation of the carboxylic group (–COOH) is less than that of the ester group (–COOCH$_3$), leading to the higher C=C electron density of methacrylic acid compared to methyl methacrylate. Thus, methacrylic acid exhibits higher steady-state uptake coefficients than methyl methacrylate.

For methacrylic acid and methyl methacrylate, the atmospheric lifetimes of this process were estimated and compared with that of homogeneous oxidation. Aerosols are often neutralized by NH_3 in the troposphere, but higher aerosol acidity approaching that used in this article has also been reported in the troposphere (Cobourn et al., 1980; Ferek et al., 1983; Curtius et al., 2001). Hung and Wang (2001) reported that the H_2O_2 concentration in the aerosol phase was up to 63 ng/m^3. Given that the typical aerosol mass loadings at that site are in the range of 10–200 μg/m^3 and the water generally comprises less than 50% of aerosol mass loading, the concentration of H_2O_2 is a little lower than that used in this study. The steady-state uptake coefficients at 70 wt.%–80 wt.% acidity were used to calculate the atmospheric lifetimes by the following equation:

$$\tau = \frac{4}{\gamma_{ss}\omega\sigma} \tag{5}$$

where ω is the mean molecular speed of the reactant, and σ is the area density of atmospheric sulfate aerosol, about 2×10^{-7} cm^2/cm^3 (Godin and Poole, 1998). For methacrylic acid, the lifetime is 3–12.9 days, which is comparable to the lifetime of homogeneous oxidation by O_3 (3.8 days estimated using the rate constant of 4.1×10^{-18} cm^3/(molecule·sec) and O_3 concentration of 7.4×10^{11} molecule/cm^3) (Neeb et al., 1998; Weber et al., 1998). This means that multiphase acid-catalyzed oxidation by H_2O_2 is an effective loss pathway for methacrylic acid and plays a role in SOA formation. However, the lifetime of methyl methacrylate is more than 70 days or even 2 years, which is very much longer than the homogeneous oxidation (a few days) (Teruel et al., 2006). Thus, the multiphase acid-catalyzed oxidation of methyl methacrylate by H_2O_2 is not important in the troposphere.

4 Conclusions

Multiphase acid-catalyzed oxidation by H_2O_2 was suggested to be a potential route to SOA formation, and the importance of this process was determined by the partitioning and reaction. In this work, uptake measurements of isoprene, methacrylic acid and methyl methacrylate into aqueous solutions of H_2SO_4 and H_2O_2 were carried out to investigate in detail the kinetics of this multiphase acid-catalyzed oxidation. Isoprene cannot partition appreciably into solution due to its high volatility and low solubility, which hinders the following reaction in the solution. Methacrylic acid and methyl methacrylate can partition into the solution, and partially irreversible uptake was observed for acidity above 30 wt.% and 70 wt.%, respectively. The steady-state uptake coefficient of methacrylic acid is much larger than that of methyl methacrylate for a solution with same acidity. This can be explained by the different reactivity of these two compounds. The atmospheric lifetimes were estimated based on the calculated steady-state uptake coefficients. These results demonstrate that the multiphase acid-catalyzed oxidation of methacrylic acid by H_2O_2 plays a role in SOA formation in the troposphere, while the loss of isoprene and methyl methacrylate through this process is not significant. However, more liquid-phase chemical mechanism research

is needed to further explain how multiphase acid-catalyzed oxidation contributes to SOA formation.

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