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## In-cloud multiphase behaviour of acetone in the troposphere: Gas uptake, Henry's law equilibrium and aqueous phase photooxidation

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### ABSTRACT

Acetone is ubiquitous in the troposphere. Several papers have focused in the past on its gas phase reactivity and its impact on tropospheric chemistry. However, acetone is also present in atmospheric water droplets where its behaviour is still relatively unknown. In this work, we present its gas/aqueous phase transfer and its aqueous phase photooxidation. The uptake coefficient of acetone on water droplets was measured between 268 and 281 K ( $\gamma = 0.7 \times 10^{-2}$ – $1.4 \times 10^{-2}$ ), using the droplet train technique coupled to a mass spectrometer. The mass accommodation coefficient  $\alpha$  (derived from  $\gamma$ ) was found in the range  $(1.0\text{--}3.0 \pm 0.25) \times 10^{-2}$ . Henry's law constant of acetone was directly measured between 283 and 298 K using a dynamic equilibrium system ( $H_{(298\text{K})} = (29 \pm 5) \text{ M atm}^{-1}$ ), with the Van't Hoff expression  $\ln H(T) = (5100 \pm 1100)/T - (13.4 \pm 3.9)$ . A recommended value of  $H$  was suggested according to comparison with literature.

The OH-oxidation of acetone in the aqueous phase was carried out at 298 K, under two different pH conditions: at pH = 2, and under unbuffered conditions. In both cases, the formation of methylglyoxal, formaldehyde, hydroxyacetone, acetic acid/acetate and formic acid/formate was observed. The formation of small amounts of four hydroperoxides was also detected, and one of them was identified as peroxyacetic acid. A drastic effect of pH was observed on the yields of formaldehyde, one hydroperoxide, and, (to a lesser extent) acetic acid/acetate. Based on the experimental observations, a chemical mechanism of OH-oxidation of acetone in the aqueous phase was proposed and discussed. Atmospheric implications of these findings were finally discussed.

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### 1. Introduction

Due to its high emission fluxes and low reactivity, acetone is an ubiquitous compound in the troposphere where it is considered as one of the major oxygenated volatile organic compounds (VOCs) (Singh et al., 2000; Jacob et al., 2002). The global sources of acetone are estimated to be 40–60 Tg y<sup>−1</sup> (Singh et al., 1994) and a background acetone concentration of 350 ppt has been reported in the Southern Hemisphere (Singh et al., 2001). Acetone is directly emitted by plants (Fall et al., 2001; Janson and de Serves, 2001; Custódio et al., 2010), marine photochemistry (Zhou and Mopper, 1997; Staehelin et al., 1998; Holzinger et al., 1999; Jacob et al.,

2002) and anthropogenic sources: incomplete combustion and evaporation of solvents (Staehelin et al., 1998; Holzinger et al., 1999). Acetone is also a key species for atmospheric chemistry. It is one of the major reaction products of the gas phase photooxidation of VOCs such as propane (Singh and Hanst, 1981; Rosado-Reyes and Francisco, 2007) and monoterpenes (Alvarado et al., 1999; Baker et al., 2001; Wisthaler et al., 2001; Spaulding et al., 2003). Its atmospheric photooxidation in the presence of NO<sub>x</sub> leads to the formation of peroxyacetyl nitrate (PAN), a very stable compound, and its photolysis at high altitudes produces substantial amounts of HO<sub>x</sub> radicals (Singh et al., 1995).

Due to its ubiquity in the troposphere, acetone has also been frequently observed in tropospheric waters in rain, cloud and fog droplets (Grosjean and Wright, 1983; Valsaraj et al., 1993; Houdier et al., 2000; van Pinxteren et al., 2005). In particular (van Pinxteren et al., 2005) found that the concentrations of many carbonyls as well as acetone inside cloud droplets are higher (by a factor of 2 to 1000) than predicted by their Henry's law constant. The explanations for such supersaturations are not obvious: among several possibilities, uncertainties on gas-to-liquid transfer

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**Table 1**

Henry's law constants of acetone: comparison with the previous experimental determinations and the recommended values available in the literature.

$H_{298K}$ (M atm <sup>-1</sup> )	$-\ln(H)/d(1/T)$ (K)	$T$ range (K)	Type <sup>a</sup>	Reference
28	–	–	M	Burnett (1963)
25	–	–	M	Buttery et al. (1969)
22	5000	–	R	Schaffer and Daubert (2002)
25	–	–	M	Vitenberg et al. (1975)
26	4800	273–298	M	Snider and Dawson (1985)
3.0	3300	–	R	Janini and Qaddora (1986)
30	–	–	M	Gaffney et al. (1987)
35	3800	283–318	M	Zhou and Mopper (1990)
32	5800	288–318	M	Betterton (1991)
27	–	–	M	Hoff et al. (1993)
27	5300 ± 100	278–313	M	Benkelberg et al. (1995)
30	4600	–	R	Staudinger and Roberts (1996)
22	5000	–	R	Schaffer and Daubert (2002)
26 ± 6	6400 ± 1600 <sup>b</sup>	276–293	M	Strekowski and George (2005)
29 ± 6	5000 ± 1100 <sup>b</sup>	283–298	M	This work
33 ± 3	5 300 ± 500 <sup>b</sup>	273–318	R	This work

<sup>a</sup> M: experimental measurements; R: review.

