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Henry's Law Constant measurements for formaldehyde and benzaldehyde as a function of temperature and water composition.

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Abstract

Henry's Law Constants H of formaldehyde and benzaldehyde were determined using a dynamic system based on the water/air equilibrium at the interface within the length of a microporous tube. The measurements were conducted over the range 273 – 293 K in (i) deionized water, (ii) 35 g L⁻¹ solution of NaCl simulating seawater and (iii) two nitric acid solutions, i.e. 0.63 and 6.3 wt %.

In pure water, the obtained data were used to derive the following Arrhenius expressions: $\ln H = (6423 \pm 542)/T - (13.4 \pm 2.0)$ and $\ln H = (6258 \pm 280)/T - (17.5 \pm 1.0)$ for formaldehyde and benzaldehyde, respectively. The H values, calculated at 293 K from Arrhenius expressions cited below, were the following (in units of M atm⁻¹) : $H = 5020 \pm 1170$ (formaldehyde), $H = 47 \pm 5$ (benzaldehyde). The temperature dependence of H permits then to derive the solvation enthalpies for both compounds : $\Delta H_{solv} = -(53.4 \pm 4.5)$ kJ mol⁻¹ and $\Delta H_{solv} = -(52.0 \pm 2.3)$ kJ mol⁻¹ for formaldehyde and benzaldehyde, respectively.

In 35 g L⁻¹ salt solution, the H values were 27 to 66% and 12 to 21% lower than their respective determinations in deionised water, for formaldehyde and benzaldehyde respectively. The observed salt effect was used to estimate the following Setschenow coefficients at 293 K for 0.6 M NaCl: formaldehyde (0.21) and benzaldehyde (0.09).

In 6.3 wt % nitric acid solution, H values of benzaldehyde were approximately 30 % higher than those found in pure water although no significant influence was observed for formaldehyde.

Finally, our experimental data were then used to estimate the fractions of formaldehyde and benzaldehyde in atmospheric aqueous phase and their derived atmospheric lifetimes.

Keywords: Henry's law constant, formaldehyde, benzaldehyde, temperature, salinity, acidity, salt effect, nitric acid.

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Introduction

Aliphatic and aromatic aldehydes constitute an abundant class of volatile organic compounds (VOCs) encountered in air and precipitations (rain, fog). Aldehydes are emitted into the atmosphere as primary pollutants from motor vehicles and industrial emissions, or produced *in situ* as environmentally intermediates in the photooxidation of other hydrocarbons (Atkinson, 1994; Müller, 1997). They play a key role in the tropospheric chemistry, since they lead photochemically to many products such as radical species that contribute to ozone (O₃) and nitrate acetic peroxy (PAN) productions (Atkinson, 2000).

Formaldehyde (FA) and benzaldehyde (BA) represent the dominant species of aliphatic and aromatic carbonyl compounds, respectively.

Formaldehyde is an atmospherically relevant carbonyl compound with an active and important role in the tropospheric photochemistry (Smith et al., 2006). It is formed in the oxidation pathways of many biogenic and anthropogenic VOCs (Sprengnether et al., 2002) and emitted directly from biomass fires. It is an efficient precursor of HO_x radicals (OH and HO₂) which are the major tropospheric oxidant. Formaldehyde is also the main contributor to catalytic ozone loss in the lower stratosphere (McElroy et al., 1992). In addition, formaldehyde affects strongly the capacity of atmosphere waters (fog, clouds) because it inhibits the oxidation of S(IV) to sulfuric acid and because it is a precursor of formic acid (Khare et al., 1997; Kieber et al., 1999; Munger et al., 1986).

Consequently, gaseous formaldehyde concentrations have been measured at different locations. Field measurements have shown concentration of 0.05 ppbv in clean Antarctic tropospheric air in winter (Riedel et al., 1999), a value varying between 15 and 20 ppbv in London (Williams et al., 1996) and up to 70 ppbv in Los Angeles (Williams et al., 1996).

Benzaldehyde can be considered as a model of simple aromatic aldehydes. It can be found in fruit, and is used as a soil fumigant and in the manufacturing of deodorants/air fresheners and loose mineral wool fiber (Atkinson, 1994).

