Uptake coefficient of H$_2$O$_2$ on ice

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Abstract

H$_2$O$_2$ uptake coefficients on ice surfaces, over a temperature range from 190 to 220 K, have been studied in a flow reactor coupled with a differentially pumped quadrupole mass spectrometer. The initial uptake coefficient increases with an increase in H$_2$O$_2$ pressure and a decrease in temperature. The results were analyzed using surface kinetics, and the analysis shows that the uptake involves both H$_2$O$_2$ adsorption and surface aggregation. H$_2$O$_2$ desorption kinetics supports lateral attractive interactions among adsorbed H$_2$O$_2$ on ice. The result can be used to model the heterogeneous H$_2$O$_2$ loss on snow/ice surfaces and cirrus clouds as a function of the H$_2$O$_2$ concentration and temperature.

1 Introduction

Hydrogen peroxide (H$_2$O$_2$) is found both in air and in condensed phases such as clouds and aerosols, as well as on the ground-level snow and icepacks at higher latitudes, with the deposition of H$_2$O$_2$ from the atmosphere as a major source (Sigg and Neftel, 1991; Bales et al., 1995; Hutterli et al., 2001; Vione et al., 2003; Seinfeld and Pandis, 2006). Field measurements have shown that snow/ice has large capacity to take up H$_2$O$_2$ (Bales et al., 1995). H$_2$O$_2$ is known to be a source of OH radicals, produced photochemically from Reaction (R1) in/on the icepack and cirrus cloud ice (Chu and Anastasio, 2005; Jacobi et al., 2006; France et al., 2007).

\[
\text{H}_2\text{O}_2(\text{ad}) + h\nu \rightarrow 2\text{OH}
\]  \hspace{1cm} (R1)

The photochemically produced OH radicals alter the OH concentration and oxidative capacity in/on the icepack, cirrus clouds and the atmosphere above ice interfaces. This changes the lifetimes of atmospheric species, such as organics and halogens, and affects tropospheric chemistry. The rate of H$_2$O$_2$ taken up on ice surfaces can affect the amount of H$_2$O$_2$ on ice surfaces so as to affect the subsequent H$_2$O$_2$ photolysis
product yield in Reaction (R1). Recent studies show the reactivity of photochemically produced OH toward aromatics bimolecular reactions at the air-ice interface is significantly suppressed relative to that in veins and packets within bulk ice (Kahan et al., 2010). The poor OH partition on ice surfaces and the recombination of OH to H$_2$O$_2$ are suggested to be a cause. A better understanding of H$_2$O$_2$-ice surface interactions is necessary to shed light on the nature of OH and H$_2$O$_2$ on the ice surface. In addition, heterogeneous reaction of H$_2$O$_2$ with bromide on the icepack is suggested to activate bromide to photochemically active halogens (Grannas et al., 2007). This pathway may alter the partitioning of halogen species and affect the distribution of ozone. To assess the significance of the heterogeneous reaction of H$_2$O$_2$ with bromide on ice surfaces and to fully understand the nature of H$_2$O$_2$-ice surface photochemistry, one needs to know the rate of H$_2$O$_2$ taken up on ice surfaces and adsorption of H$_2$O$_2$ on ice. Thus, it is necessary to gain the knowledge of the uptake coefficient of H$_2$O$_2$ on ice surfaces, to reveal the nature of H$_2$O$_2$-ice surface photochemistry and mechanism of H$_2$O$_2$ reaction with bromide on ice surfaces.

Currently, studies are mainly concentrated on the amount of H$_2$O$_2$ taken up by ice surfaces and interactions between ice and H$_2$O$_2$. Clegg and Abbatt (2001) have determined that the uptake amount of H$_2$O$_2$ on ice surfaces increases with an increase in [H$_2$O$_2$]. Pouvesle et al. (2010) showed that uptake amount of H$_2$O$_2$ on ice surfaces increases with an increase in [H$_2$O$_2$] and a decrease in temperature from 233 to 203 K. However, studies of the rate of H$_2$O$_2$, uptake coefficient, taken up by ice surfaces are infrequent. Conklin et al. (1993) showed that the proportion of H$_2$O$_2$ taken up by ice at low temperatures is higher than that at higher temperatures (from 228 to 270 K). A sticking coefficient was estimated to be on the order of 0.02, from the advection-dispersion model (Conklin et al., 1993). To the best of our knowledge, no study in literature has reported a value for uptake coefficient of H$_2$O$_2$ on ice at temperatures lower than 228 K, a temperature range found in the upper troposphere and polar region. The effects of temperature and H$_2$O$_2$ partial pressure on the uptake coefficient at low temperature are unknown. Thus, the objective of this study is to determine H$_2$O$_2$ uptake coefficient
In this paper, we report the $\text{H}_2\text{O}_2$ uptake coefficient as a function of temperature and pressure, and shed light on the nature of $\text{H}_2\text{O}_2$ interaction with ice surfaces. In the following sections, we briefly describe the experimental procedures, and then present our results for the initial uptake coefficient of $\text{H}_2\text{O}_2$ on ice surfaces. Following a discussion of our findings, we compare our results with literature values, and present the implications of this study for atmospheric chemistry.

2 Experimental

The uptake coefficient, $\gamma$, is defined as the ratio of the number of $\text{H}_2\text{O}_2$ molecules that are taken up by the ice surface to the total number of $\text{H}_2\text{O}_2$ molecules colliding with that surface. $\gamma$ was determined when an ice film was freshly prepared and the ice surface was clean; thus, it is termed the initial uptake coefficient, $\gamma_w$. The determinations of $\gamma_w$ were performed in a flow reactor coupled with a differentially pumped quadrupole mass spectrometer, QMS (Extrel; C50 Electronics). The details of the apparatus have been described in our previous publications (Chu and Heron, 1995; Chu and Chu, 1999; Yan et al., 2009). A brief summarization, noting modifications of the apparatus that were used in the present work, follows.

2.1 Flow reactor

The double-jacketed cylindrical flow reactor (35 cm in length, with 1.7 cm inner diameter) was made of Pyrex glass. The outer jacket was a vacuum layer to maintain the temperature of the reactor. Temperature of the reactor was regulated by a liquid-nitrogen-cooled methanol circulator (Neslab) and was measured with a pair of J-type thermocouples located in the middle and at the downstream end of the reactor. The experimental temperature was reported as the average from the two thermocouple readings. During the experiment, temperature was maintained within the range of 190
to 220 K; the stability of temperature was better than ±0.2 K. Pressure inside the reactor was controlled by a downstream throttle valve (MKS Instruments; Model 653B), and was measured with a high-precision Baratron pressure gauge (MKS Instruments; Model 690A). The typical total pressure used was 0.270 Torr. The stability of the pressure was better than 0.001 Torr in the experiments. A double-capillary movable injector was used to admit gaseous H$_2$O$_2$ and H$_2$O vapor into the flow reactor individually, for determinations of the initial uptake coefficient. The injector was sealed to the reactor by O-rings. Room-temperature dry air was passed through the outside of the capillary, to keep it warm so as to prevent condensation of the water vapor and H$_2$O$_2$ on the capillary wall.