<sup>b</sup> The quoted errors correspond to ±2σ.

properties can be one explanation, and in-cloud production can be another, thus illustrating the need for such studies. In the aqueous phase, acetone may be an important product of OH-oxidation of soluble VOCs (Mitani et al., 2002; Guillard et al., 2003; Warneck, 2005). Acetone photooxidation studies have previously been performed with different types of set-ups, in particular by Zegota et al. (1986), using radiolysis of N<sub>2</sub>O/O<sub>2</sub> to produce OH radicals and by Stefan et al. (1996) and Stefan and Bolton (1999) using UV photolysis of H<sub>2</sub>O<sub>2</sub>. However, their experimental conditions were far from atmospheric relevance, especially due to the low wavelengths (<290 nm) used. Besides, if the Henry's law constant of acetone at room temperature is well established in the literature, its temperature dependency  $-\ln(H)/d(1/T)$  shows variations between 3800 and 6400 K depending on the experimental studies (Zhou and Mopper, 1990; Strekowski and George, 2005) as shown in Table 1. Therefore, in order to have a better estimation of the impact of the multiphase behaviour of acetone, we have investigated its gas-to-liquid transfer properties (Henry's law constant and uptake coefficient) and its aqueous phase photooxidation mechanisms.

## 2. Experimental section

### 2.1. Uptake measurements

The uptake rate of a trace gas by a liquid is a multi-step process that can be related to fundamental properties of the gas, the interface and the condensed phase, such as mass accommodation coefficient  $\alpha$ , solubility or reactivity. The rate at which a trace gas molecule may be transferred into the condensed phase can be obtained from the kinetic theory of gases. The net flux  $\Phi_{\text{net}}$  of a trace gas into a surface is expressed in terms of a measured uptake coefficient  $\gamma$  as:

$$\Phi_{\text{net}} = \frac{1}{4} \langle c \rangle n \gamma \quad (1)$$

where  $\langle c \rangle$  is the trace gas average thermal velocity,  $\gamma$  is the uptake coefficient (which takes into account all processes potentially affecting the uptake rate) and  $n$  is the number density of the trace gas.

In order to measure uptake rates, we used the droplet train technique which has already been described elsewhere (Magi et al., 1997; Schweitzer et al., 1998) and therefore we will only provide a brief summary of the experimental procedure. The uptake coefficient is determined by measuring the decrease of the gas phase concentration of the trace species, due to its exposure to a vertical monodisperse train of droplets. These latter are generated by a vibrating orifice (70 μm diameter) leading to droplet diameters of about 140 μm. The interaction time between the gas and the droplets can be changed from 0 to 20 ms by moving the inner injector (up to 20 cm). Since the uptake process is directly related to the total surface  $S$  exposed by the droplets, any change  $\Delta S$  in this surface results in a change of the trace gas density  $\Delta n$  at the exit ports of the flow tube. Considering the kinetic gas theory, the overall uptake coefficient  $\gamma_{\text{meas}}$  can be obtained by measuring the fractional change of acetone concentration in the gas phase as a function of the total droplet surface area, at a given temperature (Worsnop et al., 1989):

$$\gamma_{\text{meas}} = \frac{4F_g}{\langle c \rangle \Delta S} \ln \left( \frac{n}{n - \Delta n} \right) \quad (2)$$

where  $F_g$  is the carrier gas volume flow rate,  $n$  and  $(n - \Delta n)$  are respectively the trace gas density at the inlet and outlet port of the interaction chamber.

The uptake coefficient  $\gamma_{\text{meas}}$  can be determined as a function of the gas/liquid contact time, composition of the liquid used to produce the droplets or total pressure that was in the range 15–25 Torr. These last measurements are necessary to decouple the overall process into individual steps. The carrier gas (helium) is always saturated, at a given temperature, with water vapour before entering the flow tube, in order to avoid any droplets evaporation.

The gas stream coming out of the flow tube was analyzed using a differentially pumped mass quadrupole spectrometer Pfeiffer Vacuum QMS with ionization energy of 60 eV. Acetone was monitored at 43 amu (CH<sub>3</sub>C(O)<sup>+</sup>) and the signal was averaged over a second.

### 2.2. Henry's law constants

Henry's law constants for acetone were measured using a dynamic equilibrium system used in recent studies (Gautier et al., 2003; Feigenbrugel et al., 2004a,b; Dievart et al., 2006).

Clean dry air (Alphagas, ≥99.99%) was passed through a microporous PTFE membrane tube (160 cm length × 0.8 cm i.d. Sumitomo Corporation) at a highly controlled flow rate (0.1–0.4 L min<sup>-1</sup>). The tube was immersed in about 0.6 L of a diluted acetone aqueous solution of about 100 mg L<sup>-1</sup>. Phase equilibrium was achieved for the dissolved compound at the gas/water interface along the inner surface of the tube. At the exit of the reactor, the gas phase containing acetone at equilibrium concentration was diluted using additional dry clean air (0.5–1 L min<sup>-1</sup>). Acetone present in the gas phase was trapped using two DNPH-impregnated cartridges connected in series and prepared as suggested by Zhou and Mopper (1990). At least 98% of acetone was trapped in the first cartridge. A sampling time of 10–45 min were required to concentrate enough acetone in the cartridges. Note that the mass of acetone trapped in the cartridges was always negligible compared to that in the total aqueous solution so that the concentration of the latter was effectively constant during the experiment. Upon passing through the cartridges, acetone reacts with DNPH to form the corresponding 2,4-dinitrophenylhydrazone which was extracted by passing 20 mL of acetonitrile. A volume of 10 μL of the obtained solution was then injected into a HPLC equipped with a C18 col-

umn (300 × 3.9 mm Waters). The sample was eluted by a mixture of acetonitrile–water (60/40%) at a flow rate of 1 mL min<sup>−1</sup> and was detected by an UV detector at 360 nm.