Both FA and BA are polar molecules having high solubilities in water and are expected to be efficiently scavenged from the gas phase by rain and fog (Gunz and Hoffmann, 1990; Jayne et al., 1996). Significant levels of formaldehyde ranging between 0.01 and 13 µM were found in rain and fog (Gunz and Hoffmann, 1990; Jayne et al., 1996) confirming its efficient scavenging from gas phase. Atmospheric deposition represents a significant sink since its

concentrations in rain water are approximately three orders of magnitude higher than those in surface waters (Nuccio et al., 1995).

The partitioning of a given species between the gas and aqueous phases is given by its Henry's law constant H . This latter is a key physical characteristic to describe the behavior of a component in the environment (Rice et al., 1997) particularly in order to better understand its fate, its transport, and its removal in the lower troposphere. A detailed inspection of literature data shows a substantial variation in the previous quoted values for formaldehyde (Betterton and Hoffmann, 1988; Chameides, 1984; Gaffney and Senum, 1984; Seinfeld, 1986; Seyfioglu and Odabasi, 2007; Staudinger and Roberts, 1996; Warneck, 1988; Zhou and Mopper, 1990) whereas only few determinations have been reported in the case of benzaldehyde (Allen et al., 1998; Betterton and Hoffmann, 1988; Gaffney and Senum, 1984; Hine and Mookerjee, 1975; Staudinger and Roberts, 1996; Zhou and Mopper, 1990). In addition, only few determinations have been obtained as a function of the water composition for both compounds.

In this study, direct experimental determinations of H for both formaldehyde and benzaldehyde in pure water have been therefore performed *via* a dynamic equilibrium system between 273 and 293 K. The effects on Henry's law constant of a 35 g L⁻¹ solution of NaCl simulating seawater or 0.63 and 6.3 wt% nitric acid solutions chosen as maximal concentrations of HNO₃ reported in tropospheric cloud droplets (Gao et al., 2004), have been investigated over the same temperature range. Our experimental determinations have been then compared with literature data and used to discuss the atmospheric lifetimes of both aldehydes.

Experimental Section

Reagents

Aqueous solutions of formaldehyde and benzaldehyde were prepared using Milli-Q Water (18 m Ω cm). Pure benzaldehyde (GC grade, $\geq 99\%$) and aqueous formaldehyde solution (30%) were obtained from Fluka Chemical Company and used without further purification. Sodium chloride ($\geq 99.8\%$) was obtained from Riedel-de Haën Chemical Company. The aqueous concentrations used for the experiments were in the range 13.7 – 97.6 mg L⁻¹ for formaldehyde and 8.7– 50.5 mg L⁻¹ for benzaldehyde, given that their water solubilities are 55×10^4 mg L⁻¹ (at 293 K) and 0.46×10^4 mg L⁻¹ (at 298 K), respectively. To investigate the effects of acidity and salinity on H values, aqueous solutions of containing either 0.63 – 6.3 wt% of HNO₃ or 35 g L⁻¹ of NaCl were used.

Dynamic equilibrium system

The measurements of H were conducted using a dynamic equilibrium system shown in Figure 1 and already used in previous work (Feigenbrugel et al., 2004a; Feigenbrugel et al., 2004b; Gautier et al., 2003; Katrib et al., 2003). Compressed air was passed through a microporous PTFE membrane tube (180 cm $\times$ 0.8 cm i.d., Sumitomo Corporation) at a highly controlled flow rate of 0.2 – 0.5 L min⁻¹. The tube was immersed in about 1.0 L of the diluted aqueous solution containing either formaldehyde or benzaldehyde. Phase equilibrium was achieved, for the dissolved compound, at the gas/water interface along the inner surface of the tube. The contact time between the two phases varied between 7 and 36 s depending on the flow rate. At the exit of the reactor, the gas phase containing the studied compound at equilibrium concentration was then diluted using clean dry air (0.5 L min⁻¹). The compound present in the gas phase was trapped using two cartridges connected in series and filled with a 2,4-dinitrophenylhydrazine (2,4-DNPH) coated silica gel as derivatises. Benzaldehyde was collected for 20 – 60 min whereas intervals of 4 to 6 hours were required to concentrate enough formaldehyde in cartridges.

After sampling, aldehyde was eluted three times by passing 20 mL, 10 mL and 10 mL of acetonitrile through the cartridge. The mass of acetonitrile which stayed in the cartridge was measured after each extraction in order to know the dead volume in the cartridge. The experiments revealed that for benzaldehyde more than 97% of the compound was trapped in

the first cartridge while for formaldehyde the percentage was about 92%. It should be noted that the mass of aldehyde trapped in the cartridges was always negligible compared to their total mass in the aqueous solution and consequently, their aqueous concentration were effectively constant during the course of the experiment.

