



# Theoretical evaluation of different factors affecting the HO<sub>2</sub> uptake coefficient driven by aqueous-phase first-order loss reaction

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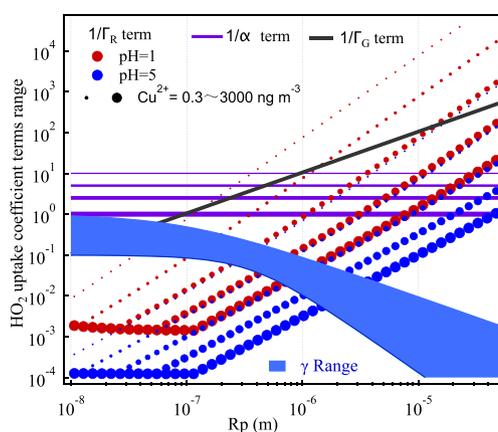
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## HIGHLIGHTS

- Systematic evaluation of factors affecting HO<sub>2</sub> uptake on ambient aerosols
- Accommodation process controls the HO<sub>2</sub> uptake on smaller aerosols.
- Aerosol pH and metal abundance influence  $\gamma_{\text{HO}_2}$  for large particles/droplets.
- The  $\gamma_{\text{HO}_2}$  decreased with increasing aerosol size.
- Adoption of an accurate  $\alpha_{\text{HO}_2}$  in model is crucial for HO<sub>2</sub> heterogeneous simulation.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The heterogeneous loss on aerosols is an important sink of HO<sub>2</sub>, affecting the radical chemistry and cycling, and thus it plays a key role in the atmospheric photochemistry. Gaining a reasonable HO<sub>2</sub> uptake coefficient ( $\gamma_{\text{HO}_2}$ ) would be of great importance in evaluating the heterogeneous loss rate of HO<sub>2</sub> on aerosols. This work was motivated by the large variance of reported HO<sub>2</sub> mass accommodation coefficients ( $\alpha_{\text{HO}_2}$ ) in laboratory studies (0.1–1), which can cause consequent bias in the parameterized HO<sub>2</sub> uptake coefficient ( $\gamma_{\text{HO}_2}$ ). We conducted a theoretical analysis of the roles of several key factors or parameters in determining  $\gamma_{\text{HO}_2}$  on a sphere droplet with adjustable Cu<sup>2+</sup> ion concentration including  $\alpha_{\text{HO}_2}$ , aqueous-phase acidity, the first-order loss-rate constant  $K^l$  value, and the aqueous phase production of HO<sub>2</sub>. The results intuitively demonstrate that utilizing a single  $\gamma_{\text{HO}_2}$  value for aerosols of different sizes, compositions or hygroscopic states is unsafe in atmospheric models. The theoretical analysis indicated that for a single aerosol experiencing hygroscopic growth,  $\gamma_{\text{HO}_2}$  decreased with increasing aerosol size, because of the increased gas phase diffusion resistance and dilution of aqueous-phase HO<sub>2</sub> consuming ions. Aerosol pH and metal abundance influence  $\gamma_{\text{HO}_2}$  by determining the aqueous-phase loss-rate constants, and these two factors were found to be only predominant for large particles/droplets ( $R_p > 1 \mu\text{m}$ ). For small and middle size aerosols, the mass accommodation process plays the determining role in controlling HO<sub>2</sub> uptake. Considering ambient aerosols rarely grow to cloud droplet size on sunny days when

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photochemical budget of HO<sub>2</sub> radicals is of more concern, it is crucial to adopt appropriate  $\alpha_{\text{HO}_2}$  in models, as arbitrarily choosing the  $\alpha_{\text{HO}_2}$  value can lead to large bias when simulating HO<sub>2</sub> heterogeneous process on ambient aerosols.

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## 1. Introduction

The atmospheric uptake process refers to gaseous molecules being removed from the gas phase upon collision and absorption into the aerosol interface, which includes both chemical and physical processes. The heterogeneous uptake of gases changes the concentrations and lifetimes of gaseous species, and also modifies the composition of aerosols. Thus, there has been growing research interest in atmospheric heterogeneous chemistry and its impact on air quality (Abbatt et al., 2012; Ammann et al., 2013; George et al., 2013; Jacob, 2000; Kolb et al., 2010; Schwartz, 1984; Tang et al., 2017). As the core species in atmospheric chemistry, HOx radicals can also undergo heterogeneous uptake process which further influence photochemical processes. Previous studies have suggested that deliquescent aerosols can act as sources or sinks of OH radicals, depending on detailed physico-chemical character of the aerosol (Herrmann et al., 2015; Tilgner et al., 2013). For HO<sub>2</sub>, studies have usually indicated that uptake loss onto aerosols is significant enough to be an important HO<sub>2</sub> sink (Mao et al., 2013; Thornton et al., 2008). Although many studies have been performed to investigate the detailed heterogeneous uptake process of HO<sub>2</sub> on different aerosol surfaces, our knowledge of its heterogeneous chemistry is still far from complete because of the complex processes involved.

The mass accommodation coefficient ( $\alpha$ ) represents the possibility of a molecule sticking to aerosol surface after a collision, whereas the uptake coefficient ( $\gamma$ ) represents the fraction which is permanently trapped or irreversibly reacted in the condensed phase.  $\gamma$  is a function of droplet/particle size, composition and the presence of dissolved reactive gases (Mozurkewich et al., 1987).  $\alpha$  can be considered as the upper limit of the uptake coefficient  $\gamma$ , when there is no desorption after colliding on the surface of the aerosol. For a species with a fast aqueous loss rate and without limitations from the gas-phase diffusion (e.g., the particle size is small), the  $\gamma$  value would approach to its mass accommodation coefficient. In some studies,  $\alpha$  was used in place of  $\gamma$  of HO<sub>2</sub>, which would result in an overestimation of the HO<sub>2</sub> uptake rate.