### 2.3. OH-oxidation experiments

OH-oxidation of acetone was studied in an aqueous phase photoreactor described in details in [Monod et al. \(2005\)](#). Briefly, it is a 450 mL Pyrex thermostated reactor, equipped with an irradiation source (a 300 W Xenon arc lamp Lot-Oriel), which mimics the sun irradiance spectrum. OH radicals were produced by H<sub>2</sub>O<sub>2</sub> photolysis and a Pyrex filter was employed to remove the UV irradiation below 300 nm, thus avoiding direct photolysis of acetone which was controlled through a specific experiment. Similarly, it was verified that the reaction of acetone towards H<sub>2</sub>O<sub>2</sub> can be neglected under our experimental conditions. The reaction was studied at 25 °C under two different pH conditions: one experiment was performed at pH = 2 (experiment A), and four experiments were performed in unbuffered solutions, i.e. at “free” pH (experiments B–E). For all experiments, the initial conditions are presented in [Table 2](#).

For each experiment, an aliquot of 2 mL was sampled from the photoreactor at periodic time intervals prior to analysis. The sampling time intervals were below 5 min at the beginning, and increased gradually up to 90 min after the first 3 h of experiment. In order to minimize artefact reactions, all samples were stored at 1–2 °C or frozen at −18 °C.

### 2.4. Analytical procedures

Each sample was divided into five aliquots corresponding to the five different analytical methods used to identify and quantify as much reaction products as possible (see [Table S1 Supplementary material](#) for more details on the analytical conditions).

- Acetone, methylglyoxal and hydroxyacetone were analyzed by GC-FID (HP 5890 series II) equipped with a semi-polar capillary column (HP INNOWAX 15 m × 0.25 mm × 0.50 μm) which allowed us direct sample injections without prior extraction or derivatization steps.
- Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and organic hydroperoxides were analyzed using HPLC equipped with fluorescence detection and post column *p*-hydroxyphenylacetic acid (POPHA) derivatization catalysed by peroxidase in the same conditions as those described by [François et al. \(2005\)](#).
- Carbonyl compounds (acetone, methylglyoxal, formaldehyde and hydroxyacetone) were derivatized with 2,4-DNPH with internal standard of benzaldehyde phenylhydrazone. The analyzes were performed using HPLC-UV and/or HPLC-ESI-MS (triple quadrupole Varian 1200).
- Organic acids (formic and acetic acids) were analyzed by a ionic chromatography Dionex DX-100 (IC) in isocratic mode. All aliquots for IC analysis were frozen (at −18 °C) just after sampling.

**Table 2**

Experimental conditions and initial concentrations of reactants for the study of the OH-oxidation of acetone.

Experiment name	pH	[Acetone] <sub>0</sub> (10 <sup>−3</sup> M)	[H <sub>2</sub> O <sub>2</sub> ] <sub>0</sub> (10 <sup>−3</sup> M)	[O <sub>2</sub> ] (10 <sup>−4</sup> M)	T (°C)	Duration
A	2	1.4	4.5	n.m. <sup>a</sup>	24.5	5 h
B	Free	1.0	10	1.3 (±0.4)	(±0.6)	8.5 h
C	Free	0.082	1.1	3.2 (±1.9)		21 h
D	Free	0.25	1.0	n.m. <sup>a</sup>		16 h
E	Free	0.28	1.0	n.m. <sup>a</sup>		14 h

<sup>a</sup> n.m. = Not measured.

Each analytical technique gave rise to sharp peaks, and calibration of each compound (in the range covering the concentrations encountered in the experiments) gave statistical error limits and detection limits that are summarized in [Table S2 \(Supplementary material\)](#).

## 3. Results and discussion

### 3.1. Uptake measurements

The uptake rate of a trace gas by a liquid is known to be a function of several processes including gas phase diffusion, mass accommodation, solubility and reactivity in the liquid phase. Each of these processes may introduce a resistance ( $\gamma_{\text{diff}}$ ,  $\alpha$ ,  $\gamma_{\text{sat}}$  and  $\gamma_{\text{rxn}}$ ) to the mass transfer from the gas phase into the aqueous phase and then the overall rate of uptake is obtained by summing up all these resistances according to [Kolb et al. \(1995\)](#):

$$\frac{1}{\gamma} = \frac{1}{\gamma_{\text{diff}}} + \frac{1}{\alpha} + \frac{1}{\gamma_{\text{sat}} + \gamma_{\text{rxn}}} \\ = \frac{< c > d_{\text{eff}}}{8D_g} - \frac{1}{2} + \frac{1}{\alpha} + \frac{< c >}{4HRT\sqrt{D_a}} \left( \frac{2}{\sqrt{\pi t}} + \sqrt{k} \right)^{-1} \quad (3)$$

In this equation,  $d_{\text{eff}}$  is the effective droplet diameter which takes into account the fact that a droplet train may not be considered as a sum of individual droplets (note however that its value is very close to the real diameter),  $H$  the Henry's law constant,  $R$  the perfect gas constant,  $T$  the droplets temperature,  $D_g$  and  $D_a$  the gas and aqueous phase diffusion coefficients respectively,  $t$  the gas/liquid contact time and  $k$  the first-order rate constant for a given reaction in the liquid phase.

The observed curvature in [Fig. S1 \(Supplementary material\)](#) characterises the existence of a surface saturation effect for the uptake of acetone on pure water at 269 K. This is confirmed by [Fig. S2 \(Supplementary material\)](#) that shows the inverse of uptake coefficient as a function of the gas/liquid contact time for acetone. It can be clearly seen that  $\gamma$  is time dependent, which means that saturation of the droplets' surface occurs in the studied temperature range 268–281 K. The uptake coefficients were therefore determined by using the first linear data. The quoted errors for  $\gamma$  include then an estimated error of 10% and  $2\sigma$  from the least-squares analysis and the corresponding results are shown in [Table S3 \(Supplementary material\)](#).