Analysis

The extracted solutions containing the hydrazones were weighed and analysed by HPLC/UV. For this, 20 μL of the extracted solution containing the hydrazones were injected into a reversed-phase column C-18 and were detected at a 360 nm wavelength (Marchand et al., 2006; Marchand et al., 2008). The hydrazones were separated with a mobile phase of acetonitrile–water (60/40) isocratically pumped at a flow-rate of 1.5 mL min^{-1} and quantified from external calibration curves (Marchand et al., 2008). For this, both aldehyde derivatives were prepared according to the method previously described (Levart and Veber, 2001). Known concentrations of hydrazone were then prepared in acetonitrile and 20 μL of the obtained solution were then injected into the HPLC in order to plot concentration curves versus HPLC peak areas. The calibration curves were linear for the concentration ranges used in this study i.e. between 0.1 and 25 mg L^{-1} for hydrazone solutions and the correlation coefficients were larger than 0.99. Note that for each series of measurements, two blank cartridges of 2,4-DNPH were used to determine the background aldehydes concentrations.

Results and discussion

Effect of temperature

The Arrhenius plots of the Henry's Law Constants measured for benzaldehyde and formaldehyde in deionized water for a temperature range 273-293 K are presented in Figures 2 and 3. The H values (in M atm^{-1}) are also listed in Table 1 where the quoted uncertainties vary between 8 and 20 %. These values represent the sum of the uncertainties on the calibration curves (ranging from 1% to 9% for formaldehyde and 1% to 7% for benzaldehyde), on the extraction process estimated to be around of 5% by a series of reproducibility tests, on the flow rates (less than 2.5 % under our experimental conditions) and on the aqueous concentration of the formaldehyde and benzaldehyde (up to 3%). Within these experimental errors, H values of both aldehydes are shown to be not sensitive to their aqueous concentration over the ranges stated in the experimental section and to the changes in

air flow rate (0.2 – 0.5 L min⁻¹) as shown in Figure 4. Since H does not vary with contact time, the equilibrium between solution and vapour is really achieved at the exit of reactor.

In Tables 2 and 3, our experimental H values obtained at 293 K and those calculated at 298 K for formaldehyde and benzaldehyde respectively, are compared with previous determinations and estimated values reported in the literature.

For formaldehyde (see Table 2) and in spite of the different techniques used, our value of H agrees reasonably well, within experimental errors, with those reported by Betterton et Hoffmann (1988), Zhou and Mopper (1990) and Staudinger and Roberts (1996). However, our H value of 3500 ± 900 M atm⁻¹ (calculated at 298 K) is 4 times lower than that reported by Warneck (1998) and approximately 2 times lower than those determined by Seinfeld (1986) or Gaffney and Senum (1984). Figure 2 shows our obtained data compared with previous experimental ones.

For benzaldehyde, our average H value of 47 M atm⁻¹ calculated at 298K is in very good agreement with the previous ones reported by several studies (Allen et al., 1998; Betterton and Hoffmann, 1988; Gaffney and Senum, 1984; Hine and Mookerjee, 1975; Staudinger and Roberts, 1996; Zhou and Mopper, 1990) as illustrated in Table 3. However, as shown in Figure 3, the values of H at low temperatures and particularly that obtained at 273 K are significantly higher than those reported by Betterton and Hoffmann (1988), Zhou and Mopper (1990) or Staudinger and Roberts (1996), but are similar, within experimental errors, to those recently obtained by Allen et al. (1998).

The following Arrhenius expressions can be derived from our data using a weighted analysis fit: $\ln H$ (FA) = $(6423 \pm 542)/T - (13.4 \pm 2.0)$; $\ln H$ (BA) = $(6258 \pm 280)/T - (17.5 \pm 1.0)$. The quoted errors are given at the 2σ level from the least-squares analysis. Our recommended H values at 293 K, derived from the Arrhenius expressions using a weighted analysis fit, are the following (in units of M atm⁻¹) : $H_{FA} = 5020 \pm 1170$ and $H_{BA} = 47 \pm 5$. The quoted errors correspond to 2σ level and are determined from the standard deviations on both slope and intercept of Arrhenius expression. In addition, the temperature dependence are very similar for the two studied compounds meaning that their enthalpies of solvation are approximately the same.