A large range of HO<sub>2</sub> mass accommodation coefficient ( $\alpha_{\text{HO}_2}$ ) values (ranging from <0.1 to 1.0) has been reported in laboratory studies and adopted in different models. Mozurkewich et al. (1987) reported a fast loss rate of HO<sub>2</sub> in deliquescent aerosols containing Cu<sup>2+</sup> and suggested that  $\alpha_{\text{HO}_2}$  would be higher than at least 0.2. Cooper and Abbatt (1996) measured  $\alpha_{\text{HO}_2} > 0.2$  on 55 wt% solutions doped with 0.1 M CuSO<sub>4</sub> at 223 K. In later laboratory studies, Thornton and Abbatt (2005) determined the lower limit of  $\alpha_{\text{HO}_2}$  to be  $0.8 \pm 0.3$  for H<sub>2</sub>SO<sub>4</sub> and  $0.5 \pm 0.1$  for (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> particles. George et al. (2013) reported a measured  $\alpha_{\text{HO}_2}$  of  $0.4 \pm 0.3$  on Cu(II)-doped (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> aerosols. Using aerosol flow tube, the  $\alpha_{\text{HO}_2}$  was measured to be  $0.65 \pm 0.17$  on (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and NaCl aerosols, and  $0.55 \pm 0.19$  on sea salt aerosols (Taketani et al., 2008; Taketani et al., 2009). Ammann et al. (2013) reviewed the kinetic data for atmospheric heterogeneous reactions and suggested that the  $\alpha_{\text{HO}_2}$  value should be higher than 0.5. Because of the large variation of reported  $\alpha_{\text{HO}_2}$  values from laboratory studies, the adopted  $\alpha_{\text{HO}_2}$  values in modeling studies also spread a large range. By assuming an  $\alpha_{\text{HO}_2}$  of 0.2 for the heterogeneous removal of HO<sub>2</sub>, de Reus et al. (2005) reported good agreement between the modeled and observed H<sub>2</sub>O<sub>2</sub> concentrations. Guo et al. (2014) adopted  $\alpha_{\text{HO}_2}$  of 0.4 in the multiphase modeling study of heterogeneous TMI-HOx reactions on deliquescent particles in Hong Kong. Moreover, a higher  $\alpha_{\text{HO}_2}$  value (1.0) was used in some recent modeling studies (Liang et al., 2013; Mao et al., 2013), and this unity value was consistent with the molecular dynamics calculation of

the HO<sub>2</sub> water interaction (Morita et al., 2004). The discrepancies and controversies about  $\alpha_{\text{HO}_2}$  values suggest the significant possibility of inaccurate modeling of the HOx photochemical budget in previous studies, and a lack of comprehensive understanding of atmospheric chemistry.

In order to further ascertain the potential bias caused by using such varied  $\alpha_{\text{HO}_2}$  values (0.1–1) in HOx uptake studies, in the present work, we performed tests and evaluations of the HO<sub>2</sub> uptake coefficient based on the parameterization equation (Schwartz, 1988; Schwartz, 1990; Schwartz and Freiberg, 1981). The parameterization assumes that HO<sub>2</sub> loss in the aqueous phase is driven by first-order reactions, and it takes gas phase diffusion, surface accommodation and aqueous phase reactions into consideration. We investigated the effects of different factors, including aerosol size, the aqueous-phase consuming-substances amount, acidity, and varied  $\alpha_{\text{HO}_2}$  values on the HO<sub>2</sub> uptake coefficient, and tried to identify the dominant factor controlling the HO<sub>2</sub> uptake coefficient value. The parameterization of the HO<sub>2</sub> uptake coefficient with consideration of the aqueous phase HO<sub>2</sub> production is also discussed in the present work.

## 2. Parameterization of the HO<sub>2</sub> uptake coefficients on spherical droplets

The comprehensive description of the uptake coefficient given below includes several fundamental physical chemical terms, i.e., gas phase diffusion, aerosol surface accommodation, and aqueous-phase reactions (Schwartz, 1988; Schwartz, 1990; Schwartz and Freiberg, 1981). It describes the overall uptake process by analogy to an electrical circuit consisting of three resistors. The uptake coefficient  $\gamma$  is viewed as a conductance, whose reciprocal is the overall resistance for a gaseous molecule experiencing an uptake process.

$$\frac{1}{\gamma} = \frac{1}{\Gamma_G} + \frac{1}{\alpha} + \frac{1}{\Gamma_R} \quad (1)$$

$1/\Gamma_G$  refers to the resistance arising from gas phase diffusion. By treating atmospheric aerosols as spherical particles,  $\Gamma_G$  can be determined by the Fuchs and Sutugin (1970) approach (Eq. (2)).

$$\Gamma_G = Kn \frac{1 + Kn}{0.75 + 0.28Kn} \quad (2)$$

$$Kn = \frac{3Dg}{Rp\omega} \quad (3)$$

The diffusivity of HO<sub>2</sub> in the air (or N<sub>2</sub>/O<sub>2</sub>) hasn't been experimentally determined yet, and was only measured in He, which should be higher than the HO<sub>2</sub> diffusivity in the air (or N<sub>2</sub>/O<sub>2</sub>) (Tang et al., 2014; Tang et al., 2015). In the current work, we use the  $D_{\text{gHO}_2}$  value of  $1.04 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$  following the estimation of (Ervens et al., 2003; Hanson et al., 1992). The tested values of the mass accommodation coefficient ( $\alpha$ ) of HO<sub>2</sub> here were 0.1, 0.2, 0.4 and 1.0, which basically covers the ranges from previous laboratory and modeling studies.

