Reinvestigation of the Henry's law constant for hydrogen peroxide with temperature and acidity variation

Daoming Huang, Zhongming Chen*

*The State Key Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering,
Peking University, Beijing 100871, China. E-mail: hdm708@163.com*

Abstract

Hydrogen peroxide is not only an important oxidant in itself; it also serves as both sink and temporary reservoir for other important oxidants including HOx (OH and HO$_2$) radicals and O$_3$ in the atmosphere. Its partitioning between gas and aqueous phases in the atmosphere, usually described by its Henry's law constant (K_H), significantly influences its role in atmospheric processes. Large discrepancies between the K_H values reported in previous work, however, have created uncertainty for atmospheric modelers. Based on our newly developed online instrumentation, we have re-determined the temperature and acidity dependence of K_H for hydrogen peroxide at an air pressure of (0.960 ± 0.013) atm (1 atm $= 1.01325 \times 10^5$ Pa). The results indicated that the temperature dependence of K_H for hydrogen peroxide fits to the Van't Hoff equation form, expressed as $\ln K_H = a/T - b$, and $a = -\Delta H/R$, where K_H is in M/atm (M is mol/L), T is in degrees Kelvin, R is the ideal gas constant, and ΔH is the standard heat of solution. For acidity dependence, results demonstrated that the K_H value of hydrogen peroxide appeared to have no obvious dependence on decreasing pH level (from pH 7 to pH 1). Combining the dependence of both temperature and acidity, the obtained a and b were 7024 ± 138 and 11.97 ± 0.48, respectively, ΔH was (58.40 ± 1.15) kJ/(K·mol), and the uncertainties represent σ. Our determined K_H values for hydrogen peroxide will therefore be of great use in atmospheric models.

Key words: hydrogen peroxide; Henry's law constant; atmosphere; acidity

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Introduction

Hydroperoxides, including hydrogen peroxide (H$_2$O$_2$), and organic hydroperoxides (ROOH), such as methylhydroperoxide (CH$_3$OOH) and peroxyacetic acid (CH$_3$C(O)OOH), play significant roles in the atmospheric processes of acid precipitation, cycling of HOx radicals, and formation of secondary organic aerosols (SOA) (Hua et al., 2008; Zhang et al., 2010). Hydrogen peroxide is considered the most important oxidant for the conversion of S(IV) to sulfuric acid and secondary sulfate in clouds, fog, and rain water at pH < 5, and thus contribute significantly to the acidification of clouds and rain (Penkett et al., 1979; Calvert et al., 1985; Fung et al., 1991; Pena et al., 2001). Both H$_2$O$_2$ and CH$_3$OOH can serve as temporary reservoirs for odd-hydrogen radicals (OH, HO$_2$, CH$_3$O$_2$) in the troposphere, as their photolysis and other reactions lead to the regeneration of OH radicals, and are also intimately involved in the production of odd-oxygen (e.g., O, O$_3$) (Madronich and Calvert, 1990; Lightfoot et al., 1992; Reeves and Penkett, 2003). Furthermore, hydroperoxides are believed to be plant and human toxins because of their strong oxidizing

property that can render enzymes useless and damage cells (Gurtner et al., 1987; Hewitt et al., 1990), although their efficacy in this regard is not completely clear (Gäb et al., 1985; Hewitt and Kok, 1991; Miller and Kester, 1994). The partitioning of these reactive species between gas and aqueous phases in the atmosphere, usually described by the Henry's law constant, is an important aspect of their role in atmospheric processes. Large discrepancies between the K_H values reported in previous work, however, have created uncertainty for atmospheric modelers. In the present study, we have re-determined the temperature and acidity dependence of the Henry's law constant for hydrogen peroxide at an air pressure of about 0.960 atm (1 atm $= 1.01325 \times 10^5$ Pa), based on our newly developed online instrumentation.

1 Experimental methods

1.1 Reagents

The H$_2$O$_2$ solution (Sigma-Aldrich Chemical, 35%) was commercial-grade and was standardized against permanganate solution before use. The H$_2$SO$_4$ (98%), purchased from the Beijing Chemical Factory, was used to adjust pH. The H$_3$PO$_4$ solution (Sigma-Aldrich, 85% for HPLC)

* Corresponding author. E-mail: zmchen@pku.edu.cn

was diluted to 5×10^{-4} mol/L and used as HPLC (high performance liquid chromatography) mobile phase. All solutions were prepared with 18 MΩ water.