Acetone does not react in the aqueous phase on our experimental time scale (0–20 ms) so that it is therefore possible to neglect the resistance related to any aqueous phase reaction. The uptake coefficient on liquid droplets is then controlled by gas diffusion  $\gamma_{\text{diff}}$ , mass accommodation  $\alpha$  and aqueous phase saturation, i.e. [Eq. \(3\)](#) can be simplified and written as:

$$\frac{1}{\gamma} - \frac{1}{\gamma_{\text{diff}}} = \frac{1}{\alpha} + \frac{< c > \sqrt{\pi t}}{8HRT\sqrt{D_a}} \quad (4)$$

The gas phase diffusion coefficient ( $D_g$ ) is not known and therefore has been estimated by the method of [Reid et al. \(1987\)](#). In addition, since our carrier gas is a mixture of helium and water vapour, it was necessary to compute the diffusion coefficient in this background. This was done according to the following equation:

$$\frac{1}{D_g} = \frac{P_{\text{H}_2\text{O}}}{D_{g-\text{H}_2\text{O}}} + \frac{P_{\text{He}}}{D_{g-\text{He}}} \quad (5)$$

where  $P_{\text{H}_2\text{O}}$  and  $P_{\text{He}}$  are the partial pressures of water and helium respectively,  $D_{g-\text{H}_2\text{O}}$  and  $D_{g-\text{He}}$  are the binary diffusion coefficients of the trace gases in water and helium respectively. For acetone,  $D_{g-\text{H}_2\text{O}}$  and  $D_{g-\text{He}}$  are respectively 0.14 and 0.37 atm cm<sup>2</sup> s<sup>−1</sup> at 298 K and 1 atm while  $D_a$  was calculated to be  $1.36 \times 10^{-5}$  cm<sup>2</sup> s<sup>−1</sup>. The raw data ( $1/\gamma$ ) were corrected for gas phase diffusion according to [Eq. \(5\)](#) recommended by [Kolb et al. \(1995\)](#).

In this work, gaseous acetone concentrations varied typically between 10 and 100 ppmv. The uptake coefficients  $\gamma$  decreases respectively from  $1.4 \times 10^{-2}$  to  $0.7 \times 10^{-2}$  between 268 and 281 K (Table S3, Supplementary material).

By plotting  $1/\gamma - 1/\gamma_{\text{diff}}$  versus  $t^{1/2}$ , a linear response was found (Fig. S2, Supplementary material). The mass accommodation  $\alpha$  was therefore extracted from the intercept according to Eq. (5) when it was possible. The derived values of  $\alpha$  decrease from  $3 \times 10^{-2}$  to  $1 \times 10^{-2}$ , between 268 and 281 K. As shown in Fig. S2 (Supplementary material), the intercepts are very small (i.e. the mass accommodation coefficients are in fact very large) and therefore introduces large uncertainties.

Since the accommodation is not a kinetic limiting step, we have then used a technique allowing direct determination of Henry's law constants, in order to estimate the partitioning of acetone between air and water droplets in the atmosphere.

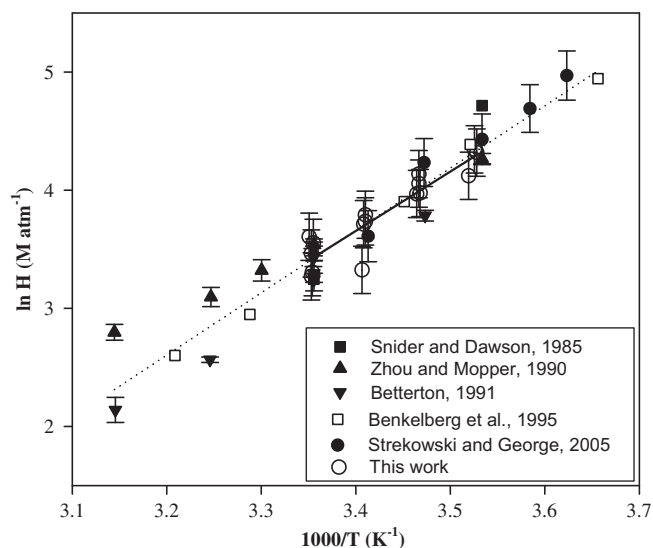
### 3.2. Direct measurements of Henry's law constant

The Henry's law constants  $H$  ( $\text{M atm}^{-1}$ ) were determined according to Eq. (6):

$$H = \frac{[X]}{P_x} \quad (6)$$

where  $[X]$  is the aqueous concentration of the studied compound and  $P_x$  its partial pressure (atm).

The Arrhenius plot of the Henry's Law constants measured for acetone between 283 and 298 K is presented in Fig. 1. The  $H$  values expressed in  $\text{M atm}^{-1}$  are listed in Table S4 (Supplementary material) where the quoted uncertainties are about 15%. The latter corresponds to the sum of the uncertainties on the calibration curve estimated to approximately 5%, on the extraction process determined to be of the order of 5% by a series of reproducibility tests, on the flow rates (less than 2.5% in our conditions) and on the aqueous concentration of acetone ( $\sim 2\%$ ). All the experiments were performed with an aqueous concentration of acetone equal to  $100 \text{ mg L}^{-1}$ . Within these experimental errors,  $H$  values of acetone are shown to be independent of the changes in air flow rate in the range  $0.2\text{--}0.4 \text{ L min}^{-1}$  (Table S4 in Supplementary material). This confirms that the equilibrium between solution and vapour is achieved before the exit of the reactor.



**Fig. 1.** Plot of the Henry's law constant  $H$  ( $\text{M atm}^{-1}$ ) versus  $1000/T$  for acetone. Comparison with the experimental temperature dependence found in the literature. The solid line is the linear fit obtained from our experimental data and the dotted line corresponds to the fit using all experimental data reported in this plot.

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

$$\ln H(T) = A - \left( \frac{\Delta H_{\text{soln}}}{RT} \right) \quad (7)$$

where  $\Delta H_{\text{soln}}$  is the solvation enthalpy ( $\text{J mol}^{-1}$ ),  $T$  is the temperature (K) and  $R$  is the ideal gas constant.