$\Gamma_R$  is the most complex term in uptake coefficient parameterization. Gas species loss can occur on the particle/liquid interface or in the bulk aqueous phase. In the present work, a simple case was assumed, that the loss of species only happens in the bulk aqueous phase. The corresponding  $\Gamma_R$  value can be calculated by Eq. (4).  $R_p$  is the particle radius (units:

m),  $K^I$  is the pseudo-first-order reaction rate constant (units:  $s^{-1}$ ),  $H$  is the dimensionless Henry's Law constant for the gas species, and  $Q$  is a correcting factor for calculating the average reaction rate in droplets by integrating the loss rate of  $Cr(x)$  along radius direction.  $q$  represents the ratio of droplet size to the distance of the species moves from surface into the droplets before loss by the pseudo-first-order reaction.

$$\Gamma_R = \frac{4.Rp.Q.K^I.H}{3.\omega} \quad (4)$$

$$Q = 3.\left(\frac{\coth q}{q} - \frac{1}{q^2}\right) \quad (5)$$

$$q = \frac{Rp}{l} = \frac{Rp}{\sqrt{D_l/K^I}} \quad (6)$$

The final parameterization for the uptake coefficient of  $HO_2$  driven by first-order reactions in aqueous sphere droplets is given by Eq. (7). Parameters used here include the molecule velocity  $\omega$  of  $HO_2$  as  $437.25 \text{ ms}^{-1}$  at 298 K,  $D_{gHO_2}$  of  $1.04 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ ,  $D_{liqHO_2}$  of  $1.00 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ , and the dimensionless Henry's law constant  $H_{HO_2}$  of  $2.20 \times 10^5$ .

$$\frac{1}{\gamma} = \frac{Rp\omega}{4Dg} + \frac{1}{\alpha} + \frac{3\omega}{4Rp.Q.H.K^I} \quad (7)$$

### 3. Key factors affecting the $HO_2$ uptake coefficient

#### 3.1. Aqueous $HO_2$ loss rate constant $K^I$ and its related factors

The continuous uptake of  $HO_2$  on aerosols relies on the sustaining aqueous reactions between  $HO_2$  radicals and the depleting substances.  $Cu^{2+}$  ions are ubiquitous in atmospheric aerosols and can quickly react with  $HO_2$  and  $O_2^-$  ion. Other transitional metal ions, such as  $Fe^{3+}$ ,  $Fe(OH)^{2+}$ ,  $Fe(OH)_2^+$ ,  $Fe^{2+}$ ,  $Cu^+$  and  $MnO_2^+$  are also abundant in ambient aerosols and able to promote similar chemistry, but their reaction rate constants are about one or two orders of the magnitude lower than

that for  $Cu^{2+}$  (Ervens et al., 2003). Previous multiphase modeling studies also suggest that  $Cu^{2+}$  ion serves as the dominant consumption agent of  $HO_2$  in ambient aerosols (Deguillaume et al., 2004; Long et al., 2010). In the present work, aqueous-phase  $HO_2$  was assumed to be mainly consumed by the reaction with aerosol  $Cu^{2+}$  ions, and the aqueous-phase first-order loss rate constants  $K^I$  of  $HO_2$  was estimated based on the reported  $Cu^{2+}$  concentration range in aerosols from ambient observation.

The literature has reported that the dissolved  $Cu^{2+}$  amount in ambient aerosols ranged from 3 to  $300 \text{ ng m}^{-3}$  (Deguillaume et al., 2005; Mao et al., 2013). We enlarged the tested range of  $Cu^{2+}$  by a factor of ten in this work, i.e., from 0.3 to  $3000 \text{ ng m}^{-3}$ , to cover the cases that part of the  $Cu^{2+}$  ion being bound in the highly ionic organic-rich matrix and/or other dissolved TMI species jointly depleting the  $HO_2$  radical as equivalent  $Cu^{2+}$ . The concentration of dissolved  $Cu^{2+}$  in the droplet is inversely proportional to the change in droplet volume upon hygroscopic growth or efflorescence. With typical liquid water content (LWC) of  $3 \text{ g m}^{-3}$  for clouds, the corresponding  $Cu^{2+}$  concentration estimated for typical cloud droplets will range from 0.0016 to  $16 \text{ }\mu\text{M}$ , which is close to the reported soluble  $Cu^{2+}$  range of 0.001– $0.3 \text{ }\mu\text{M}$  in clouds (Jacob, 2000). For deliquescent particles, the aqueous  $Cu^{2+}$  concentration increases with decreasing LWC, and when the solution is further condensed, the metal salts precipitate at their dissolution point. Considering the solubility of a saturated  $CuSO_4$  solution at  $20 \text{ }^\circ\text{C}$  of  $1.27 \text{ mol L}^{-1}$ , the tested aqueous-phase  $Cu^{2+}$  concentration in deliquescent aerosols in this work was assumed to be no higher than  $1.27 \text{ mol L}^{-1}$  in the highly condensed deliquescent aerosols.