1.2 Measurement method

The experimental equipment used for determining the Henry's law constant of H_2O_2 contained three main parts: a saturated vapor generator, a vapor collector, and a HPLC (1100, Agilent, USA) for quantifying H_2O_2. The schematic diagram of vapor saturator is shown in Fig. 1.
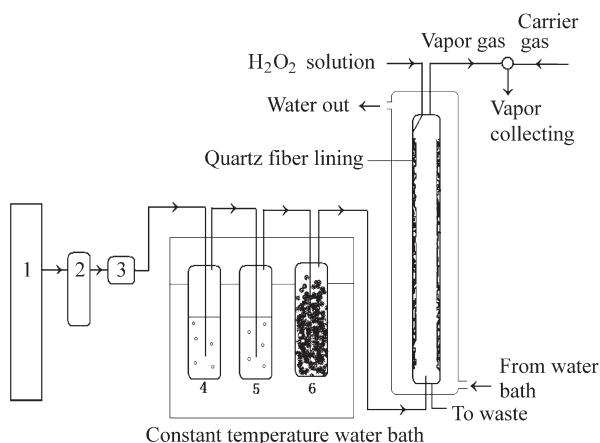

Fig. 1 Schematic diagram of the apparatus used for generation and collection of saturated H_2O_2 vapor. (1) highly purified synthetic air supply; (2) drying column; (3) flow meter; (4) and (5) humidity equilibration bubblers; (6) a glass wool filled tube to remove entrained water droplets.

1.2.1 Vapor saturator

First, the highly purified synthetic air (hereafter referred to as air) was flowed through a drying and purifying column, which was filled with silica gel, and was then flowed through a mass flow controller to control the gas at a flow rate of 0.50 slm (standard liter per minute).

Second, the air was introduced into two glass bubblers in series to obtain saturated water vapor. The entrained water droplet was then removed by passing through a glass tube tightly packed with pre-cleaned glass wool. The glass tubes were placed into a constant temperature water bath.

Third, the water vapor saturated air flowed into the bottom of a saturator, a 750-mm long piece of jacketed glass tubing lined with quartz fiber paper (Graseby Gmn, USA) and with an internal diameter of 16.5 mm. The H_2O_2 solution was introduced into the top of the saturator using a peristaltic pump and then flowed down the inner tube wall. The supplied air flowed countercurrent to the aqueous flow. The temperature of the solution and vapor was controlled by a constant-temperature water bath surrounding the saturator tube.

Finally, a carrier gas (highly purified N_2) with 2.20 slm was added into the vapor flow, to use a glass coil scrubber (see below) to collect the vapor effectively. Combined with the vapor flow at 0.50 slm from the saturator, the total gas flow was 2.70 slm. In order to reduce the H_2O_2 loss on the wall of the tubing and avoid a pressure higher than 1 atm, the combined gas was pumped by a vacuum pump through

the coil scrubber at a rate of 2.76 slm. We measured the air pressure in the saturator and found it was slightly lower than 1 atm by about 0.04 atm.

The concentration loss of H_2O_2 solution, which flowed down from the top of the 750 mm long tube covered by quartz fiber paper, was estimated. As H_2O_2 is more unstable at a higher temperature and lower acidity, we tested its stability at 298 K and pH 7.0. The results indicated that the H_2O_2 concentration changed from 2.28×10^{-3} mol/L at inlet (at the top of tube) to 2.20×10^{-3} mol/L at outlet (on the bottom of tube), leading to a minor loss of 4%. Therefore, the loss of H_2O_2 in the tube could be neglected in the present study.

Henry's law constant for H_2O_2 was determined at different temperatures of 277, 283, 288, 293, and 298 K, and at different pH levels of 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, and 7.0. At each temperature and pH level, the experiments were performed eight times.

1.2.2 Vapor collection and analysis

The combined H_2O_2 vapor and carrier gas was introduced into a glass coil scrubber by a vacuum pump. The total gas flow rate was 2.70 slm, while the pumping flow rate was 2.76 slm, as mentioned above. The H_2O_2 in the gas was absorbed at 277 K by the stripping solution (H_3PO_4 solution with pH 3.5) supplied by a peristaltic pump at a rate of 0.23 mL/min. The collection efficiency was estimated to be approximately 100%. Details on the coil scrubber can be seen in our previous work (Hua et al., 2008).