The behaviour of henry's law constants as a function of temperature can be conveniently expressed with a Van't Hoff equation:

$$H(T) = H_{293} \times \exp(-\Delta H^{\circ}_{\text{sol}}/R (1/T - 1/293)) \quad (1)$$

where $\Delta H^\circ_{\text{solv}}$ is the solvation enthalpy (J mol^{-1}), T is the temperature (K) and R is the ideal gas constant. Assuming that $\Delta H^\circ_{\text{solv}}$ is not temperature dependent between 273 and 293 K, the values of $\Delta H^\circ_{\text{solv}}$ for both constituents have been calculated from a plot of $\ln H$ versus $1/T$, where the slope is $-\Delta H^\circ_{\text{solv}}/R$. The linearity of these plots, within experimental uncertainties confirms the validity of equation (1). The derived enthalpies of solvation are the following (in units of kJ mol^{-1}) : $\Delta H^\circ_{\text{solv}}$ (FA) = $-(52.0 \pm 4.5)$ and $\Delta H^\circ_{\text{solv}}$ (BA) = $-(52 \pm 2.3)$ where the quoted errors correspond to 2σ obtained from the least-squares analysis.

Effect of nitric acid

The measured H values of formaldehyde and benzaldehyde in 0.63 – 6.3 wt% nitric acid solutions (maximal acid concentrations of tropospheric cloud droplets) in the range 273 – 293 K for HNO_3 0.63 wt% (0.1 N) and 268 – 293 K for HNO_3 6.3 wt% (1N), are reported in Figures 5 and 6.

As shown in Figure 6, the experimental Henry's law constants of benzaldehyde are approximately the same for pure water and the lower nitric acid concentration of 0.63 wt%. Nevertheless, all H values of benzaldehyde in 6.3 wt% nitric acid solution were 30 % higher than their respective values in deionised water. In opposite to benzaldehyde, Henry's law constants of formaldehyde in both nitric acid solutions are approximately the same than those measured in pure water, as displayed in Figure 5.

The question, of course, arises as to why a such difference is observed between the formaldehyde and benzaldehyde uptake behavior in acid medium. First, let us remind that in liquid solution, aldehydes (RCHO) react with water to form gem diol ($\text{RCH(OH)}_2 \text{aq}$) which is greatly more water-soluble than its precursor. This hydration pathway increases effective aldehyde solubility in water since its hydration coefficient k_{hyd} is very higher (in case of FA, $k_{\text{hyd}} \approx 2000$ at 298 K) (Betterton and Hoffmann, 1988) but smaller for larger molecules ($k_{\text{hyd}} = 7.7$ at 298 K for phtalaldehyde (McDonald and Martin, 1979). The partitioning between gas and aqueous phases is then governed by the equilibrium constants as illustrated as follows:

Therefore, hydration subsequently increases the effective Henry's Law Constant of aldehydes. For formaldehyde, this effect can be expressed by the following equation:

$$H_{eff} = \frac{[HCHO_{aq}] + [CH_2(OH)_{2aq}]}{[HCHO_g]} = H \times (1 + k_{hyd}) \quad (3)$$

If the medium is strongly acid, an additional way affects the set of equilibria mentioned above (see Eq. 2) since a protonated form of aldehydes RCH_2O^+ is formed as shown below:

In this latter equation, the stability of RCH_2O^+ cation strongly depends on the nature of alkyl group R.

As expected, our measured H value of benzaldehyde is quite low in pure water, confirming that its value of k_{hyd} is relatively limited, similarly to phthalaldehyde (McDonald and Martin, 1979). This is in agreement with the observations made by McDonald and Martin (1979) who concluded that no hydration was detected for benzaldehyde.

At low acidity, the protonated form RCH_2O^+ is still negligible as it was observed by Jayne et al. (1992) for both formaldehyde and acetaldehyde. In very low pH, our results suggest that the protonated form seems to be important and partially governs the partitioning of benzaldehyde between the gas and liquid phases.

The equilibrium (4) leads to the soluble cation RCH_2O^+ which is thermodynamically more stable when R is an efficient electron donor group such as a phenyl group (benzaldehyde). In opposite to benzaldehyde, HCH_2O^+ is unstable and break up quickly to regenerate $HCHO_{aq}$ so that the Henry's law constant of formaldehyde is not sensitive to the pH effect. However, at very low pH, the decreasing of H_2O activity reduces gem diol formation but supports inevitably the protonated form. Broadly, a compensation of the two effects takes place and finally, the observed Henry law constant does not undergo significant modification.