2.2 Ice film preparation

High-purity deionized water (> 18 MΩ cm, Barnstead; Model D11931) was degassed by a passage of helium carrier gas (Matheson; 99.9995 %) through the reservoir, which was maintained at 293.2 ± 0.1 K by a refrigerated circulator (Neslab; Model RTE-100LP), to remove dissolved gases in water. Helium saturated with the water vapor was introduced to the reactor, maintained at a temperature of the experiment, through an inlet of the double-capillary injector. The injector was then pulled out at a slow, constant speed, to allow a uniform ice film to form on the inner wall of the reactor. The amount of ice deposited was determined from the mass flow rate of the H$_2$O-He mixture (as measured by a Hasting mass flow meter), the H$_2$O-He mixing ratio, and the deposition time. The average film thickness, $h$, was calculated from the mass of ice, the geometric area of the ice film on the flow reactor, and the bulk density ($\rho_b = 0.63 \text{ g cm}^{-3}$) of vapor-deposited ice (Keyser and Leu, 1993a). The effect of the ice-film volatile nature on the film thickness is negligible because of the short experimental time scale (minutes) to measure $\gamma_w$. 
2.3 H$_2$O$_2$ preparation and calibration

Highly concentrated H$_2$O$_2$ solution (93 ± 1 wt %) was prepared by vacuum distillation of a 50 wt % H$_2$O$_2$ (Sigma-Aldrich) solution (Maass and Hatcher, 1920). A 98 wt % H$_2$SO$_4$ trap was used during the vacuum distillation, to assist in the removal of H$_2$O and to overcome a eutectic point (61.2 wt % and 217.1 K; Giguère and Masee, 1940; Schumb et al., 1955). Teflon tubing and connectors were used in the distillation system to avoid potential wall-catalyzed H$_2$O$_2$ decomposition. The temperature of the H$_2$O$_2$ solution was controlled with the use of a water-bath varying from 278 to 293 K during the distillation. The pressure in the distillation system was controlled by a needle valve.

The concentrated H$_2$O$_2$ solution was kept in dark at 265.3 K, since low temperature reduces the propensity for H$_2$O$_2$ decomposition.

Determination of the H$_2$O$_2$ concentration in the gas and aqueous phase of the prepared solution entailed two steps. First, [H$_2$O$_2$] in solution was determined to be 93 ± 1 wt % from the measurements of the refractive index at 293.2 K (Giguère and Geoffrion, 1949), using a refractometer (Bausch & Lomb; Model 33.46.10). The density of the H$_2$O$_2$ solution was determined to confirm the [H$_2$O$_2$] in solution (Huckaba and Keyes, 1948). Second, using (i) the vapor-liquid equilibrium data of 93 wt % H$_2$O$_2$ at 273.2 K and 283.2 K (Scatchard et al., 1952; Schumb et al., 1955); and (ii) the QMS signals of the H$_2$O$_2$ vapor above the solution, determined at 265.3, 273.2 and 283.2 K, the gaseous [H$_2$O$_2$] of the 93 wt % H$_2$O$_2$ solution was determined, from a linear plot of the H$_2$O$_2$ QMS signals versus the gaseous H$_2$O$_2$ concentration, to be 0.106 ± 0.02 Torr at 265.3 K. However, taking the uncertainties of H$_2$O$_2$ vapor-liquid data (Manatt and Manatt, 2004) and the measurements into consideration, the accuracy of the gaseous [H$_2$O$_2$] was estimated to be ± 30 %.

The H$_2$O$_2$-He mixture was prepared by bubbling helium through the 93 wt % H$_2$O$_2$ solution in a glass bubbler at 265.3 K. The total pressure in the bubbler was measured by a Baratron pressure gauge (MKS Instruments; Model 722A). The typical H$_2$O$_2$-to-He mixing ratio was $10^{-4}$ to $10^{-5}$. The flow rate of the H$_2$O$_2$-He mixture was controlled
by a metering valve. The H$_2$O$_2$-He mixture, along with additional helium carrier gas, was admitted to the flow reactor via PFA tubing. The tubing was passivated by the H$_2$O$_2$-He mixture, to enable equilibrium to be established, as monitored by the QMS prior to every measurement.

2.4 Determination of initial uptake coefficient

The initial uptake coefficient, $\gamma_w$, of H$_2$O$_2$ on ice was determined as follows. First, a fresh ice film (~20 cm in length) was prepared by water-vapor deposition on the inner wall of the flow reactor for each determination. The background QMS signal at $m/z = 34$ was recorded. Second, the H$_2$O$_2$-He mixture was admitted to the other inlet of the double capillary injector. Before H$_2$O$_2$ molecules came in contact with the ice surface, the initial H$_2$O$_2$ signal, [H$_2$O$_2$]$_i$, was measured by the QMS. After the [H$_2$O$_2$]$_i$ stabilized, the sliding injector was pulled out toward the upstream end of the flow reactor, 1 cm at a time. The loss of H$_2$O$_2$ was monitored at $m/z = 34$ by the QMS as a function of the injector distance $z$. Figure 1 shows a typical plot of the QMS signal for the H$_2$O$_2$ loss on an ice-film surface. The initial H$_2$O$_2$ signals were determined under the conditions both with and without the ice film in the reactor, and the difference in H$_2$O$_2$ signals was subtracted for the plot. For the first-order loss rate under laminar flow conditions, the following equation holds for H$_2$O$_2$:

$$\ln[\text{H}_2\text{O}_2]_z = -k_s(z/v) + \ln[\text{H}_2\text{O}_2]_0$$

(1)

where $z$ is the injector position, $v$ is the average flow velocity, $z/v$ is the duration of contact (time) of H$_2$O$_2$ with the ice surface, [H$_2$O$_2$]$_z$ is the gaseous H$_2$O$_2$ concentration measured by the QMS at position $z$, and the subscript 0 is the initial injector reference position. The first-order loss rate constant ($k_s$) was determined to be $444 \pm 13$ s$^{-1}$, from the slope of the least-squares fit to the experimental data (Fig. 1). The $k_s$ value was corrected for gas-phase radial diffusion using a method outlined by Brown (1978), and the corrected rate constant was termed $k_w$. This correction worked well for our long and thin flow reactor (Davis, 2008). A diffusion coefficient for H$_2$O$_2$ in helium was used...
for the gas-phase diffusion correction; it was calculated, from the Chapman-Enskog
equation (Cussler, 1984), to be $698 \text{ cm}^2 \text{s}^{-1}$ at 0.270 Torr and 190 K. Assuming that
there is no other major gas-phase $\text{H}_2\text{O}_2$ loss besides the heterogeneous loss on ice, then the observed gas-phase $\text{H}_2\text{O}_2$ loss rate is equal to the heterogeneous loss rate. Figure 1 shows that there is no measurable $\text{H}_2\text{O}_2$ loss on the cold Pyrex wall surface and ensures that the assumption is valid.

The initial uptake coefficient can be calculated from $k_w$ as follows, using the geometric area of the flow reactor (Motz and Wise, 1960; Keyser et al., 1991; Chu and Chu, 1999):

$$\gamma_w = \frac{2rk_w}{\omega + r k_w}$$  \hspace{1cm} (2)

where $\omega$ is the mean molecular velocity, and $r$ (0.85 cm) is the radius of the flow reactor.

It is generally accepted that a vapor-deposited ice film has internal surface areas and is porous (Keyser and Leu, 1993a,b). In order to obtain a “true” uptake coefficient $\gamma_t$, assuming the film is a geometrically smooth surface, we have corrected $\gamma_w$ for contributions from the internal surface areas. On the basis of findings from previous studies conducted at similar conditions (Keyser et al., 1991, 1993; Keyser and Leu, 1993a), $\text{H}_2\text{O}$-ice films can be approximated as stacked layers of hexagonally close-packed spherical granules, and cylindrical pores are assumed. The true uptake coefficient, $\gamma_t$, is related to $\gamma_w$ by Keyser et al. (1993):

$$\gamma_t = \frac{\sqrt{3}\gamma_w}{\pi\{1 + \eta[2(N_L - 1) + (3/2)^{1/2}]\}}$$  \hspace{1cm} (3)

where the effectiveness factor, $\eta = \varphi^{-1}\tanh \varphi$, is the fraction of the film surface that participates in the reaction, $\varphi = \left(\left(N_L - 1\right)\left(\frac{2}{3}\right)^{1/2} + \left(\frac{1}{2}\right)\right) \left[\frac{3\rho_b}{2(\rho_t - \rho_b)}\right] (3\tau\gamma_t)^{1/2}$, $\rho_t$ (0.925 g cm$^{-3}$) and $\rho_b$ are true density and bulk density of the ice, $\tau$ is the tortuosity factor, and $N_L$ is the number of granule layers (Chu et al., 1993; Keyser et al., 1993).
Detailed calculations can be found in Keyser et al. (1991, 1993). \( \tau = 3.3 \) (see Sect. 3.1) was used in the above calculation. This value is within the typical recommended range of 2 to 6 for porous solids (Satterfield, 1970). The true uptake coefficient was subsequently determined to be \( \gamma_t = 3.9 \times 10^{-3} \) (Fig. 1).