The stripping solution containing H_2O_2 was introduced, by a peristaltic pump, into the auto-sampler of the HPLC system for automatic online analysis. This analysis applied the post-column derivatization method using *p*-hydroxyphenylacetic acid (POPHA) and fluorescence detection developed by our laboratory. The basis of this method is to quantify the fluorescent dimmer produced by the stoichiometric reaction of POPHA and hydroperoxides through catalysis of hemin. The mobile phase, pumped by an Agilent 1100 pump, was a H_3PO_4 solution at pH 3.5. The hydroperoxides were separated in a 5-μm reversed-phase C_{18} HPLC column (4.6 mm × 250 mm, ZORBAX, SB-Aq, Agilent, USA), which was cooled to 2°C to stabilize the hydroperoxide. After separation, the eluate was introduced into a 3-m Teflon coil, where it reacted with a fluorescent reagent that contained hemin (≥ 98%, Fluka, the Netherlands) and POPHA (≥ 98%, Acros Orgnics, USA), and was pumped by an Agilent 1100 pump. The fluorescence signal of the biphenyl derivative formed during the derivatization reaction was determined at wavelengths of $\lambda_{Ex} = 315$ nm and $\lambda_{Em} = 400$ nm using a fluorescence detector (Agilent 1100). This method is described in detail in our previous work (Hua et al., 2008; Chen et al., 2008).

1.3 Equilibrium between gas and liquid

Two kinds of vapor saturator are usually used to determine the Henry's law constant for a compound. One lets the air stream pass through a porous tube immersed

in a solution of known concentration. The other lets the air stream flow over the glass fabric membrane that is saturated by the solution. The present study applied a variation on the second method that we used a quartz fiber membrane characterized with stronger inertia. Lind and Kok (1986) have demonstrated that the air stream should be less than 1 L/min to ensure the Henry's law equilibrium. In our experiments there was no statistically noticeable change (less than 6%) in gas concentration in the speed range of 0.5–1.0 slm. This study selected 0.50 slm to ensure ample time for the gas/liquid partition of the peroxide to attain equilibrium.

2 Results and discussion

The Henry's law describes the partitioning of a compound between the gas and liquid phase at equilibrium, relating the gas-phase partial pressure of a compound to its mole fraction in solution in the limit of zero concentration. Henry's law is approximately valid for any solute in a dilute aqueous solution and can be applied to the solubility expressed as (Eq. (1)):

$$K_H = \frac{C}{P} \quad (1)$$

where, the proportionality K_H is the Henry's law constant, P is the partial pressure of a particular compound in equilibrium with its aqueous solution containing the molar concentration C. K_H can have different values according to the selected definitions and units (P is in atm, C in M (mol/L), and thus K_H is in M/atm in the present study). Obviously, the application of Eq. (1) needs two assumed conditions: (1) the compound has ideal behavior in both gas and aqueous phases; and (2) its chemical form is identical in both phases. The temperature dependence of the Henry's law constant can be expressed by Van't Hoff equation (Eq. (2)):

$$K_H = \exp\left(\frac{a}{T} - b\right) \quad (2)$$

where, T (K) is the equilibrium temperature, and a, as a parameter, is a function of the standard heat of solution ΔH:

$$a = -\frac{\Delta H}{R} \quad (3)$$

where, R is the ideal gas constant. For an exothermic solution reaction, the standard heat of solution is negative and thus K_H decreases with increasing temperature.

2.1 Concentration dependence

The partial pressure of equilibrium gas phase H_2O_2 in air versus the generation solution concentration at 288 K and pH 3.0 is plotted in Fig. 2. The measurements of the gas phase H_2O_2 at each concentration of generation solutions were performed four times. The linear relationship was observed with the slope being equal to the K_H (the correlation coefficient $r = 0.996$, $n = 16$). Within the uncertainty of our measurements, the resulting
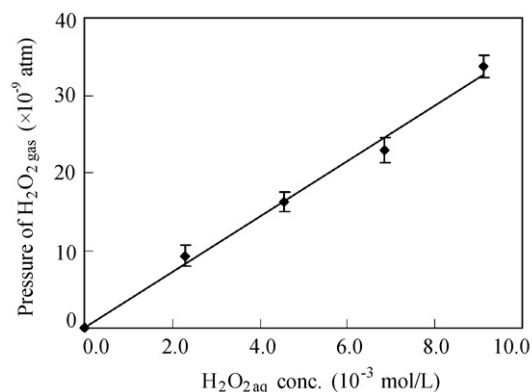

Fig. 2 Vapor pressure of H_2O_2 in equilibrium with its solution of different concentrations at 288 K and pH 3.0.