With the above copper abundance assumption ( $0.3\text{--}3000 \text{ ng m}^{-3}$ ), the estimated aqueous-phase  $Cu^{2+}$  concentration as a function of droplet size is given in Fig. 1. The  $Cu^{2+}$  concentrations in droplets with  $Rp$  of  $10 \text{ }\mu\text{m}$  (typical cloud droplet size) range from  $1 \times 10^{-10}$  to  $1 \times 10^{-5} \text{ mol L}^{-1}$ , whereas for typical deliquescent aerosols with  $Rp$  of  $100 \text{ nm}$ , the  $Cu^{2+}$  concentrations were much higher, ranging from  $1 \times 10^{-4}$  to  $1.27 \text{ mol L}^{-1}$ . The reactions rate between  $HO_2$  and  $Cu^{2+}$  also varies with aqueous-phase acidity, because the pH value determines the partition between  $HO_2$  and  $O_2^-$ , which have different reaction rate constants with  $Cu^{2+}$ .  $O_2^-$  reacts 80 times faster than the  $HO_2$  with  $Cu^{2+}$  (Cabelli et al., 1987). A higher pH value in the aqueous phase

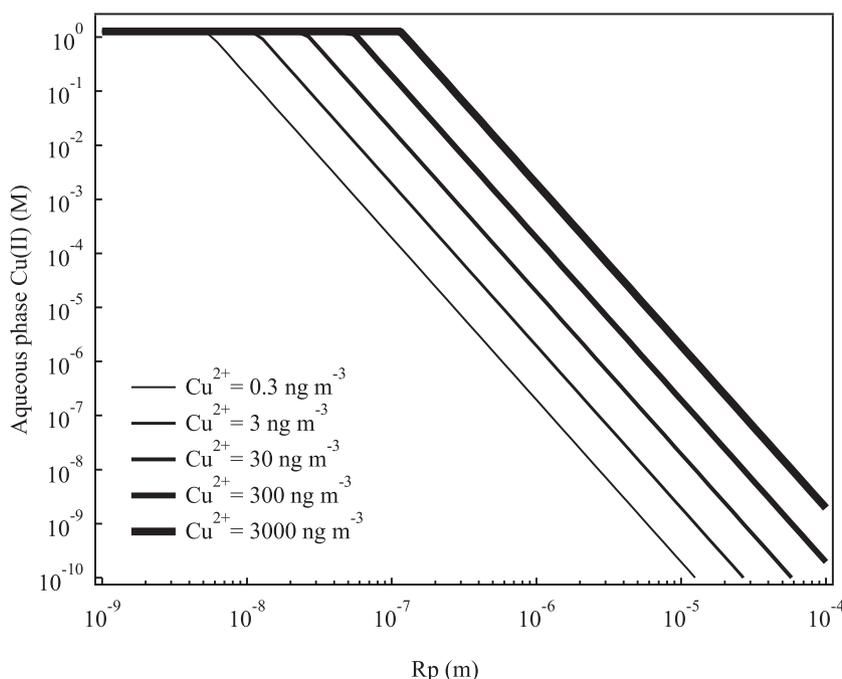


Fig. 1. The derived aqueous-phase  $Cu^{2+}$  concentration from the assumed  $Cu^{2+}$  abundance range as a function of droplet size.

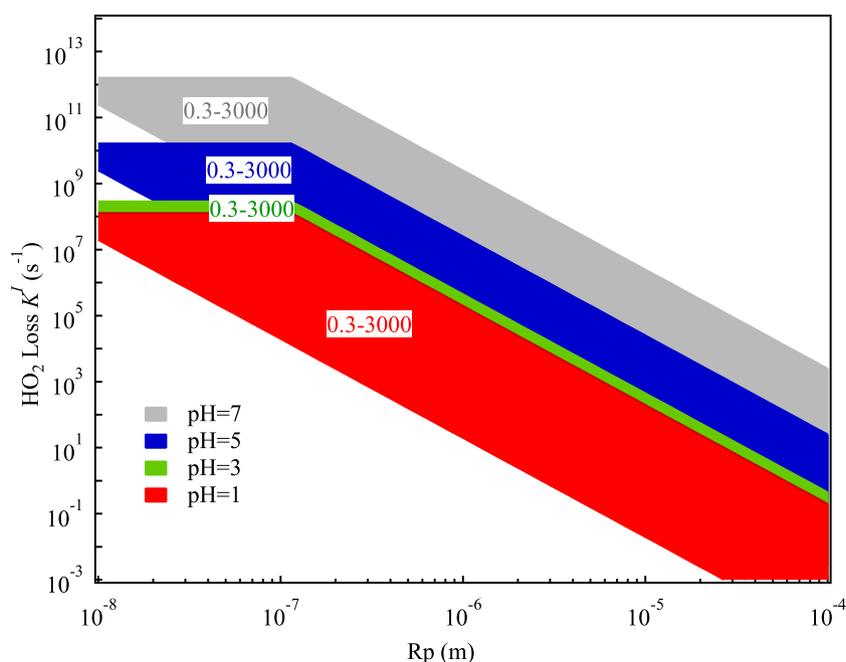


Fig. 2. The estimated  $\text{HO}_2$  loss rate constant  $K^l$  for the assumed  $\text{Cu}^{2+}$  abundance ( $0.3\text{--}3000 \text{ ng m}^{-3}$ ) under different pH values.

makes the equilibrium shift towards  $\text{O}_2^-$ , which would result in a higher  $\text{HO}_2$  loss rate constant than in low pH conditions. Fig. 2 compares the calculated  $\text{HO}_2$  loss rate constants for the same assumed  $\text{Cu}^{2+}$  values under different acidity conditions and droplet sizes. The large range of  $K^l$  caused by metal loading and acidity results in significant complexity in determining the uptake coefficient of ambient aerosols.