As displayed by the solid line in Fig. 1, our experimental determinations were then fitted according to Eq. (8) using a linear square analysis fit:

$$\ln H = (5100 \pm 1100)/T - (13.4 \pm 3.9) \quad (8)$$

where the quoted error is given at the  $2\sigma$  level from the least-squares analysis.

The Henry's law constant at 298 K derived from this Van't Hoff equation is  $29 \pm 5 \text{ M atm}^{-1}$ . Note that the relatively low values of  $H$  explain the saturation observed using the droplet train technique, during the study of the incorporation kinetics of acetone into water droplets.

#### 3.2.1. Comparison with the literature

At 298 K, our  $H$  value of  $29 \pm 5 \text{ M atm}^{-1}$  is in very good agreement with those reported in the literature where all values are in the range  $25\text{--}35 \text{ M atm}^{-1}$  (Table 1). Table 1 and Fig. 1 show that our temperature dependence is also in good agreement with most of those reported in the previous experimental studies (Snider and Dawson, 1985; Betterton, 1991; Benkelberg et al., 1995) where  $-\text{d}(\ln H)/\text{d}(1/T)$  varied between 4800 and 5800 K. However, our temperature dependences of  $H$  is 20–25% higher than those reported by Janini and Qaddora (1986) or Zhou and Mopper (1990) as shown in Table 1. Besides, our study does not confirm the higher value of  $-\text{d}(\ln H)/\text{d}(1/T) = 6400 \text{ K}$  found by the last reported study (Strekowski and George, 2005). Finally, by fitting our values together with all experimental temperature dependence found in the literature (Snider and Dawson, 1985; Zhou and Mopper, 1990; Betterton, 1991; Benkelberg et al., 1995; Strekowski and George, 2005) as illustrated by the dot line in Fig. 1, the Henry's law constant of acetone for temperature ranging between 273 and 318 K can be expressed as follows:

$$\ln H = (5300 \pm 500)/T - (14.3 \pm 1.6) \quad (9)$$

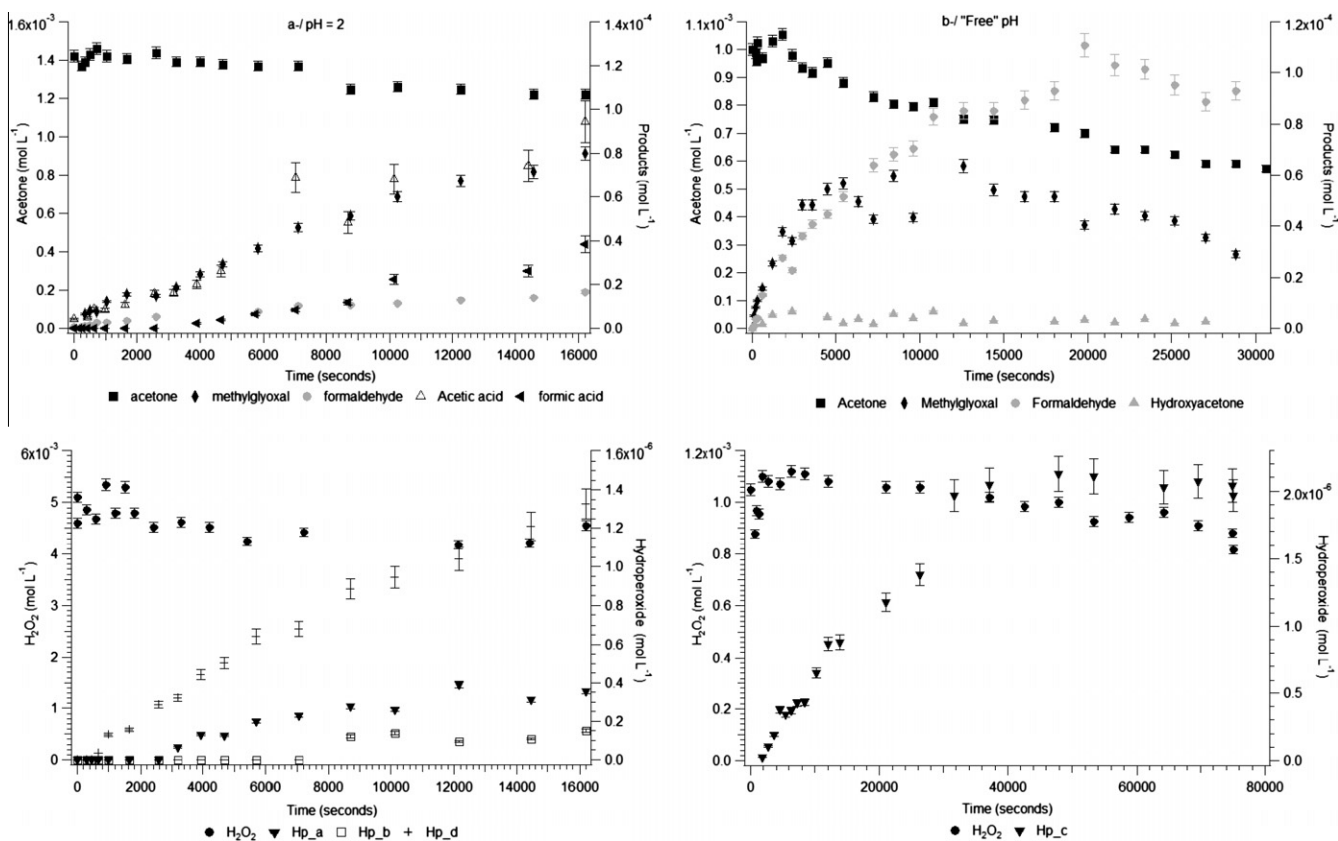
where the quoted error is given at the  $2\sigma$  level from the least-squares analysis. Consequently, a value of  $H = 33 \pm 3 \text{ M atm}^{-1}$  can be recommended at 298 K.