intercept was not distinctively different from zero, which indicates that H_2O_2 solutions obey Henry's law at a low concentration range of 2.28×10^{-3}–9.12×10^{-3} mol/L. Measurements of H_2O_2 in cloud water and rain water have been made by several researchers (Jackson and Hewitt, 1999). Atmospheric concentrations as high as 1×10^{-4} mol/L were observed, although levels of less magnitude are more typical. In principle, the experimental concentration of H_2O_2 generation solutions should be close to the actual level in the atmosphere. The corresponding low concentration of equilibrium vapor, however, is difficult to analyze accurately, even lower than the detection limit. Integrating various factors and considering the sensitivity of HPLC, the concentration of 4.56×10^{-3} mol/L of generation solutions was used for the investigation of temperature and acidity dependence in this study. Although this concentration is far higher than the level in the atmosphere, the experimental result shows that Henry's law was still complied with for H_2O_2, so that the rule can be extrapolated to the lower concentrations observed in the atmosphere.

2.2 Temperature dependence

Figure 3 shows a plot for H_2O_2 in water as a function of temperature at pH 3.0. The data sets were fit by linear regression analysis to the equation of $\ln K_H = a/T - b$. The correlation coefficient r was found as 0.996 ($n = 40$), which indicates a good linear relationship. Obviously, the
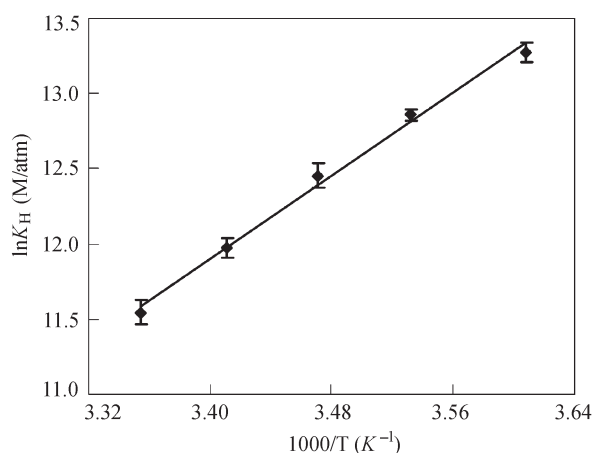

Fig. 3 Temperature dependence of K_H for H_2O_2 at pH 3.0. M: mol/L

Table 1　Comparison of Henry's law constants for H_2O_2

K_H (M/atm)		$K_H = \exp(a/T - b)$		Reference
283.15 K	298.15 K	a	b	
2.49×10^5	0.715×10^5	–	–	Martin and Damschen, 1981*
2.77×10^5	0.678×10^5	7920	15.44	Hwang and Dasgupta, 1985
3.10×10^5	1.00×10^5	6338	9.74	Lind and Kok, 1986, 1994
4.03×10^5	1.06×10^5	7514	13.63	Staffelbach and Kok, 1993
3.09×10^5	0.832×10^5	7379	13.42	O'Sullivan et al., 1996
3.76×10^5	1.08×10^5	7024**	11.97**	This work

* Calculated by their given data at 286.15 and 292.15 K; ** described in Section 2.3

parameters a and b are equal to the slope and intercept of the line, respectively. Based on the a and b values, which are taken from Section 2.3, where the temperature and acidity dependence are considered together, the K_H values for H_2O_2 at 283 and 298 K were estimated as 3.76 $\times 10^5$ and 1.08×10^5 M/atm, respectively. The K_H value for H_2O_2 decreased with increasing temperature.

As the partition ratio of H_2O_2 between gas and aqueous phases is important for understanding the atmospheric hydroperoxide transformation, a number of studies have been carried out to determine the Henry's law constant of H_2O_2, as shown in Table 1.

The earliest study examining the Henry's law constant of H_2O_2 is by Scatchard et al. (1952). A problem arose, however, as this study measured the Henry's law constant from vapor pressure measurements over solution compositions from 5 to 1400 mol/L H_2O_2 and from 318 to 378 K, namely, the experimental conditions were far from those of the real atmosphere. Martin and Damschen (1981) extrapolated these measurements to the temperature range 273–298 K, and the accuracy was estimated at only 40% as a result of the uncertainty in the vapor pressure of H_2O_2. Hwang and Dasgupta (1985) conducted the first study of Henry's law behavior of H_2O_2 in dilute aqueous solutions as a function of temperature. They employed a novel technique for generating gas-phase H_2O_2, as well as several different analytical techniques, to determine H_2O_2 concentration. Lind and Kok (1986, 1994) and Staffelbach and Kok (1993) determined the temperature dependence of K_H for H_2O_2, and obtained results higher than Hwang and Dasgupta (1985). At lower temperatures, however, there is a large difference between the K_H of Lind and Kok (1986, 1994) and Staffelbach and Kok (1993), for example, a discrepancy of 43% at 277 K. O'Sullivan (1996) also re-determined the temperature dependence of the K_H for H_2O_2 with a nearly 40% discrepancy. Recently, Chung (2005) determined the K_H for H_2O_2 in pure water and concentrated salt solutions, and obtained results for K_H in the pure water similar to that of Hwang and Dasgupta (1985).