2.5 \( \text{H}_2\text{O}_2 \) QMS signal

As shown below, the measured QMS signal at \( m/z = 34 \) was indeed from \( \text{H}_2\text{O}_2 \) molecules. We have determined that QMS signal ratio of \( m/z = 34 \) to \( m/z = 32 \) was \( (6 \pm 2) \times 10^{-3} \) and \( 0.15 \pm 0.05 \), before and after admitting \( \text{H}_2\text{O}_2 \) (\( 4 \times 10^{-5} \) Torr) to the flow reactor, respectively. The value, \((6 \pm 2) \times 10^{-3}\), was close to the expected signal ratio of \( 4 \times 10^{-3} \) for \( ^{34}\text{O}_2 : ^{32}\text{O}_2 \), calculated from the natural abundance of \( ^{18}\text{O} : ^{16}\text{O} \) (0.2 : 100) (Lide, 2008). \( 0.15 \pm 0.05 \) was approximately 25-fold higher than \( (6 \pm 2) \times 10^{-3} \), suggesting that the \( m/z = 34 \) signal was from \( \text{H}_2\text{O}_2 \) rather than \( ^{18}\text{O}^{16}\text{O} \). In addition, the contribution of \( ^{34}\text{O}_2 \) to the \( m/z = 34 \) signal was determined to be \(< 2.7 \% \) of the total \( m/z = 34 \) signal. \( k_s \) was calculated from the difference in logarithm signals (cf. Eq. (1)), and we found that the \( k_s \) value increased approximately 3.5 \%, after taking the \( ^{34}\text{O}_2 \) signal correction into consideration. The correction is smaller than the experimental uncertainty. In order to reduce the data acquisition time, we did not measure \( m/z = 34 \) and \( m/z = 32 \) signals simultaneously in all experiments, but we did correct the measured \( k_s \) value by 3.5 \% for the results in Tables 1 and 2.

We observed that the measured initial \( \text{H}_2\text{O}_2 \) signal, with the ice deposited in the reactor, was higher than that without the ice film, suggesting that the \( \text{H}_2\text{O}_2 \) signals were affected by the presence of the ice film. The \( \text{H}_2\text{O}_2 \) signal enhancement is not due to the interference of \( \text{H}_2\text{O} \) signal since \( \text{H}_2\text{O} \) has no \( m/z = 34 \) fragment. Furthermore, we found that the \( \text{H}_2\text{O}_2 \) signal increased with an increase in the \( \text{H}_2\text{O} \) vapor pressure. The nature of this \( m/z = 34 \) signal enhancement by the \( \text{H}_2\text{O} \) vapor pressure is not clear to us, however, it is possible that this observation was due to the formation of \( \text{H}_2\text{O}_2 -(\text{H}_2\text{O})_n \) clusters (Kulkarni et al., 2006) in the ionization region, and altered the
H2O2 QMS fragmentation pattern, leading to an enhanced H2O2 signal at m/z = 34. We have subtracted the enhancement of the initial H2O2 signal due to the presence of ice films, from the measured initial m/z = 34 signals. However, during the uptake coefficient measurement, when the injector was pulled out, the temperature of ice films varied slightly (1 to 2 K). As a result, this affected the measured H2O2 signal slightly. We have constructed a calibration curve of the H2O2 QMS signal versus the H2O vapor pressure, and the H2O2 signal changes due to the temperature effect were then corrected.

It was estimated that < 0.5 % of the H2O2 vapor would be decomposed over the 93 wt % H2O2 solution (Manatt and Manatt, 2004). The heterogeneous decomposition rate of H2O2 on a Pyrex glass could be ignored since the rate constant was estimated to be 10^-2 – 10^-5 s^-1 at 220 K (Schumb et al., 1955). Thus, the effect of the H2O2 decomposition on measured [H2O2] was negligible.

2.6 Temperature programmed desorption

Temperature programmed desorption (TPD) experiments were conducted to investigate the desorption kinetics of H2O2 on ice. An ice film was prepared on the inner wall of reactor first, followed by the exposure of the ice surface to gaseous H2O2 at 190 K. The surface was then heated with a linear heating rate of ~ 1.2 K min^-1, up to 283 K. The signals of the desorbed species, H2O2 and H2O, were collected and plotted as a function of temperature. The temperature resolution was approximately 0.5 K.

3 Results

3.1 The effect of ice-film thickness on uptake coefficient

The effect of ice-film thickness on the initial H2O2 uptake coefficient was studied to investigate the morphology of the ice film. We varied the ice-film thickness, h, from 1.0 to 51 µm, at 190 K. Figure 2 shows that the initial uptake coefficient, \( \gamma_w \), of H2O2 on
ice surfaces increased rapidly from $8.8 \times 10^{-3}$ to $1.3 \times 10^{-2}$ when $h \leq 4.0 \mu m$, but then $\gamma_w$ remained nearly constant, $(1.3 \pm 0.1) \times 10^{-2}$, for $h > 4.0 \mu m$. This pattern suggests that the ice film is porous and has internal surface areas. $H_2O_2$ molecules can gain access to the internal surfaces via pore diffusion. The results were modeled using the hexagonally close-packed spherical granule pore diffusion model (Keyser et al., 1993), Eq. (3). The solid line in Fig. 2 shows the result of nonlinear least-squares fit to the experimental data. Since $N_L$ in Eq. (3) is a function of thickness, an empirical relationship between $N_L$ and $h$ is assumed to be $N_L = a + b \log(h + c)$, where $a$, $b$, and $c$ are fitting parameters (Keyser et al., 1993; Jin and Chu, 2007). On the basis of the least-squares fit ($\gamma_w$ vs. $h$), we have determined that $\tau = 3.3 \pm 1.0$ and $N_L = 17$ for a $36.1 \pm 1.8 \mu m$ thick ice film, and $N_L = 13$ for a $14.7 \pm 1.5 \mu m$ thick ice film. The true uptake coefficient $\gamma_t$ of $H_2O_2$ on ice was also determined, from the nonlinear least-squares fit, to be $(1.1 \pm 0.2) \times 10^{-3}$ at 190 K.

3.2 The effect of $H_2O_2$ concentration on uptake coefficient

The uptake coefficient of $H_2O_2$ on ice was determined as a function of $H_2O_2$ partial pressure at $189.9 \pm 0.5 K$, and the results are shown in Fig. 3. When the $H_2O_2$ partial pressure was increased from $7.9 \times 10^{-6}$ to $4.7 \times 10^{-5}$ Torr, the $\gamma_w$ value increased from $1.4 \times 10^{-2}$ to $4.7 \times 10^{-2}$; and $\gamma_t$ increased from $1.3 \times 10^{-3}$ to $8.8 \times 10^{-3}$ (Fig. 3 and Table 1). The solid line in Fig. 3 is a fit to the experimental data (see details in Sect. 4.1). The results show that the higher the partial $H_2O_2$ pressure, the greater the initial uptake coefficient on the ice surface, suggesting that there is attractive interaction among adsorbed $H_2O_2$ molecules. The detailed experimental conditions are listed in Table 1, and the $\gamma_t$ values presented in Table 1 were calculated using $\tau$ and $N_L$ values from Sect. 3.1. The error bars in Fig. 3 and the errors listed in Table 1 include the systematic errors related to the pressure gauges, digital thermometers, mass flow meters, and the $m/z = 34$ signal corrections, estimated collectively to be approximately 10%, and 1 standard deviation $\pm \sigma$ of the mean value. Every $k_s$ value listed in Table 1 is
an average of two to five measurements, and each measurement was conducted on a freshly prepared ice film.