Effect of salinity

The Arrhenius plots of the Henry's Law Constants, measured for formaldehyde and benzaldehyde in aqueous solutions of NaCl (35 g L⁻¹) simulating seawater for a temperature

range 273 – 298 K, are presented in Figures 7 and 8. The following Arrhenius expressions can be derived from our data using a linear fit: $\ln H_S(\text{FA}) = (5548 \pm 1320)/T - (10.7 \pm 4.8)$ and $\ln H_S(\text{BA}) = (6015 \pm 424)/T - (16.7 \pm 1.4)$. The quoted errors are given at the 2σ level from the least-squares analysis.

As shown in both Figures 7 and 8, our H values of benzaldehyde and formaldehyde in salt solutions were respectively 12 to 21% and 27% to 66% lower than their respective values in deionized water. For instance, the determined H values at 293 K in salt solution obtained from Arrhenius expression given above, can be compared with those measured in pure water (in parentheses): formaldehyde, $H_S = 3770 \pm 2590$ ($H = 5020 \pm 1170$); benzaldehyde, $H_S = 46 \pm 7$ ($H = 47 \pm 5$) (in units of M atm^{-1}) where the quoted errors correspond to 2σ obtained from the least-squares analysis. This phenomenon is related to the salting-out effect which impacts on the water solubility (reduction in solubility).

The salt effect on the solubility of gases in seawater has been studied theoretically for a variety of small gas molecules (Danckwerts, 1970). The presence of a salt in an aqueous solution changes the water structure in the vicinity of the solute. An empirical relation for the effect of ionic strength on a Henry's law constant H for a given compound in an aqueous solution was given by (Setschenow, 1889):

$$\log(H/H_S) = h(\text{NaCl}) \quad (5)$$

where H and H_S are the Henry's law coefficients of the compound in pure water and in the salt solution, respectively, (NaCl) is the molarity of the NaCl solution and h is the Setschenow's salting-out coefficient (L mol^{-1}). Our results of H and H_S at 293 K were used to estimate the following Setschenow coefficients for $[\text{NaCl}] = 0.6\text{M}$: $h(\text{FA}) = 0.21$ and $h(\text{BA}) = 0.09$. The solubility at 293 K is then reduced by a factor of 0.34 and 0.13 for formaldehyde and benzaldehyde, respectively.

In the study performed in pure water and natural seawater by Zhou and Mopper (1990), the values of Setschenow's coefficients h for benzaldehyde were found to be 0.20 and 0.15 at 298 and 283K, respectively. These values are relatively higher than that of 0.09 derived in this work at 293 K. Besides, our h value of formaldehyde disagrees with some observations made in previous studies (Dong and Dasgupta, 1986; Zhou and Mopper, 1990) since both studies report H/H_S ratios close to 1. No salt effect on formaldehyde solubility have been detected by Dasgupta and Dong (1986) in their experiments conducted with aqueous solution containing

either 2M of NaCl or 1M of Na₂SO₄ or 1M of (NH₄)₂SO₄. However, Swartz et al. (1997) have observed a low Setschenow's coefficient, equal to 0.07 at 293 K with NaCl concentration ranging from 0 to 4 M (Swartz et al., 1997).

Atmospheric implications

The distribution of soluble gases between the gaseous and droplet phases in the atmosphere is strongly dependent on their Henry's law constant.

Once released in the atmosphere, VOCs can react in the gas phase or can be taken up by liquid water in clouds where they can also be oxidized. For most of them, OH radical is the most efficient oxidizing species in both gas phase (Atkinson, 2000) and aqueous phase (Ervens et al., 2003). To evaluate the impact of a cloud on the atmospheric chemistry of formaldehyde and benzaldehyde, we compare in this section their atmospheric lifetimes under clear sky (τ_{gas}) and cloudy conditions ($\tau_{\text{multiphase}}$).