### 3.3. OH-oxidation of acetone in the aqueous phase

#### 3.3.1. Reaction products

During the OH-oxidation of acetone, the formation of methylglyoxal, formaldehyde, hydroxyacetone, acetic acid/acetate and formic acid/formate was observed (Fig. 2), in good agreement with Stefan et al. (1996) and Stefan and Bolton (1999). The formation of small amounts of four hydroperoxides (named Hp\_a, Hp\_b, Hp\_c and Hp\_d) was also detected (Fig. 2). Hydroperoxide Hp\_b was identified as peroxyacetic acid (PAA) using the HPLC-POPHA-fluorimetry technique, by comparison of its retention time with synthesized PAA. Using the HPLC-POPHA-fluorimetry technique, most of hydroperoxides are converted into  $\text{H}_2\text{O}_2$  prior to analysis (François et al., 2005). The quantification of unidentified hydroperoxides (Hp\_a, Hp\_c and Hp\_d) was performed (Fig. 2) assuming each of these compound was quantitatively converted into  $\text{H}_2\text{O}_2$ . To our knowledge, the formation of hydroperoxides was experimentally evidenced here for the first time, in good agreement with the assumptions of Zegota et al. (1986). For experiments B–E, the pH of the unbuffered solution, which started at 5.9, decreased





**Fig. 2.** Time profiles of reactants and main identified reaction products (link) and  $\text{H}_2\text{O}_2$  and organic hydroperoxides (Hp) (right) during the OH-oxidation of acetone in the aqueous phase (a) at pH = 2 (experiment A), and (b) at “free pH” (experiments B and C).

down to 4.2 within 5 h due to the formation of organic acids. Fig. 2 shows that methylglyoxal, formaldehyde, hydroxyacetone, acetic acid/acetate, and hydroperoxides Hp\_c and Hp\_d were primary reaction products, while formic acid/formate, and hydroperoxides Hp\_a and Hp\_b were secondary reaction products. This figure also shows a clear difference in the yields of formaldehyde and hydroperoxides between pH = 2 and unbuffered experiments. A chemical mechanism explaining the formation of the identified products is discussed below.

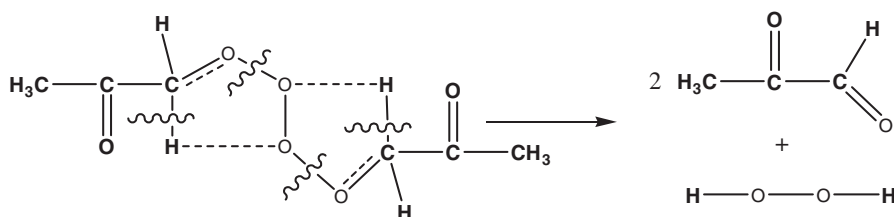
### 3.3.2. OH-oxidation mechanism

OH-oxidation of acetone proceeds via a hydrogen abstraction mechanism, leading to an acetyl radical (Zegota et al., 1986; Ervens et al., 2003; Monod et al., 2005) which undergoes a fast  $\text{O}_2$  addition to form an acetylperoxy radical (Fig. 3).

The acid/base radical  $\text{HO}_2/\text{O}_2^-$  has a pKa of 4.8 (Bielski et al., 1984), its basic form  $\text{O}_2^-$  can react with an acetylperoxy radical to produce acetylhydroperoxide,  $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{OOH}$ . This first

generation hydroperoxide should be one of the most abundant hydroperoxides at “free pH”, which corresponds to hydroperoxide Hp\_c (Fig. 2b). However, this assumption could not be verified with standards. The acetylperoxy radical can also undergo a self-reaction, leading to a tetroxide (Zegota et al., 1986; Von Sonntag and Schuchmann, 1997), which can undergo three different pathways (a–c) (Fig. 3):

- Pathway a leads to the formation of methylglyoxal, hydroxyacetone and oxygen through the Russell’s mechanism, which proceeds via the formation of a six atoms cycle (Russell, 1957).
- Pathway b corresponds to the degradation mechanism described by Bennet in 1974 (which can be found in Zellner and Herrmann (1995)) and leads to the formation of methylglyoxal and  $\text{H}_2\text{O}_2$ . As for the Russell’s mechanism, this reaction can proceed via a cyclic transition state: (i) two five-membered rings Eq. (10) or (ii) a double cycle of six atoms including two molecules of water (Eq. (11)).



(10)