3.3 The effect of temperature on uptake coefficient

The values of the initial uptake coefficient were determined at a number of ice-film temperatures. We employed a thicker ice film, $36.1 \pm 1.8 \, \mu m$, to cover the entire temperature range from 190 to 220 K. Table 2 summarizes the results. The initial uptake coefficient for $H_2O_2$, $\gamma_w$, decreased from $1.4 \times 10^{-2}$ to $2.6 \times 10^{-3}$, as temperature of the ice film increased from 190 to 220 K. This trend is clearly consistent with the $H_2O_2$ heterogeneous loss on ice surfaces. The true uptake coefficient, $\gamma_t$, also decreased from $1.2 \times 10^{-3}$ to $6.6 \times 10^{-5}$ when temperature increased from 190 to 220 K (Fig. 4). The solid line in Fig. 4 was a fit to the experimental data (see Sect. 4.1).

3.4 Consecutive determinations of $\gamma$

Figure 5 shows four repetitions of the determination of an uptake coefficient at 190.0 K. The first measurement was conducted on a freshly prepared ice surface. Once the initial $H_2O_2$ signal was stable, the injector was pulled out 1 cm at a time toward the upstream end of the flow reactor. $\gamma_w$ of $H_2O_2$ on the ice surface was determined to be $1.8 \times 10^{-2}$. The injector was then pushed back to the downstream end to enable subsequent measurements to be made on the same ice film. We allowed the $H_2O_2$ signal to be stabilized for subsequent measurements, and the 2nd, 3rd and 4th determinations of the uptake coefficient were made on the same ice surface. The corresponding uptake coefficients were $1.8 \times 10^{-2}$, $1.8 \times 10^{-2}$ and $1.7 \times 10^{-2}$. Within the uncertainty of the measurement ($\sim 15 \%$), $\gamma$ is constant. The results suggest that the adsorption of a small amount of $H_2O_2$ on the ice surface, in a short uptake time period, does not deactivate the ice surface.
3.5 Temperature programmed desorption

Panel (a) in Fig. 6 depicts a series of TPD profiles of H₂O₂, at various H₂O₂ exposures on ice surfaces. The H₂O₂ exposed ice surface was heated from 190 to 283 K; and since no H₂O₂ signal was found above 260 K, we only present data obtained from 190 to 260 K. Panel (a) shows that as the H₂O₂ exposure time increased from 5, 10, 20, 30 to 45 min at 2.2×10⁻⁵ Torr (5-min exposure is equivalent to 6600 L), the desorption temperature, \( T_d \), of the first peak of each given desorption profile increased from 201.5, 206.0, 210.5, 213.0 to 216.0 K, correspondingly. This suggests that adsorbed H₂O₂ has lateral attractive interaction to aggregate H₂O₂ together on the surface. Also, TPD profiles suggest there is a considerable amount of H₂O₂ molecularly adsorbed on the surface, since the parent peak of H₂O₂ was detected. However, the \( T_d \) for a desorption peak centered at 225.0 K in each desorption profile remained unchanged, 225.0 ± 0.5 K, with an increase in H₂O₂ exposure (Panel (a) in Fig. 6). By varying the ice film thickness, we found that \( T_d \) of this desorption peak increased with an increase in ice-film thickness and \( T_d \) in each H₂O₂ desorption profile was the same as the ice \( T_d \), i.e., 225.0 K for 14.3 µm ice film and 229.5 K for 36.0 µm ice film (Panel (b) of Fig. 6). The \( T_d \) value of the middle desorption peak in each H₂O₂ desorption profile was approximately at 219.0 ± 0.5 K.

4 Discussion

4.1 Uptake coefficient of H₂O₂ on ice

Figure 3 shows that \( \gamma_t \) of H₂O₂ on ice films increases with increasing \( P_{H_2O_2} \), and this observation cannot be explained by the precursor model (Masel, 1996), which predicts that \( \gamma_t \) decreases as \( P_{H_2O_2} \) increases (see details below). \( P_{H_2O_2} \) used in Fig. 3 is higher than the saturation vapor pressure of solid H₂O₂ at 190 K, \( \sim 1 \times 10^{-6} \) Torr (Dean, 1999), providing a condition for H₂O₂ to aggregate or associate on the surface, and
the aggregation is also supported by results of TPD. Bowker and King (1979) shows that the sticking coefficient of nitrogen on W(110) increases with increasing nitrogen coverage at 90 and 120 K, and the observation is attributed to the attractive lateral interaction between the adsorbed nitrogen. Aggregation is also used to explain the trend for the sticking coefficient increases with increasing water coverage on Pt{110}-(1×2) (Panczyk et al., 2009). By analogous, we may explain the increase in uptake coefficient with increasing \( P_{H_2O_2} \) by considering both adsorption and aggregation of \( H_2O_2 \) on ice surfaces. The process is illustrated using the following equations.

\[
\begin{align*}
H_2O_2(g) & \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} H_2O_2(p) \\
1 - f & \times H_2O_2(p) \overset{k_2}{\underset{k_{-2}}{\rightleftharpoons}} H_2O_2(a) \\
f & \times H_2O_2(p) \overset{k_3}{\underset{k_{-3}}{\rightleftharpoons}} \frac{1}{n(H_2O_2)_n}
\end{align*}
\]

Reaction (R2) represents that gaseous \( H_2O_2 \) forms a weakly bounded precursor state, \( H_2O_2(p) \), on the surface, and \( H_2O_2(p) \) can be either desorbed back to the gas phase, or proceed to an adsorption state \( H_2O_2(a) \) (Reaction R3). At the same time, \( (H_2O_2)_n \) aggregation is allowed on the surface (Reaction R4). Furthermore, we assume that a small fraction, \( f \), of \( H_2O_2(p) \) is aggregated to form islands on the surface, and \( H_2O_2(g) \) is only adsorbed on the unoccupied surface.

Experimentally, the net loss of gas-phase \( H_2O_2 \) onto the ice-film surface was observed, and can be expressed as:

\[
- \frac{d[H_2O_2]}{dt} = k_1P_{H_2O_2} - k_{-1}[H_2O_2(p)]
\]

\([H_2O_2(p)]\) can be solved using the steady-state approximation, \( d[H_2O_2(p)]/dt = 0 \), and \( [H_2O_2(p)] = \frac{k_1P_{H_2O_2}}{k_{-1} + k_2(1-f) + k_3f} \), where we assume the reverse rates of Reactions (R3) and (R4) are slow. Since the amount of \( H_2O_2 \) adsorbed on the ice surface is 30104
low ($\theta < 0.1$), we assume $f$ is proportional to $\mathrm{H}_2\mathrm{O}_2$ surface coverage $\theta$ by $f = c\theta$, and $\theta$ can be expressed as $\theta \approx bP_{\mathrm{H}_2\mathrm{O}_2}$, where $b$ is a Langmuir adsorption constant. The uptake coefficient can then be expressed as:

$$
\gamma_t = \frac{-d[\mathrm{H}_2\mathrm{O}_2]}{dt} = \frac{4Vk_1}{\omega S} \frac{k_2(1 - f) + k_3f}{k-1 + k_2(1 - f) + k_3f} \quad (5)
$$

where $S/V$ is the surface-to-volume ratio of the flow reactor. Furthermore, when we combine constants together, $a = \frac{4Vk_1}{\omega S} \frac{k_3}{k-1+k_3}$, $m = \frac{4Vk_1}{\omega S} \frac{k_2-k_3}{k-1+k_3}$, $n = \frac{k_2-k_3}{k-1+k_3}$ and $K = bc$, Eq. (5) can be written as:

$$
\gamma_t = \frac{a + me^{-KP_{\mathrm{H}_2\mathrm{O}_2}}}{1 + ne^{-KP_{\mathrm{H}_2\mathrm{O}_2}}} \quad (6)
$$