Complexity also comes from the diffusion of  $\text{HO}_2$  molecules in the aqueous phase. The size and composition of aerosols can influence the speed of  $\text{HO}_2$  molecules moving from the aerosol surface to the bulk and result in a steady-state profile of  $\text{HO}_2$  concentration, with its concentration higher at the surface and lower in the core region. A correcting parameter  $Q$  that considers the aqueous-phase concentration profile of  $\text{HO}_2$  was therefore used (Jacob, 1986; Schwartz and Freiberg, 1981) to calculate the integrated loss rate of  $\text{HO}_2$  by multiplying  $Q$  (c. f. Eq. (5)) with  $K^l$  and the  $\text{HO}_2$  concentration at the aqueous-phase surface ( $C_{s(\text{aq})}$ ). The  $Q$  values under conditions of different acidities,  $\text{Cu}^{2+}$  concentration ranges, and aerosol size are given in Fig. 3. For the same  $\text{Cu}^{2+}$  and acidity conditions, the  $Q$  values of large droplets are mostly higher than those for small droplets, i.e., the concentration profile of  $\text{HO}_2$  radicals in the large droplet is flatter than that in smaller ones. This is because large droplets have lower depleting species ( $\text{Cu}^{2+}$ ) concentration than small droplets due to the dilution effect, which makes the  $\text{HO}_2$  radicals experience less loss upon its diffusion into larger droplets than its diffusion into small droplets. However, under very high metal-loading conditions or when the aerosol aqueous phase is highly condensed, the  $\text{Cu}^{2+}$  would reach its saturation point, and thus the  $\text{HO}_2$  loss rate constant value  $K^l$  would not increase with decreasing aerosol water amount. Thus, with the same  $K^l$  value, the long distance of the  $\text{HO}_2$  radical diffusing from the surface to the core region for large droplets makes the  $\text{HO}_2$  concentration in the core region lower in large droplets than in small droplets. Therefore, the  $Q$  value is higher in small droplets than in large droplets for the  $\text{Cu}^{2+}$  loading cases (Fig. 3).

### 3.2. Comparing the key terms determining the uptake coefficient

Based on the above estimation of the loss rate constant  $K^l$  and  $Q$  values, we compared the roles of the three resistance processes (i.e., in Eq. (1)) on  $\text{HO}_2$  uptake for different droplet sizes, different copper

loadings, and the four tested  $\alpha_{\text{HO}_2}$  cases. The comparison of accommodation term and gas diffusion term is shown in Fig. 4a. The  $1/\alpha$  values range from 1 to 10, which are all higher than the gas-phase diffusion term for particles with a radius smaller than 100 nm. This means that for smaller particles, the uptake process is limited by the accommodation process rather than by the gas-phase diffusion process. These two terms overlap at the radius size range of 100 nm to 1  $\mu\text{m}$ , which is a transition region. As for particles with a radius larger than 1  $\mu\text{m}$ , the gas-phase diffusion term becomes higher than all possible  $1/\alpha$  values, suggesting a stronger role for the diffusion term in limiting the  $\text{HO}_2$  uptake for large particles. The reaction term as a function of particle/droplet size is shown in Fig. 4b. The value of the  $1/\Gamma_R$  term exhibits large variation from  $10^{-5}$  to  $10^2$ , depending on the particle/droplet size, acidity, and metal loading of the aerosols. The larger size, higher pH value, and lower metal-loading aerosols have much larger reaction term resistance than the smaller size, lower pH value, and higher metal-loading aerosols.

Fig. 4c shows the comparison of these three resistance terms. Overall, the limiting process for  $\text{HO}_2$  uptake is different for different droplet sizes. For aerosols with a radius smaller than 100 nm, the reaction term ( $1/\Gamma_R$ ) ranges from  $1 \times 10^{-5}$  to 1, and the gas diffusion term ( $1/\Gamma_G$ ) ranges from 0.1 to 1, both of which are lower than the range of the  $1/\alpha$  term (from 1 to 10). The comparison suggests that the accommodation process dominates the  $\text{HO}_2$  uptake for droplets smaller than 100 nm. In the transition region with particles radius from 100 nm to 1  $\mu\text{m}$ , the reaction term also overlaps with the accommodation and gas-phase diffusion terms under the low metal-loading and low pH-value cases, whereas the reaction term for other conditions is mostly lower than the other two terms. In this region, the accommodation and gas-phase diffusion terms are the dominant limiting factors of the uptake process. For particles with a radius larger than 1  $\mu\text{m}$ , the  $1/\alpha$  term can be ignored in comparison to the gas-phase diffusion term.

The derived  $\text{HO}_2$  uptake coefficient from the above three terms at different droplet sizes is shown by the blue color area in Fig. 4d. The blue area gives an intuitive reference for the feasible  $\gamma_{\text{HO}_2}$  range set for different size aerosols in atmospheric modeling studies. Generally, lower  $\gamma_{\text{HO}_2}$  values should be used for larger size aerosols.  $\gamma_{\text{HO}_2}$  for particles radius smaller than 100 nm ranges from 0.1 to 1, and the variation

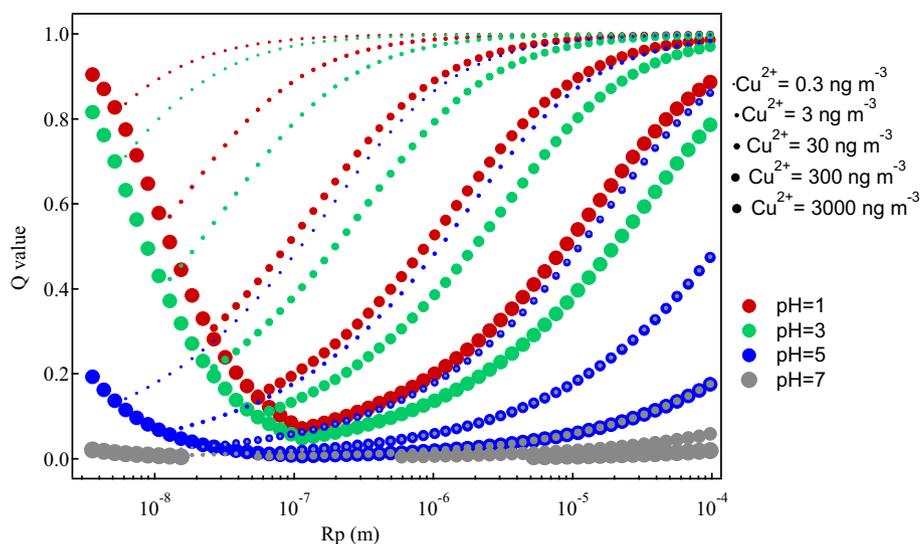


Fig. 3. The estimated Q values for aerosols with different  $\text{Cu}^{2+}$  loadings and different pH values.

mostly depends on the selected  $\alpha_{\text{HO}_2}$  value. For droplets with a radius larger than  $1 \mu\text{m}$ , the  $\gamma_{\text{HO}_2}$  should be no higher than 0.1. The  $\gamma_{\text{HO}_2}$  value for typical cloud droplets ( $R_p > 5 \mu\text{m}$ ) is about 0.02.