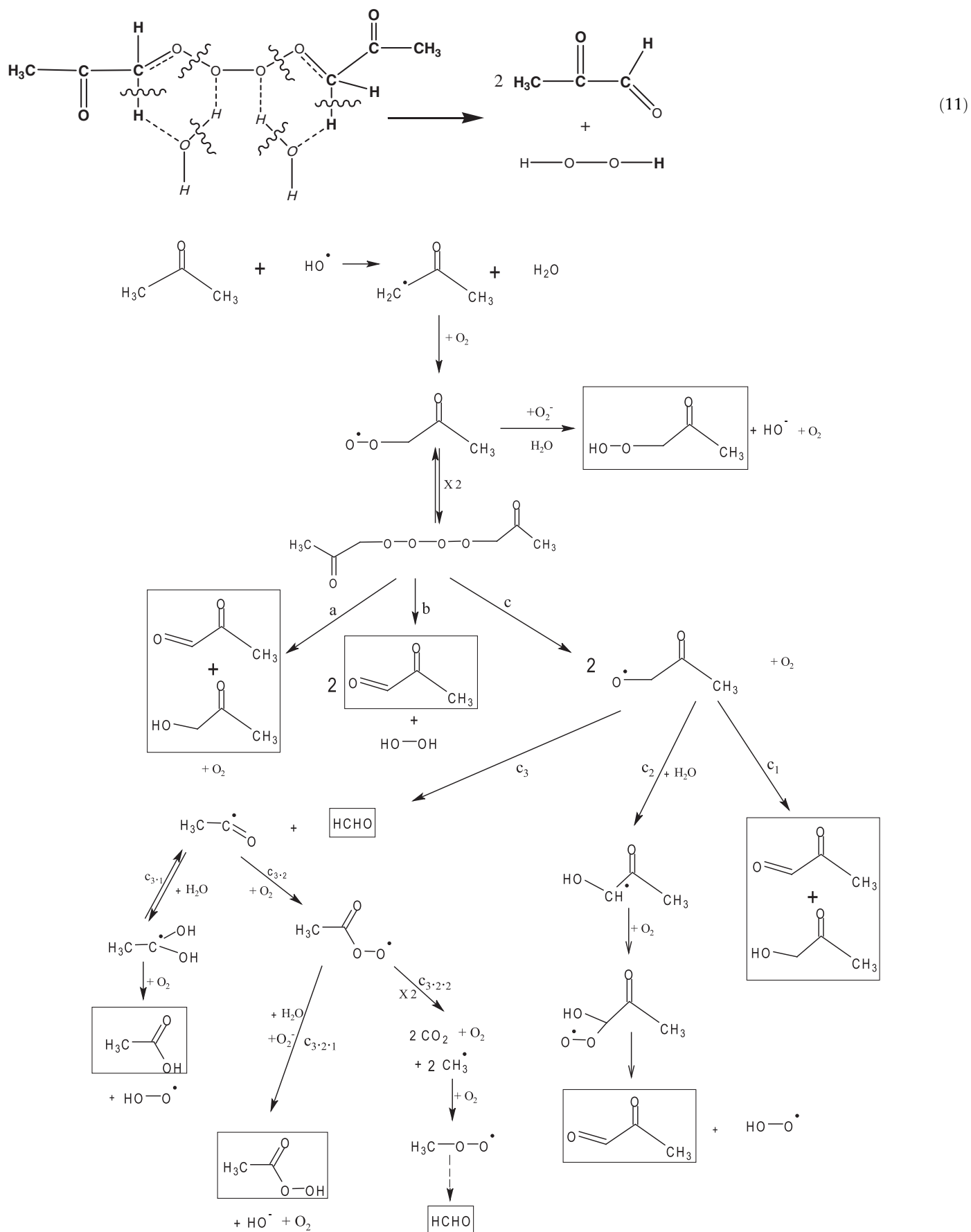


Fig. 3. OH-oxidation mechanism of acetone in the aqueous phase. The reaction products observed are framed.

- Pathway c forms an alkoxy radical  $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}^\bullet$  and oxygen by fragmentation of the tetroxide. The alkoxy radical can, in turn, undergo three different pathways:
  - Pathway  $c_1$ , corresponds to a self-reaction mechanism leading to the formation of methylglyoxal and hydroxyacetone (Zegota et al., 1986).
  - In pathway  $c_2$ , the alkoxy radical  $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}^\bullet$  rearranges in water solution to form the corresponding hydroxyalkyl radical  $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}^\bullet$  (von Sonntag and Schuchmann, 1997), which undergoes a fast  $\text{O}_2$  addition. The resulting  $\alpha$ -hydroxyperoxyl radical eliminates  $\text{HO}_2/\text{O}_2^-$  radicals (as observed for most of the  $\alpha$ -hydroxyperoxyl radicals) to produce methylglyoxal.
  - In pathway  $c_3$ , the  $\beta$ -bond fragmentation of the alkoxy radical leads to formaldehyde and acetyl radical, which can hydrate (pathway  $c_{3,1}$ ) ( $K_{\text{hyd}} \sim 0.66$ , Schuchmann and Von Sonntag, 1988). The resulting hydrated acetyl radical rapidly adds oxygen leading to hydrated acetylperoxyl radical which eliminates  $\text{HO}_2/\text{O}_2^-$  radicals, leading to acetic acid/acetate (Schuchmann and Von Sonntag, 1988). Nonhydrated acetyl radicals add oxygen (pathway  $c_{3,2}$ ) to form acetylperoxyl radicals ( $\text{CH}_3\text{CO}(\text{OO}^\bullet)$ ), which oxidize superoxide radicals ( $\text{O}_2^-$ ) leading to peracetic acid (pathway  $c_{3,2,1}$ ). In competition, acetylperoxyl radicals react bimolecularly (pathway  $c_{3,2,2}$ ), leading to  $\text{CO}_2$ , oxygen and  $\cdot\text{CH}_3$  radicals. The latter radicals add oxygen to form methylperoxy radicals ( $\text{CH}_3\text{OO}^\bullet$ ), which mainly lead to formaldehyde (Monod et al., 2007).

Pathways a, b,  $c_1$  and  $c_2$  explain the observed formation of methylglyoxal and hydroxyacetone as primary reaction products, but these four pathways cannot be differentiated under our experimental conditions. Pathway  $c_3$  is the only pathway able to explain the observed formation of formaldehyde, acetic acid and peroxyacetic acid. Furthermore, primary acetic acid/acetate can only be formed via pathway  $c_{3,1}$ , and peroxyacetic acid via pathway  $c_{3,2,1}$ .

### 3.3.3. Carbon balance and pH effect on reaction products

The molar yield of the primary reaction products was determined by plotting their concentration versus the concentration of consumed acetone at the same reaction time. The slope of the linear regression gives the molar yield of each product, presented in

**Table 3**

Molar yield and carbon yield of the reaction products identified during the OH-oxidation of acetone in the aqueous phase.