Results for the measured K_H values for H_2O_2, e.g., at 283.15 and 298.15 K (Table 1) are slightly larger than those from most previous research, but are similar to the results of Staffelbach and Kok (1993). We suggest that, in addition to the difference between the measurement methods, the total gas pressure in the vapor saturator might be a cause for this gap between our findings and previous results. We performed the measurement for the K_H of H_2O_2 under conditions of (0.960 ± 0.013) atm pressure, slightly less than 1 atm, although the pressure was usually unmentioned in the previous works. Clouds, rain, and fog, which are the aqueous phases partitioning H_2O_2, usually exist under a gas pressure slightly less than 1 atm. Therefore, our measured K_H values for H_2O_2 seem to be more consistent with real atmospheric conditions.

2.3 Acidity dependence

In the atmosphere, the aqueous phase likely encounters a wide variation in acidity, thus acidity dependence of the Henry's law constant should be considered carefully. Although several studies have attempted to determine the acidity dependence for hydrogen peroxide, it remains unclear. Staffelback and Kok (1993) reported that the K_H value generally decreased with increasing pH for H_2O_2 in pH range 2.2–6.4. They also stated, however, that there was considerable scatter in the data, reflecting the difficulty in adjusting and maintaining the pH of the hydroperoxide mixture. Conversely, O'Sullivan et al. (1996), who performed determinations with pH 3 and 6 generation and collection solutions, observed no statistically significant pH dependence.

The experimental results (Fig. 4) showed that the K_H value for H_2O_2 appeared to have no obvious dependence on decreasing pH levels (from 7 to 1).

This pH independence seems to indicate that the standard heat of solution for H_2O_2 and then the coefficient a, as shown in the Van't Hoff equation forms Eqs. (2) and (3), are almost independent from the acidity of the solution in the pH range of 1 to 7. Accordingly, by fitting
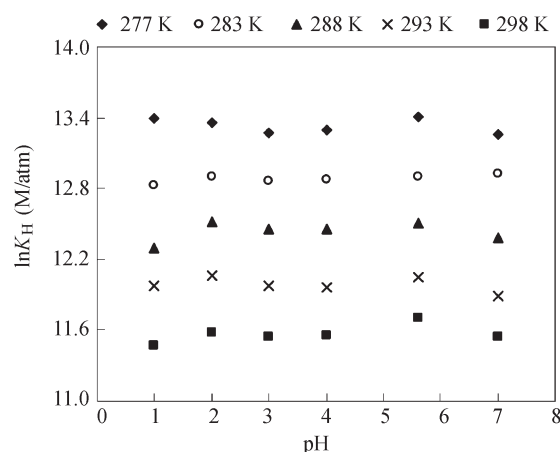

Fig. 4　Henry's law constants for H_2O_2 determined at different pH and temperature

the experimental data in Fig. 4, we find that a was (7024 ± 138), b was (11.97 ± 0.48). The standard heat of solution, ΔH, was estimated as (58.40 ± 1.15) kJ/(K·mol). The uncertainties represent σ. A comparison of a and b values determined for H_2O_2 between our and previous studies can be seen in Table 1.

3 Conclusions

We have determined the temperature and acidity dependence of the Henry's law constant for hydrogen peroxide at an air pressure of (0.960 ± 0.013) atm. In addition to validating that the temperature dependence of the Henry's law constant for hydrogen peroxide obeys the Van't Hoff equation form, $\ln K_H = a/T - b$, in 273–298 K, we have found that the K_H value of hydrogen peroxide appears to have no obvious dependence on decreasing pH levels (from 7 to 1). For the atmospheric aqueous phases, such as cloud and fog, both their temperature and acidity change frequently. In this regard, the K_H values for hydrogen peroxide determined in the present study are useful for atmospheric models.

Acknowledgments

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