Furthermore, we want to emphasize that more attention should be paid to small and middle aerosol sizes ( $R_p < 1 \mu\text{m}$ ). Atmospheric  $\text{HO}_2$  radicals are a product of the photochemical process. On

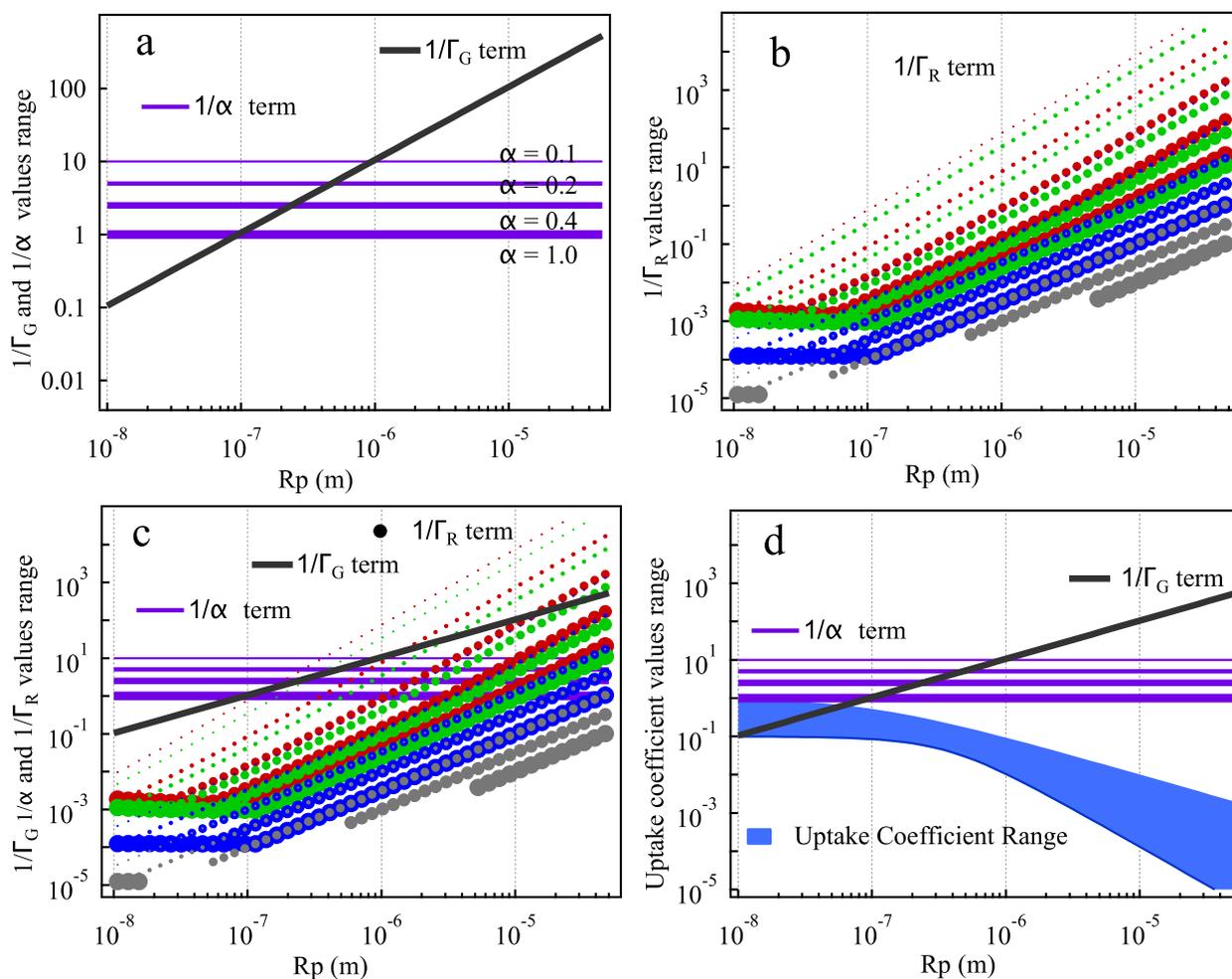


Fig. 4. The comparison of the roles of accommodation ( $\alpha$ ), gas-phase diffusion ( $1/\Gamma_G$ ), and reaction terms ( $1/\Gamma_R$ ) on determining the uptake coefficient ( $\gamma$ ) of  $\text{HO}_2$  radicals as a function of droplet/particle size. The size of markers represents the  $\text{Cu}^{2+}$  loadings and the marker colors represent the pH values, are the same as in Fig. 3.

photochemically active days (normally also sunny days), ambient aerosols rarely grow up to cloud droplet size. HO<sub>2</sub> uptake, with high probability, occurs on small- and middle-size aerosols. The results here indicate that for small and middle size aerosols, the accommodation process is the critical factor controlling HO<sub>2</sub> uptake. Then, the large uncertainties existing in the reported and employed  $\alpha$  values, may result in significant bias in the modeled HO<sub>2</sub> budget, leading to a discrepancy between observed and modeled results for the photochemistry process. Although we think the  $\alpha_{\text{HO}_2}$  value higher than 0.5 that suggested by Ammann et al. (2013) is more reasonable, further well-designed field/laboratory measurements of  $\alpha_{\text{HO}_2}$  under different and real ambient conditions are critically needed, and a more accurate representation of  $\alpha_{\text{HO}_2}$  in atmospheric multiphase chemistry modeling is needed to better evaluate the radical budget.