Equation (6) was used to fit the data of $\gamma_t$ versus $P_{\mathrm{H}_2\mathrm{O}_2}$, and the fitted result is shown as a solid line in Fig. 3. The solid line replicates the experimental results very well, suggesting that the uptake of $\mathrm{H}_2\mathrm{O}_2$ on ice surfaces is accompanied by both adsorption and aggregation of $\mathrm{H}_2\mathrm{O}_2$ on ice surfaces.

If we ignore the aggregation of $\mathrm{H}_2\mathrm{O}_2$, i.e., $f = 0$, and assume that Reactions (R2) and (R3) are the only steps to take place on the ice surface, with Reaction (R3) as the rate-determining step, then $\gamma_t$ can be expressed as:

$$
\gamma_t = \frac{-d[\mathrm{H}_2\mathrm{O}_2]}{dt} \approx \frac{4V}{\omega S} \frac{k_2S_O}{k-1 + k_2P_{\mathrm{H}_2\mathrm{O}_2}} \quad (7)
$$

where $S_O$ is the total surface sites (Masel, 1996). Equation (7) shows that $\gamma_t$ decreases as $P_{\mathrm{H}_2\mathrm{O}_2}$ increases. Equation (7) cannot model the observation, and the fitted result is shown as the long dashed line in Fig. 3. This shows that the precursor model cannot predict our results.
On the other hand, if we assume the aggregation (island formation) of \( \text{H}_2\text{O}_2 \) on ice surfaces is the only pathway, i.e., \( f = 1 \), with Reaction (R4) as the rate-determining step, and then \([\text{H}_2\text{O}_2(p)] = \frac{k_1 P_{\text{H}_2\text{O}_2}}{k_{-1} + k_3} \), \( \gamma_t \) can be written as:

\[
\gamma_t = \frac{-d[\text{H}_2\text{O}_2]}{dt} = \frac{a - b'}{P_{\text{H}_2\text{O}_2}},
\]

where \( b' = \frac{4V}{\omega S} k_{-3} [(\text{H}_2\text{O}_2)_n]^{1/n} \). Assuming \((\text{H}_2\text{O}_2)_n\) is hydrogen bonded and is stable on the surface and the reverse reaction in Reaction (R4) is slow, and then the \([(\text{H}_2\text{O}_2)_n]\) is approximately unchanged, so as \( b' \). The result of Eq. (8) is essentially the same as the result from the condensation model (Brown et al., 1996). We used Eq. (8) to fit the data of \( \gamma_t \) versus \( P_{\text{H}_2\text{O}_2} \), and the fitted result is shown as the dotted line in Fig. 3. The dotted line cannot represent the result well. By comparing the results of three processes (Fig. 3), we conclude that the uptake of \( \text{H}_2\text{O}_2 \) on ice is accompanied by both aggregation and adsorption of \( \text{H}_2\text{O}_2 \) on ice surfaces, and this explains the observation −\( \gamma_t \) increases with increasing \( P_{\text{H}_2\text{O}_2} \) very well.

Figure 4 shows that \( \gamma_t \) decreases as temperature increases. We attribute the decrease in \( \gamma_t \) to be kinetics. Because the surface area of vapor-deposited ice reduces approximately 2-fold from 200 to 265 K (Keyser and Leu, 1993a), and the decrease in the ice surface area is substantially smaller than the decrease in \( \gamma_t \) from 190 to 220 K (18-fold). The experimental observation can be explained using Eq. (5). The data in Fig. 4 were collected at \( P_{\text{H}_2\text{O}_2} = 8.9 \times 10^{-6} \) Torr, which is lower than the \( \text{H}_2\text{O}_2 \) saturation vapor pressure at the corresponding temperature, except at 190 K. This implies that the rate of aggregation (R4) is not predominant relative to the rate of adsorption, i.e., \( k_3 f < k_2 (1 - f) \), and then \( k_2 (1 - f) + k_3 f \approx k_2 (1 - f) \) in Eq. (5). Furthermore, with low \( P_{\text{H}_2\text{O}_2} \) and the short \( \text{H}_2\text{O}_2 \) exposure time (∼minute), we can assume that the surface coverage is low, \( \theta \sim 0.1 \), and approximately constant; then we have \( f < 1 \), and \( f \) can be
approximately treated as a constant. Equation (5) can be rewritten as:

\[ \gamma_t \approx \frac{4Vk_1}{\omega S k_{-1} + k_2(1-f)} \approx \frac{4Vk_1}{\omega S} \frac{1}{k_{-1} + k_2(1-f)} \approx \frac{4Vk_1}{\omega S} \frac{1}{1 + \frac{\nu_1}{\nu_2} e^{(f-\frac{\Delta E}{RT})}} \]  

where \( \Delta E = E_{-1} - E_2 \) and \( R \) is the gas constant. \( E_{-1} \) and \( E_2 \) are the activation energy of \( \text{H}_2\text{O}_2 \) from the precursor state to the gas phase and to the adsorption state, respectively. Equation (9) was used to fit the data in Fig. 4. \( \Delta E = 28.5 \pm 7.0 \text{ kJ mol}^{-1} \) was obtained from the least-squares fit. The activation energy of the uptake, \( E_a = -\Delta E = -28.5 \pm 7.0 \text{ kJ mol}^{-1} \), indicates that a precursor \( \text{H}_2\text{O}_2 \) molecule can easily overcome the barrier and traps in the adsorption state. It is a nonactivated adsorption process. \( E_a \) of \( \text{H}_2\text{O}_2 \) on the aqueous surface was determined to be \( -26 \pm 7 \text{ kJ mol}^{-1} \) (Worsnop et al., 1989), which is close to \( E_a \) of \( \text{H}_2\text{O}_2 \) on the ice surface, suggesting that the fitted \( \Delta E = 28.5 \pm 7 \text{ kJ mol}^{-1} \) is reasonable. The analysis from Eq. (9) also suggests that more \( \text{H}_2\text{O}_2 \) molecules are adsorbed on the ice surface at a lower temperature, i.e., \( 190 \text{ K} \). At a higher temperature, i.e., \( 220 \text{ K} \), we anticipate that the desorption of precursor \( \text{H}_2\text{O}_2 \) molecules to the gas phase has a higher probability than the migration of \( \text{H}_2\text{O}_2 \) to adsorption sites, and results in lower \( \gamma_t \) values.