The lifetime of A in the gas phase ($\tau_{\text{A,gas}}$) taking into account the photolysis and the reaction of A with OH and NO₃ radicals, is defined as follows:

$$\tau_{\text{A,gas}} = \frac{[\text{A}]_{\text{g}}}{-d[\text{A}]_{\text{g}}/dt} = \frac{1}{J_{\text{g}} + k_{\text{OH,g}}[\text{OH}]_{\text{g}} + k_{\text{NO}_3\text{g}}[\text{NO}_3]_{\text{g}}} \quad (6)$$

where J_{g} , $k_{\text{OH,g}}$ and $k_{\text{NO}_3\text{g}}$ are respectively the gas-phase photolysis coefficient, the rate constant of the gas phase reaction of OH and NO₃ radicals with A, $[\text{OH}]_{\text{g}}$ is the mean concentration of OH radicals and $[\text{A}]_{\text{g}}$ is the concentration of A in the troposphere. $[\text{NO}_3]_{\text{g}}$ is the night concentration of nitrate radicals.

If we consider now the cloudy atmosphere as a multiphase reactor where both gas and aqueous phases coexist, then the multiphase lifetime of A can be defined as (Monod et al., 2005):

$$\tau_{\text{A,multiphase}} = \frac{1 + \text{HRL}_{\text{WC}}T}{J_{\text{g}} + k_{\text{OH,g}}[\text{OH}]_{\text{g}} + k_{\text{NO}_3\text{g}}[\text{NO}_3]_{\text{g}} + \text{HRL}_{\text{WC}}T \times (J_{\text{aq}} + k_{\text{OH,aq}}[\text{OH}]_{\text{aq}})} \quad (7)$$

where R the ideal gas constant (in $\text{L atm mol}^{-1} \text{K}^{-1}$), L_{wc} the dimensionless liquid water content of the cloud (typically 4.2×10^{-7}) (Kolb, 1994), J_{aq} and $k_{OH,aq}$ are respectively the photolysis coefficient of A and the rate constant of OH reaction with A in aqueous phase, $[OH]_{aq}$ is the mean concentration of OH radicals in the tropospheric aqueous phase.

The rate constants of OH reaction with formaldehyde or benzaldehyde in both aqueous and gas phases have already been reported (Chin and Wine, 1994; IUPAC, 2009; NIST, 2009; Semadeni et al., 1995), and are shown in Table 4 together with the Henry's law constants determined in this work.

These data have then been used to estimate the partitioning and then the atmospheric lifetimes of both aldehydes under clear sky (τ_{gas}), and cloudy conditions ($\tau_{multiphase}$), by using typical concentrations of OH radicals in gas and aqueous phases: $[OH]_g = 1 \times 10^6 \text{ cm}^{-3}$ and $[OH]_{aq} = 1 \times 10^{-13} \text{ M}$ (Monod et al., 2005). We assume here that the OH concentration in the gas phase is the same under clear sky and cloudy conditions although it is reduced as soon as clouds are formed, and the magnitude of the decrease strongly depends on the pH value of the droplet (Monod and Carlier, 1999).

At 293 K, the calculated aqueous fraction are the following: formaldehyde, 3.4×10^{-2} ; benzaldehyde, 3.8×10^{-4} . At 293 K which is the temperature where most of experimental rate constants were measured, the atmospheric lifetimes of formaldehyde and benzaldehyde are slightly reduced in clouds as shown in Table 4. However, the average temperature of tropospheric clouds is 283 K and therefore, the calculated aqueous fraction of formaldehyde rises from 3.4×10^{-2} to 9.6×10^{-2} when the temperature decreases from 293 to 283 K, temperature range where the H value of formaldehyde increases from 5020 to 10900 M atm^{-1} .

Assuming that the rate constants of OH reactions with formaldehyde or benzaldehyde in the gas and aqueous phases do not vary a lot between 283 and 298 K as it was already observed for many oxygenated VOCs (except when data are available at 283 K), we can then estimate the multiphase lifetimes of both aldehydes at 283 K. These calculated multiphase lifetimes at 283 K (in units of hours) can be compared to those under clear sky in July (in parentheses): formaldehyde, 7.0 (6.7); benzaldehyde, 1.2 (18.2). Considering all the uncertainties associated with the above calculations, one can conclude that the oxidation of formaldehyde might be negligible in aqueous phase although that of benzaldehyde could represent its main sink.

334

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Figure Captions

Figure 1 : Scheme of the dynamic equilibrium system used to determine Henry's law constants as a function of the temperature.