### 3.3. Impact of the aqueous production of HO<sub>2</sub> on the uptake coefficient

Production of HO<sub>2</sub> from reactions in the aqueous phase could suppress the uptake loss of HO<sub>2</sub> on aerosols. Here, we derive an uptake parameterization that includes the production process and further evaluate the possible impact of HO<sub>2</sub> aqueous-phase production on its uptake coefficient. The calculation is basically consistent with the steady-state diffusion equations expressed in previous studies (Jacob, 1986; Mao et al., 2013), and assuming the HO<sub>2</sub> production rate ( $P_{\text{HO}_2}$ ) being independent of the position ( $r$ ) in droplets. The equilibrium equation of the steady state between aqueous-phase loss and the diffusion of HO<sub>2</sub> at a certain droplet radius is described by Eq. (8).

$$d(D_{\text{liq}} \times 4\pi r^2 \times dC_r/dr) = 4\pi r^2 \times (K^I \times C_r - P) \times dr \quad (8)$$

where  $C_r$  represents the concentration of HO<sub>2</sub> at radius  $r$ , and  $P$  refers to the radial independent production rate of HO<sub>2</sub>. By solving Eq. (8), the  $C_r$  concentration can be obtained from Eq. (9), in which  $x = r/Rp$  and  $C_{s(\text{aq})}$  is the HO<sub>2</sub> concentration at the aqueous-phase surface. The meaning and evaluation of the  $q$  value are the same as those in Eq. (6).

$$C_r = \left( C_{s(\text{aq})} - \frac{P}{K^I} \right) \times \frac{sh(q \cdot x)}{shq \cdot x} + \frac{P}{K^I} \quad (9)$$

By integrating the loss rate through the droplet volume, the total loss rate of HO<sub>2</sub> in the aqueous phase is given in Eq. (10).  $Q$  is calculated from

Eq. (5). The uptake coefficient parameterization with consideration of the aqueous phase production of HO<sub>2</sub> is thus described by Eq. (11).

$$\text{Loss rate} = Q \left( C_{s(\text{aq})} - \frac{P}{K^I} \right) \times K^I \times \frac{4}{3} \pi R p^3 \quad (10)$$

$$\frac{1}{\gamma} = \frac{R p \cdot \omega}{4 D g} + \frac{1}{\alpha} + \frac{3 \omega}{4 R p \cdot H^* \cdot K^I \cdot Q \cdot \left( 1 - \frac{P}{K^I \cdot C_{s(\text{aq})}} \right)} \quad (11)$$

It should be noted that, with consideration of  $P_{\text{HO}_2}$ , the reaction term in Eq. (11) is a function of  $C_{s(\text{aq})}$ . It is because that the HO<sub>2</sub> uptake coefficient is determined by the difference between the aqueous phase production and the loss rates of HO<sub>2</sub>. The  $C_{s(\text{aq})}$  value, which is lower than Henry's law equilibrium value from the known gas phase HO<sub>2</sub> concentration, can be calculated from Eq. (13).

$$K m t \times \left( C_g - \frac{C_{s(\text{aq})}}{H} \right) = Q \times \left( C_{s(\text{aq})} - \frac{P}{K^I} \right) \times K^I \quad (12)$$

$$C_{s(\text{aq})} = \frac{Q P + K m t C_g}{Q K + \frac{K m t}{H^*}} \quad (13)$$

$$\text{in which, } K m t = \left( \frac{R p^2}{3 D g} + \frac{4 R p}{3 \omega \alpha} \right)^{-1} \quad (14)$$

According to the above equations, with the production of HO<sub>2</sub> in the aqueous phase, the HO<sub>2</sub> concentration at a certain droplet radius ( $C_r$ ) will be higher than that without the production process. Correspondingly, the concentration gradient in aerosols that drive the HO<sub>2</sub> uptake is reduced, and the HO<sub>2</sub> uptake coefficient value will be lower than that without considering the production process. To intuitively depict the impact of aqueous HO<sub>2</sub> production on the uptake coefficients, the derived uptake coefficient of HO<sub>2</sub> for a typical deliquescent aerosol case ( $Rp = 100 \text{ nm}$ ) and cloud droplet case ( $Rp = 5 \mu\text{m}$ ) were calculated, and the results are shown in Fig. 5.

The simulation was performed using different production rates of HO<sub>2</sub> in the aqueous phase. With production rates that were 30%, 60%, and 90% of the HO<sub>2</sub> loss rate on aerosols surface, the decreases of  $\gamma$  were 11%, 28%, and 66%, respectively of the original values for the deliquescent particles, and were respectively 9%, 23%, and 52% for the cloud