### 4.2 Temperature programmed desorption

Panel (a) in Fig. 6 shows that \( \text{H}_2\text{O}_2 T_d \) of the first desorption peak of each desorption profile increases with an increase in \( \text{H}_2\text{O}_2 \) exposure, consistent with the zero-order desorption kinetics. Assuming that the zero-order kinetic formalism applies to the TPD data, the leading edge of the desorption profiles of the first peak in Panel (a) of Fig. 6 can be described using (Brown et al., 1996):

\[ \text{Desorption rate} = \nu_0 e^{-\frac{E_d}{RT}} \]  

where \( \nu_0 \) is a pre-exponential factor and \( E_d \) is the desorption barrier. The long dashed line plotted in Panel (a) shows that the \( \text{H}_2\text{O}_2 \) desorption profile of the first desorption peak, at various exposures, can be perfectly described using Eq. (10), with
ν₀ = (1.0 ± 0.3)×10^{26} \text{molecules cm}^{-3} \text{s}^{-1} \text{ and } E_d = 58.3 \pm 5.0 \text{kJ mol}^{-1}. \text{ The excellent fit to the zero-order desorption kinetics suggests that H}_2\text{O}_2 \text{ is multilayer adsorbed or islanded on the ice-film surface due to the lateral attractive interaction. Multilayer adsorption is expected because the exposure of H}_2\text{O}_2 \text{ on the ice surface is high in TPD experiments. For example, for the lowest exposure (5-min H}_2\text{O}_2 \text{ exposure) at 190 K, the amount of H}_2\text{O}_2 \text{ taken up by the ice surface is } 1.4\times10^{15} \text{molecules cm}^{-2}, \text{ which is higher than a monolayer coverage of } 2.7\times10^{14} \text{molecules cm}^{-2}, \text{ estimated using the van der Waals radii of H}_2\text{O}_2 \text{ 3.42 Å (Huheey, 1983). The multilayer adsorption supports our previous assumption of the H}_2\text{O}_2 \text{ molecule can be aggregated on ice surfaces for the analysis of the uptake coefficient data.}

T_d \text{ of the H}_2\text{O}_2 \text{ desorption peak centered at 225.0 K is identical to the } T_d \text{ of ice, suggesting that H}_2\text{O}_2 \text{ desorption at 225.0 K is accompanied by the ice desorption. Since H}_2\text{O}_2 \text{ does not adsorb on the surface of the glass reactor wall (cf. Fig. 1), once H}_2\text{O} \text{ desorption takes place, H}_2\text{O}_2 \text{ desorbs along with ice. The nature of the H}_2\text{O}_2 \text{ desorption peaks at 219.0 ± 0.5 K is not exactly clear to us. It may be due to H}_2\text{O}_2 \text{ near distorted surface layers. The increase in } T_d \text{ of ice from 225.0 K to 229.5 K, as the ice-film thickness increases from 14.3 μm to 36.0 μm, is attributed to the increased total lateral interactions among H}_2\text{O} \text{ molecules for a thicker ice film (Yan and Chu, 2008).}

5 Comparison and atmospheric implication

We may compare some of our findings with results from previous studies. Conklin et al. (1993) reported the sticking coefficient, α, to be 2.2×10^{-2} \text{ for H}_2\text{O}_2 (\sim 3\times10^{-5} \text{Torr) loss on ~200-μm ice spheres at 228 K, from the analysis of the H}_2\text{O}_2 \text{ breakthrough curves, using the advection-dispersion model. Our initial uptake coefficient } γ_w \text{ is estimated to be } \sim 2\times10^{-3} \text{ at 228 K and } 3\times10^{-5} \text{Torr. This } γ_w \text{ value is lower than the } α \text{ value. A possible explanation follows: since the } α \text{ value was obtained from the overall forward rate constant of the advection-dispersion model, the model takes the adsorption of H}_2\text{O}_2 \text{ on the surface, the distribution of H}_2\text{O}_2 \text{ in the surface disor-
dered region and the diffusion of H$_2$O$_2$ into bulk ice into consideration, but the model does not separate these processes rigorously. With the long H$_2$O$_2$ exposure time to ice (up to 16 h) (Conklin et al., 1993), the transport of H$_2$O$_2$ to the near surface region and bulk cannot be ignored. In addition, co-condensation of H$_2$O with H$_2$O$_2$ also plays a role in the study of Conklin et al. (1993). The factors illustrated above cause a higher overall forward rate constant than the rate of the adsorption process alone. Our initial uptake coefficient measures the net H$_2$O$_2$ loss on the ice surface (cf. Eq. 4), since the H$_2$O$_2$ exposure time is short (∼ minutes). This may explain the higher $\alpha$ value than our $\gamma_w$ value. We also determined the amount of H$_2$O$_2$ taken up by ice surfaces (data are not shown). Our results show that the H$_2$O$_2$ uptake amount on ice films increases as temperature decreases, this is in agreement with the results of Conklin et al. (1993) and Pouvesle et al. (2010).

There is no reported $\gamma$ value for H$_2$O$_2$ on ice surfaces at $T < 228$ K. The $\gamma$ values of H$_2$O$_2$/ice may be compared to the $\gamma$ values of atmospheric oxygenated organics on vapor deposited ice (Behr et al., 2006; Romanias et al., 2010). Table 3 shows $\gamma$ values decrease gradually in an order from H$_2$O$_2$, CH$_3$COCH$_3$ to HCOOH. For these systems, the gas-surface interaction is mainly the van der Waals and hydrogen bonding interactions. The hydrogen bonding interaction for H$_2$O$_2$/ice is expected to be the strongest among the three systems, followed by HCOOH/ice and CH$_3$COCH$_3$/ice. Polarizability, $\bar{\alpha}$, of the molecules decreases from CH$_3$COCH$_3$, HCOOH, to H$_2$O$_2$ (Table 3) (Schumb et al., 1955; Giguère, 1983; Lide, 2008), suggesting that the van der Waals interaction between CH$_3$COCH$_3$ and ice is the strongest, likely due to both C=O and CH$_3$ groups interact with the ice surface. The van der Waals interaction between H$_2$O$_2$ and ice is relatively weak, and H$_2$O$_2$/ice is dominated by the strong hydrogen bonding interaction. Cyclic HCOOH dimers in the gas phase via hydrogen bonds (Allouche, 2005) may affect the hydrogen bonding between HCOOH and ice. Along with low $\bar{\alpha}$ for HCOOH, this may result in the low $\gamma$ value listed in Table 3. Although the comparison is limited by the available data, it suggests that the interactions between H$_2$O$_2$ or oxygenated organics gases and ice involve both hydrogen bonds and van der Waals forces, and
the γ value depends on the nature of gas-surface interactions. The stronger the gas-surface interaction is, the higher the γ value is. For instance, the adsorption of $\text{H}_2\text{O}_2$ on $\text{TiO}_2$ surfaces is suggested to be a dissociative chemisorption (Pradhan et al., 2010), at room temperature, its room-temperature γ value is comparable with the γ values of other compounds listed in Table 3.

The activation energy of desorption for ice was determined to be $E_d = 48.0 \pm 3.0 \text{kJ mol}^{-1}$ (Panel b, Fig. 6). This is in an excellent agreement with a value of $48.3 \pm 0.8 \text{kJ mol}^{-1}$, reported by Brown et al. (1996). Since the binding energy (26.4 kJ mol$^{-1}$) of the $\text{H}_2\text{O}_2$·$\text{H}_2\text{O}_2$ dimer is higher than that of $\text{H}_2\text{O}$·$\text{H}_2\text{O}$ dimer (20.6 kJ mol$^{-1}$) (Schütz et al., 1997; Engdahl et al., 2001), using the similar analogy, we anticipate that the measured $E_d$ of $\text{H}_2\text{O}_2$ (58.3 ± 5.0 kJ mol$^{-1}$) is higher than $E_d = 48 \text{kJ mol}^{-1}$ of ice.