Figure 2 : Plot of $\ln H$ versus $1000/T$ for formaldehyde in the temperature range 273 – 293 K in deionized water. Our determinations are compared to the experimental data of the literature. Our uncertainties on H values varied typically between 8 and 20 % and are determined as mentioned in the text. Straight lines represent Arrhenius plots derived by Staudinger and Roberts (blue dash-dot line), by Zhou and Mopper (red long dash line), by Betterton and Hoffmann (green dash-dot line), by Chameides (black dotted line) or in this work (pink solid line).

Figure 3 : Plot of $\ln H$ versus $1000/T$ for benzaldehyde in the temperature range 273 – 293 K in deionized water. Our determinations are compared to the experimental data of the literature. Our uncertainties on H values varied typically between 8 and 20 % and are determined as mentioned in the text. Straight lines represent Arrhenius plots derived by Allen *et al.* (black long dash line), by Staudinger and Roberts (blue dash-dot line), by Zhou and Mopper (red long dash line), by Betterton and Hoffmann (green dash-dot line) or in this work (pink solid line).

Figure 4 : Plot of H versus the flow rate ranging between 0.2 and 0.5 L min⁻¹ for both formaldehyde and benzaldehyde at 293 K. Our errors on H varied typically between 8 and 20 % and are determined as mentioned in the text.

Figure 5 : Plot of $\ln H$ versus $1000/T$ for formaldehyde in 0.1N (dotted line) and 1N (dash line) nitric acid solutions in the temperature range 273 – 293 K and comparison with values obtained in deionized water (solid line).

Figure 6 : Plot of $\ln H$ versus $1000/T$ for benzaldehyde in 0.1N and 1N nitric acid (dash line for 1N HNO₃) solutions in the temperature range 273 – 293 K and comparison with values obtained in deionized water (solid line).

494 **Figure 7** : Plot of $\ln H$ versus $1000/T$ in deionized water (solid line) and salt water (dash line)
495 for formaldehyde in the temperature range 273 – 293 K.

496 **Figure 8** : Plot of $\ln H$ versus $1000/T$ in deionized water (solid line) and salt water (dash line)
497 for benzaldehyde in the temperature range 273 – 293 K.

498

Table 1: Henry's Law Constants of benzaldehyde and formaldehyde as a function of the temperature determined by using the dynamic equilibrium system.

<i>T</i> (K)	<i>H</i> Formaldéhyde	<i>H</i> benzaldehyde
273.05	-	248 ± 17 ^e
273.05	-	261 ± 23
273.15	22600 ± 2200	237 ± 22
273.15	27500 ± 3200	-
273.25	29600 ± 3400	-
273.35	22800 ± 2100	-
278.05	-	144 ± 13
278.15	17100 ± 1400	-
278.25	-	150 ± 14
278.75	-	145 ± 10 ^e
283.15	11000 ± 900	100 ± 9
283.15	9940 ± 1260	-
283.45	-	97 ± 7 ^e
283.45	-	103 ± 7 ^e
288.15	7390 ± 610	73 ± 7
288.35	7300 ± 680	
288.45	-	69 ± 5 ^e
288.45	-	71 ± 5 ^e
292.95	-	50 ± 5 ^a
292.95	-	46 ± 3 ^b
293.05	5300 ± 840	46 ± 3 ^e
293.05	5330 ± 500 ^b	50 ± 4 ^e
293.15	-	49 ± 3 ^c
293.15	5230 ± 520 ^a	54 ± 5
293.15	-	46 ± 4
293.25	5530 ± 400 ^{c,d}	49 ± 3 ^e
293.35	-	49 ± 3 ^e
293.35	-	53 ± 4 ^e

By default, the experiments were carried out in deionized water with a flow rate of 0.4 L min⁻¹ and with an aqueous concentration of ~ 15 mg L⁻¹ (~ 5×10⁻⁴ M) for formaldehyde and ~ 10 mg L⁻¹ (~ 9.4×10⁻⁵ M) for benzaldehyde. Experiments carried out with an air flow rate of: ^a 0.2 L

504 min⁻¹; ^b 0.3 L min⁻¹; ^c 0.5 L min⁻¹. Experiments performed with an aqueous concentration of: ^d
505 ~ 85 mg L⁻¹ (~ 2.8×10⁻³ M) for formaldehyde; ^e ~ 25 mg L⁻¹ (~ 2.4×10⁻⁴ M) for benzaldehyde.
506

Table 2: Comparison of experimental Henry's law constants for formaldehyde with previous work.