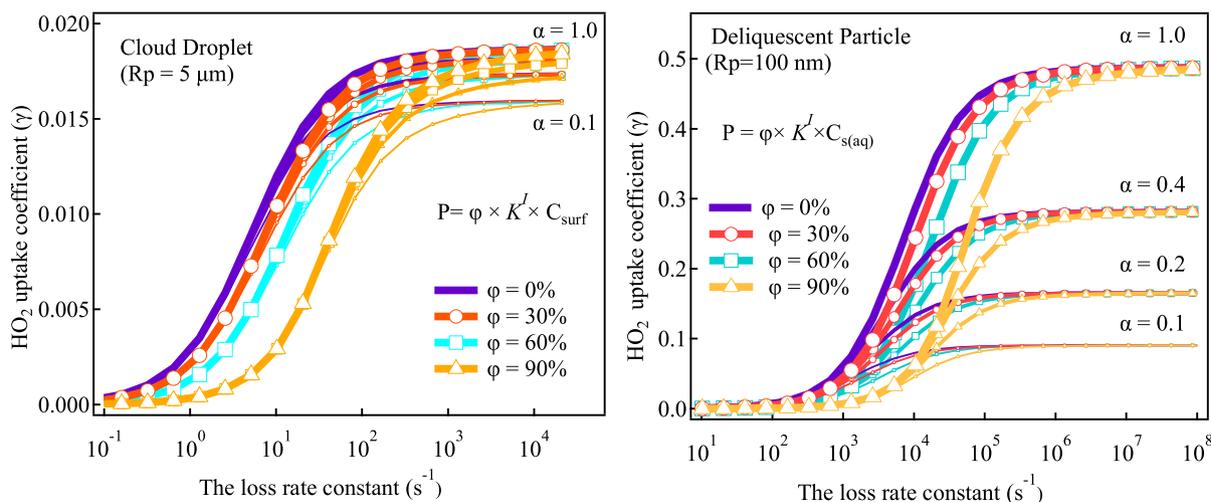


Fig. 5. The derived HO<sub>2</sub> uptake coefficient with consideration of the aqueous-phase HO<sub>2</sub> production reactions for (a) a typical deliquescent particle case ( $Rp = 100 \text{ nm}$ ) and (b) cloud droplet case ( $Rp = 5 \mu\text{m}$ ).

droplet case. For conditions with large loss-rate constant (e.g.,  $K^l > 10^6 \text{ s}^{-1}$ ), the reduction in  $\gamma$  seems not as significant as that for the middle  $K^l$  regions. This is because the production rates in the simulation were assumed to be fixed at a certain ratio of the loss rate, and thus too large  $K^l$  values indicated very large loss-production differences of  $\text{HO}_2$ , in which case the uptake coefficient values would be limited by other factors of the uptake process. For small loss rate constants, the  $\gamma$  value is very close to zero because of the small loss-reaction rate, but the impact of production still exists, even though it is difficult to distinguish in the plot.

As can be seen in Fig. 5, the determined  $\gamma$  value increases with increasing loss rate constant  $K^l$ , switching from the reaction term-limited scenario to accommodation and gas-phase diffusion-limited scenarios. It should be noted that for the cloud droplet case, the upper limit for the possible  $\gamma_{\text{HO}_2}$  values is only 0.02. By varying the  $\alpha$  values from 0.1 to 1.0, the  $\gamma_{\text{HO}_2}$  values only increased from 0.015 to 0.02, indicating a small influence of the accommodation process on the uptake rates, which is different from the case of the deliquescent aerosols. In addition, according to Fig. 4, the upper limit of  $\gamma_{\text{HO}_2}$  value for a droplet with a radius of 1  $\mu\text{m}$  is about 0.1. The indication here is that for modeling studies on estimating the uptake of  $\text{HO}_2$  under cloud or fog scenarios, the adopted accommodation coefficient will not result in critical bias on the final uptake coefficient values, and the  $\gamma_{\text{HO}_2}$  value for general cloud or fog scenarios is suggested to be no higher than 0.1 and the value would decrease to 0.02 when a 5- $\mu\text{m}$ -radius droplet is considered.

#### 4. Conclusion

Based on theoretical analysis and evaluation of the  $\text{HO}_2$  uptake coefficient on aqueous aerosols, the present work suggests that for a single aerosol particle with a fixed amount of transition metal ions (e.g.,  $\text{Cu}^{2+}$ ) dissolved in the aqueous phase, its  $\gamma_{\text{HO}_2}$  value decreases with increasing size of the aerosol upon hygroscopic growth. For small aerosols ( $R_p < 100 \text{ nm}$ ), the accommodation process is the rate-determining step for  $\text{HO}_2$  uptake. With increasing aerosol size, the resistance from gas-phase diffusion and aqueous-phase reaction loss also increase and become the dominant factors controlling the  $\text{HO}_2$  uptake when the droplet radius is larger than 1  $\mu\text{m}$ . Because of the large resistance brought about by gas-phase diffusion, the upper limit of the  $\gamma_{\text{HO}_2}$  value on a 1- $\mu\text{m}$ -radius droplet would be 0.1, which would decrease to 0.02 for a 5- $\mu\text{m}$ -radius droplet. Furthermore, parameterization of  $\gamma_{\text{HO}_2}$  on spherical droplets driven by a first-order loss reaction with consideration of the  $\text{HO}_2$  production reaction was developed, and the results suggest that the aqueous-phase production of  $\text{HO}_2$  is also an important factor that influences the  $\text{HO}_2$  uptake coefficient.

Finally, we want to emphasize the critical importance of choosing a reasonable accommodation coefficient  $\alpha_{\text{HO}_2}$  in modeling studies on the heterogeneous uptake of  $\text{HO}_2$  by ambient aerosols. The accommodation coefficient dominates the uptake coefficient for aerosol sizes with  $R_p < 100 \text{ nm}$ . Ambient aerosols rarely grow to cloud droplet size on sunny days, when the photochemical budget of atmospheric  $\text{HO}_2$  radicals is of more concern. Because using different  $\alpha_{\text{HO}_2}$  values will result in large bias in estimating the  $\text{HO}_2$  heterogeneous uptake, special attention should be paid to the selection of the  $\alpha_{\text{HO}_2}$  value in multi-phase chemical modeling studies. Further well-designed studies to more accurately parameterize the  $\text{HO}_2$  uptake coefficient and measuring the mass accommodation coefficients are needed to help reduce the discrepancy of the  $\text{HO}_2$  budget between photochemical models and observations.

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