In order to assess the importance of the heterogeneous loss of $\text{H}_2\text{O}_2$ on ice/snow surfaces, we may compare heterogeneous lifetimes of $\text{H}_2\text{O}_2$ on cirrus clouds and on the snow/icepack (dry deposition) to a lifetime of $\text{H}_2\text{O}_2$ photolysis in the atmosphere. Cirrus clouds in the upper troposphere consist mainly of ice, and are surrounded by air. Using the first-order loss rate constant of $k_t = 1.4 \text{s}^{-1}$ (calculated from $k_w = 55 \text{s}^{-1}$, and corrected for ice porosity) for $8.9 \times 10^{-6} \text{Torr} \text{H}_2\text{O}_2$ on ice surfaces at 220 K and the typical $S/V$ ratio of $10^{-3} \text{cm}^2 \text{cm}^{-3}$ for a tropospheric cloud (Seinfeld and Pandis, 2006), the heterogeneous lifetime of $\text{H}_2\text{O}_2$ is estimated to be $\sim 700 \text{s}$. The atmospheric photolysis rate constant for $\text{H}_2\text{O}_2$ is $J = 1.2 \times 10^{-5} \text{s}^{-1}$ in the upper troposphere (Barth et al., 2007), and the photolysis lifetime of $\text{H}_2\text{O}_2$ is $1/J = 8.3 \times 10^4 \text{s}$. Thus, the heterogeneous loss of $\text{H}_2\text{O}_2$ on cirrus cloud surfaces is more efficient process than that of the $\text{H}_2\text{O}_2$ photolysis. On the ground-level snow/ice surfaces, the heterogeneous lifetime of $\text{H}_2\text{O}_2$ is estimated to be $\sim 4 \times 10^{-3} \text{s}$ using the $S/V$ ratio $\sim 200 \text{cm}^2 \text{cm}^{-3}$ for the typical snow/ice surface (Dominé et al., 2002). This value is smaller than that of photolysis, $8.3 \times 10^4 \text{s}$, with an assumption that $J$ of $\text{H}_2\text{O}_2$ at ground level is similar to that in the upper troposphere. However, dry deposition consists of aerodynamic and quasi-laminar
sublayer transports, and the heterogeneous uptake (Seinfeld and Pandis, 2006). The air parcel containing H$_2$O$_2$ needs to transport to the icepack surface. With a dry deposition velocity of H$_2$O$_2$ 0.32 cm s$^{-1}$ over the snow/icepack surfaces, and the average travel length of $\sim$10 m from the air to the snow/ice surface (Seinfeld and Pandis, 2006), the dry deposition time is estimated to be $\sim 3\times 10^3$ s, which is orders of magnitude longer than the heterogeneous lifetime of H$_2$O$_2$, $4\times 10^{-3}$, on ice, suggesting that the heterogeneous loss of H$_2$O$_2$ on icepack at ground level is limited by the transport process (dry deposition), not by heterogeneous chemistry. The heterogeneous loss of H$_2$O$_2$ on snow/ice surfaces is faster than the gas-phase photolysis rate of H$_2$O$_2$. In summary, the loss of H$_2$O$_2$ to ice surfaces, such as cirrus clouds and snow/icepack, may be a sink for H$_2$O$_2$ at low temperature. However, at warmer temperature, our TPD results and other studies (Clegg and Abbatt, 2001) suggest that ice is not a permanent sink for H$_2$O$_2$.

6 Conclusions

We have determined the initial uptake coefficient of H$_2$O$_2$ on ice surfaces using the flow reactor. $\gamma_t$ of H$_2$O$_2$ increases from $1.3\times 10^{-3}$ to $8.8\times 10^{-3}$ on ice films, as the H$_2$O$_2$ partial pressure increases from $7.9\times 10^{-6}$ to $4.7\times 10^{-5}$ Torr at 190 K. The $\gamma_t$ value of H$_2$O$_2$ decreases from $1.2\times 10^{-3}$ to $6.6\times 10^{-5}$ as the temperature increases from 190 to 220 K. Uptake of H$_2$O$_2$ on ice involves both adsorption and aggregation of H$_2$O$_2$ on the ice surfaces. The study suggests that the nature of H$_2$O$_2$-ice surface interactions is mainly hydrogen bonds. The results imply that gaseous H$_2$O$_2$ can be taken up by snow/ice or icepack, with $\gamma_w \leq 0.1$ at low temperatures, and our results are useful to model the H$_2$O$_2$ loss on snow/ice and cirrus clouds.

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Uptake coefficient of H$_2$O$_2$ on ice

H. Yan and L. T. Chu


Hutterli, M. A., McConnell, J. R., Stewart, R. W., Jacobi, H.-W., and Bales, R. C.: Impact of temperature-driven cycling of hydrogen peroxide (H$_2$O$_2$) between air and snow on the

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Pouvesle, N., Kippenberger, M., Schuster G., and Crowley, J. N.: The interaction of H₂O₂ with


Table 1. Uptake coefficients for H₂O₂ on ice surfaces at 190 K.

<table>
<thead>
<tr>
<th>$P_{\text{H}_2\text{O}_2}$ (Torr)</th>
<th>$T$ (K)</th>
<th>$\nu^b$ (m s⁻¹)</th>
<th>$k_z$ (s⁻¹)</th>
<th>$k_w$ (s⁻¹)</th>
<th>$\gamma_w$</th>
<th>$\gamma_t^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(7.9 \pm 0.6) \times 10^{-6}$</td>
<td>189.9 ± 0.3</td>
<td>18.8</td>
<td>250 ± 31</td>
<td>280 ± 36</td>
<td>$(1.4 \pm 0.2) \times 10^{-2}$</td>
<td>$(1.3 \pm 0.3) \times 10^{-3}$</td>
</tr>
<tr>
<td>$(1.2 \pm 0.1) \times 10^{-5}$</td>
<td>189.8 ± 0.3</td>
<td>19.0</td>
<td>316 ± 38</td>
<td>366 ± 96</td>
<td>$(1.9 \pm 0.5) \times 10^{-2}$</td>
<td>$(2.0 \pm 0.8) \times 10^{-3}$</td>
</tr>
<tr>
<td>$(1.5 \pm 0.1) \times 10^{-5}$</td>
<td>190.1 ± 0.3</td>
<td>19.1</td>
<td>444 ± 54</td>
<td>547 ± 71</td>
<td>$(2.8 \pm 0.4) \times 10^{-2}$</td>
<td>$(3.9 \pm 0.8) \times 10^{-3}$</td>
</tr>
<tr>
<td>$(2.0 \pm 0.1) \times 10^{-5}$</td>
<td>190.0 ± 0.2</td>
<td>19.0</td>
<td>456 ± 62</td>
<td>567 ± 82</td>
<td>$(2.9 \pm 0.4) \times 10^{-2}$</td>
<td>$(4.1 \pm 1.0) \times 10^{-3}$</td>
</tr>
<tr>
<td>$(2.2 \pm 0.1) \times 10^{-5}$</td>
<td>190.1 ± 0.3</td>
<td>18.6</td>
<td>495 ± 97</td>
<td>630 ± 138</td>
<td>$(3.2 \pm 0.7) \times 10^{-2}$</td>
<td>$(4.8 \pm 1.6) \times 10^{-3}$</td>
</tr>
<tr>
<td>$(2.9 \pm 0.1) \times 10^{-5}$</td>
<td>190.2 ± 0.2</td>
<td>18.8</td>
<td>565 ± 88</td>
<td>744 ± 131</td>
<td>$(3.7 \pm 0.6) \times 10^{-2}$</td>
<td>$(6.3 \pm 1.8) \times 10^{-3}$</td>
</tr>
<tr>
<td>$(3.7 \pm 0.1) \times 10^{-5}$</td>
<td>189.9 ± 0.4</td>
<td>18.6</td>
<td>613 ± 70</td>
<td>830 ± 102</td>
<td>$(4.2 \pm 0.5) \times 10^{-2}$</td>
<td>$(7.4 \pm 1.4) \times 10^{-3}$</td>
</tr>
<tr>
<td>$(4.7 \pm 0.1) \times 10^{-5}$</td>
<td>189.8 ± 0.2</td>
<td>19.0</td>
<td>676 ± 94</td>
<td>941 ± 147</td>
<td>$(4.7 \pm 0.7) \times 10^{-2}$</td>
<td>$(8.8 \pm 2.0) \times 10^{-3}$</td>
</tr>
</tbody>
</table>