<i>T</i> (K)	<i>H</i> (M atm ⁻¹)	<i>d ln H/d(1/T)</i> (K)	<i>T</i> range (K)	Technique	Référence
298	6.0×10^3	-	-	- ^a	(Gaffney and Senum, 1984)
293	1.0×10^4	6400		TC ^b	(Chameides, 1984)
298	7.0×10^3				
298	6.3×10^3	-		- ^a	(Seinfeld, 1986)
293	4.5×10^3	7200	278 - 318	SCT ^c	(Betters and Hoffmann, 1988)
298	3.0×10^3				
298	1.4×10^4	-		- ^a	(Warneck, 1988)
293	4.5×10^3	6500	283 - 318	SCT ^c	(Zhou and Mopper, 1990)
298	3.1×10^3				
293	4.7×10^3	6800	-	SEST ^d	(Staudinger and Roberts, 1996)
298	3.2×10^3				
293	5.9×10^3	1642	278 - 323	SCT ^c	(Seyfioglu and Odabasi, 2007)
298	5.4×10^3				
293	$(5.0 \pm 1.2) \times 10^3$ ^f	6423 ± 542 ^f	273 - 293	DES ^e	This work
298	$(3.5 \pm 0.8) \times 10^3$ ^f				

^a not reported; ^b Thermodynamic calculation; ^c SCT: Stripping Column Technique; ^d SEST: Single Equilibrium Static Technique; ^e DES: Dynamic Equilibrium System; ^f The quoted errors correspond to 2σ obtained from the least-squares analysis.

Table 3: Comparison of experimental Henry's law constants for benzaldehyde with previous work.

T (K)	H (M.atm ⁻¹)	d ln H/d (1/T) (K)	T range (K)	Technique	Reference
298	36	-	-	SAR ^a	(Hine and Mookerjee, 1975)
298	36	-	-	- ^b	(Gaffney and Senum, 1984)
293 298	50 37	5100	278 - 318	SCT ^c	(Betterton and Hoffmann, 1988)
293 298	55 42	4600	283 - 318	SCT ^c	(Zhou and Mopper, 1990)
293 298	51 39	4800	-	SEST ^d	(Staudinger and Roberts, 1996)
293 298	52 35	7000	-	EPICS ^e	(Allen et al., 1998)
293 298	47 ± 5 ^g 33 ± 3 ^g	6260 ± 280 ^g	273 - 293	DES ^f	This work

^a determined from Structure Activity Relationship; ^b not reported; ^c SCT: Stripping Column Technique; ^d SEST: Single Equilibrium Static Technique; ^e Equilibrium Partitioning In Closed Systems (EPICS); ^f DES: Dynamic Equilibrium System. ^g The quoted errors correspond to 2σ obtained from the least-squares analysis.

Table 4: Rate constants of OH reaction with formaldehyde and benzaldehyde in both gas and aqueous phases and their corresponding Henry's law constants. The atmospheric lifetimes were calculated at two temperatures, i.e. 298 and 283 K.

Compound	$10^{12} \times k_{\text{OH, g}}$ (cm ³ s ⁻¹)		$10^{-8} \times k_{\text{OH, aq}}$ (M ⁻¹ s ⁻¹)		$10^5 \times J_{\text{g}}$ (s ⁻¹)		H (M atm ⁻¹)		$\tau_{\text{multiphase}}$ January (hours)		$\tau_{\text{multiphase}}$ July (hours)	
	298 K	283K	298 K	283 K	January	July	298K	283 K	298K	283 K	298 K	283 K
Formaldehyde	8.5 ^a	8.7 ^a	7.6 ^g	6.3 ^g	3.2 ^c	7.3 ^c	3480 ^h	10900 ^h	13.2	13.0	6.7	7.0
Benzaldehyde	12 ^d	13 ^d	4.4×10 ⁴ ⁱ	4.4 × 10 ⁴ ⁱ	0.15 ^f	1.5 ^f	37 ^h	111 ^h	3.1	1.2	2.9	1.2

^a (IUPAC, 2009) ; ^b (Mora-Diez and Boyd, 2002) ; ^c (Masclet, 2005) ; ^d (Semadeni et al., 1995) ; ^e (Atkinson et al., 1984) ; ^f (Zhu and Cronin, 2000) ; ^g (Chin and Wine, 1994) ; ^h This work; ⁱ (NIST, 2009).

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8