a The ice-film thickness was 14.7 ± 1.5 µm.
b Flow velocity.
c $\gamma_t$ was calculated from Eq. (3) using $N_L = 13$ at $h = 14.7$ µm.
Table 2. Uptake coefficients for H$_2$O$_2$ on ice surfaces at varying temperature$^a$.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$\nu^b$ (m s$^{-1}$)</th>
<th>$k_s$ (s$^{-1}$)</th>
<th>$k_w$ (s$^{-1}$)</th>
<th>$\gamma_w$</th>
<th>$\gamma_t^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>189.8 ± 0.2</td>
<td>19.3</td>
<td>241.4 ± 52.8</td>
<td>269.2 ± 61.8</td>
<td>$(1.4 ± 0.3) \times 10^{-2}$</td>
<td>$(1.2 ± 0.5) \times 10^{-3}$</td>
</tr>
<tr>
<td>194.6 ± 0.2</td>
<td>18.9</td>
<td>226.1 ± 34.4</td>
<td>250.2 ± 39.3</td>
<td>$(1.3 ± 0.2) \times 10^{-2}$</td>
<td>$(1.1 ± 0.4) \times 10^{-3}$</td>
</tr>
<tr>
<td>200.0 ± 0.2</td>
<td>19.4</td>
<td>162.4 ± 38.2</td>
<td>174.5 ± 46.9</td>
<td>$(8.7 ± 2.0) \times 10^{-3}$</td>
<td>$(5.4 ± 2.5) \times 10^{-4}$</td>
</tr>
<tr>
<td>204.7 ± 0.3</td>
<td>20.1</td>
<td>116.9 ± 51.8</td>
<td>123.1 ± 56.3</td>
<td>$(6.1 ± 2.7) \times 10^{-3}$</td>
<td>$(2.8 ± 1.3) \times 10^{-4}$</td>
</tr>
<tr>
<td>209.7 ± 0.3</td>
<td>20.9</td>
<td>109.3 ± 14.2</td>
<td>114.6 ± 14.9</td>
<td>$(5.6 ± 0.7) \times 10^{-3}$</td>
<td>$(2.5 ± 1.1) \times 10^{-4}$</td>
</tr>
<tr>
<td>214.2 ± 0.3</td>
<td>21.3</td>
<td>82.2 ± 24.8</td>
<td>85.2 ± 26.1</td>
<td>$(4.1 ± 1.2) \times 10^{-3}$</td>
<td>$(1.4 ± 0.7) \times 10^{-4}$</td>
</tr>
<tr>
<td>219.1 ± 0.2</td>
<td>22.0</td>
<td>53.7 ± 13.4</td>
<td>54.8 ± 13.5</td>
<td>$(2.6 ± 0.6) \times 10^{-3}$</td>
<td>$(6.6 ± 2.8) \times 10^{-5}$</td>
</tr>
</tbody>
</table>

$^a$ $R_{H_2O_2} = (8.9 ± 0.4) \times 10^{-6}$ Torr, and the thickness of ice films was 36.1 ± 1.8 µm.

$^b$ Flow velocity.

$^c$ $\gamma_t$ was calculated from Eq. (3) using $N_L = 17$ at $h = 36.1$ µm.
Table 3. Comparison of uptake coefficients on vapor deposited ice.

<table>
<thead>
<tr>
<th></th>
<th>$10^3 \gamma$</th>
<th>Surface</th>
<th>Reference</th>
<th>$\tilde{a}$ ($10^{-24}$ cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O$_2$</td>
<td>8.7</td>
<td>ice</td>
<td>This work</td>
<td>2.3</td>
</tr>
<tr>
<td>CH$_3$COCH$_3$</td>
<td>6</td>
<td>ice</td>
<td>Behr et al. (2006)</td>
<td>6.3</td>
</tr>
<tr>
<td>HCOOH</td>
<td>2</td>
<td>ice</td>
<td>Romanias et al. (2010)</td>
<td>3.4</td>
</tr>
<tr>
<td>H$_2$O$_2$</td>
<td>1.5$^b$</td>
<td>TiO$_2$</td>
<td>Pradhan et al. (2010)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ At $8.9 \times 10^{-6}$ Torr and $199.0 \pm 1.0$ K.
$^b$ At $1.3 \times 10^{-4}$ Torr, 295 K and 15% relative humidity.
Fig. 1. Plot of the log $\text{H}_2\text{O}_2$ signal versus contact time ($t = z/v$) at 190 K. The plot shows the initial $\text{H}_2\text{O}_2$ signal, before $\text{H}_2\text{O}_2$ came in contact with the ice ($t < 0$), and the loss of $\text{H}_2\text{O}_2$ onto the ice film ($t > 0$). The background $\text{H}_2\text{O}_2$ signal was subtracted. The first-order loss rate constant for $\text{H}_2\text{O}_2$ on ice was determined to be $k_s = 444 \pm 13 \text{ s}^{-1}$, and the corrected rate constant $k_w = 549 \pm 19 \text{ s}^{-1}$, and $\gamma_w = 2.8 \times 10^2$. The ice-film thickness was 13.8 µm, and $P_{\text{H}_2\text{O}_2} = 1.5 \times 10^{-5}$ Torr. The loss of $\text{H}_2\text{O}_2$ signal onto the reactor wall shows that there is no $\text{H}_2\text{O}_2$ loss to the cold glass reactor wall, $P_{\text{H}_2\text{O}_2} = 1.0 \times 10^{-5}$ Torr. Data were offset for clarity.
Fig. 2. Plot of the initial uptake coefficient of \( \text{H}_2\text{O}_2 \), \( \gamma_w \), on ice as a function of the ice-film thickness at 190.0 ± 0.2 K. Fitted parameters are \( a = -0.35 \), \( b = 11.03 \) and \( c = 1.002 \). \( P_{\text{H}_2\text{O}_2} = (8.2 \pm 0.3) \times 10^{-6} \) Torr, and the \( \gamma_t \) value was determined to be \( (1.1 \pm 0.2) \times 10^{-3} \) (see text).
Fig. 3. Plot of the true uptake coefficient of H$_2$O$_2$, $\gamma_t$, on the ice surface versus H$_2$O$_2$ partial pressure at 190 K. The ice-film thickness was 14.7 ± 1.5 µm. See text for details.
Fig. 4. Plot of the true uptake coefficient of $\text{H}_2\text{O}_2$, $\gamma_t$, on the ice surface versus $1/T$. $P_{\text{H}_2\text{O}_2} = (8.9 \pm 0.4) \times 10^{-6}$ Torr.
Fig. 5. Plot of the H$_2$O$_2$ signal versus the gas-surface contact time for four repeated measurements on an ice film at 190.0 K. The initial uptake coefficient, $\gamma_w$, calculated from the slopes of the data using the least-squares fit to Eq. (1) (solid line), to be 1.8x10$^{-2}$. After the first measurement, the injector was then pushed back to the downstream end to enable subsequent measurements to be made on the same ice film. The background H$_2$O$_2$ signal has been subtracted from the plotted values. The thickness of the ice film was 14.7 µm, and the total pressure was 0.500 Torr. See text for details.
Fig. 6. TPD of H$_2$O$_2$ on ice films. (a) H$_2$O$_2$ TPD profiles, (b) H$_2$O TPD profiles. Ice films were exposed to gaseous H$_2$O$_2$ at 190 K and $P_{H_2O_2} = (2.2 \pm 0.1) \times 10^{-5}$ Torr.