Identified compounds	Molar yield%	
Experiment	A	B, C, D, E <sup>a</sup>
pH	2	"Free" <sup>f</sup>
Methylglyoxal	58 ± 11	73 ± 15
Hydroxyacetone	n.d. <sup>b</sup>	13 ± 3
Formaldehyde	24 ± 3	74 ± 17
Acetic acid/acetate	40 ± 8	13 ± 15 <sup>c</sup>
Formic acid/formate	Secondary	Secondary
Hydroperoxide Hp_a (r.t. <sup>d</sup> = 12.3 min)	Secondary	–
Hydroperoxide Hp_b (r.t. <sup>d</sup> = 14.4 min) (PAA)	Secondary	–
Hydroperoxide Hp_c (r.t. <sup>d</sup> = 15.3 min)	–	8 ± 1
Hydroperoxide Hp_d (r.t. <sup>d</sup> = 18.1 min)	0.7 ± 0.1	–
Total carbon yield for primary reaction products (% of carbon) <sup>e</sup>	86 ± 16%	117 ± 31%

<sup>a</sup> At "free" pH, the molar yields were determined by gathering together the data for the four experiments (B–E).

<sup>b</sup> n.d.: Not determined.

<sup>c</sup> Measured during experiment C, at concentrations close to the detection limits.

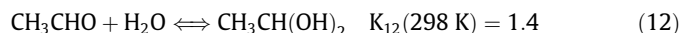
<sup>d</sup> r.t.: Retention time using HPLC equipped with fluorescence detection and post column POPHA derivatization catalysed by peroxidase (see text).

<sup>e</sup> The calculated total carbon yield does not take into account hydroperoxides.

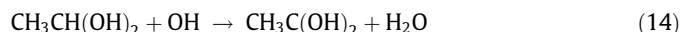
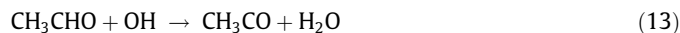
<sup>f</sup> The pH value varied from 5.9 at the beginning of the reaction, to 4.2 after 5 h of photooxidation.

Table 3, together with the total carbon yields. Although the four "free" pH experiments (B–E) were performed with different initial concentrations (Table 2), the obtained molar yields were not significantly different, and the results are presented in Table 3 by gathering together the data for the four experiments. The carbon balance was roughly complete at both pH. Table 3 also shows that pH had no significant effect on the yield of methylglyoxal, in good agreement with the study by Zegota et al. (1986) who obtained a yield of approximately 50–55% at pH = 6.5, 9.5–11.3 and 10–11. Table 3 shows that pH had a drastic effect on the yields of formaldehyde, hydroperoxide Hp\_c and (to a lesser extent) acetic acid/acetate. The amounts of hydroperoxides Hp\_a, Hp\_b and Hp\_d, were very low at both pH, and the differences observed from one pH value to the other are not considered significant.

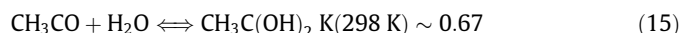
The absence of peroxyacetic acid as a primary reaction product at both pH indicates that pathway  $c_{3,2,1}$  is of minor importance compared to pathway  $c_{3,2,2}$ , thus pathway  $c_{3,2}$  mainly leads to formaldehyde. The pH effects observed on the yields of formaldehyde and acetic acid/acetate can be interpreted as a pH effect on the branching ratios between pathways  $c_{3,1}$  (which leads to acetic acid/acetate) and  $c_{3,2}$  (which mainly leads to formaldehyde). In order to verify this hypothesis, we have performed experiments of OH-oxidation of acetaldehyde at pH = 2 and pH = 7 under similar conditions as those described for acetone. In aqueous solution, acetaldehyde is partly hydrated Eq. (12) (Betterton and Hoffmann, 1988).



Both the hydrated and nonhydrated forms are oxidized by OH radicals (Eqs. (13) and (14)), and for both molecules, the H-abstraction on the methyl group represents less than 10% (Schuchmann and Von Sonntag, 1988).



The resulting radicals are also in equilibrium in the aqueous phase Eq. (15) (Schuchmann and Von Sonntag, 1988).



The subsequent pathways for these two radicals are described by pathways  $c_{3,1}$  and  $c_{3,2}$  in Fig. 3. The results obtained during the acetaldehyde experiments have shown that peracetic acid was not produced under our analytical conditions, thus confirming the results obtained for acetone. Acetic acid (or acetate ions) was the main primary reaction product, with a yield of (81 ± 9)% and (90 ± 9)% at pH = 2 and 7 respectively. Formaldehyde and formic acid (or formate ions) were also observed, but together, their yields accounted for less than 10% at both pH values. These results show that the pH effect observed during acetone photooxidation cannot be attributed to pathways  $c_{3,1}$  and  $c_{3,2}$ . An additional unknown pathway forms formaldehyde with high pH sensitivity. Concerning hydroperoxide Hp\_c, in the absence of a clear identification, it is difficult to build up a clear explanation of the observed pH effect on this compound. The formation of formic acid/formate as a secondary product can be explained by the OH-oxidation of the formed formaldehyde, following the mechanism described by McElroy and Waygood (1991).

## 4. Atmospheric implications

In regards to its mass accommodation coefficient of  $(1.0 - 3.0 \pm 0.25) \times 10^{-2}$  in the temperature range 268–281 K and its Henry's law constant of  $33 \pm 3 \text{ M atm}^{-1}$  at 298 K (recommended value), acetone can be considered as a low solubility organic compound. However, van Pinxteren et al. (2005) have found that the



concentrations of acetone (and other low soluble carbonyls) inside cloud droplets are two orders of magnitude higher than predicted by its Henry's law constant. One possible explanation may be the decreasing of the surface tension of hydrometeors which improves the gas–water transfer as suggested by [Lo and Lee \(1996\)](#) and by [Facchini et al. \(2000\)](#). For acetone, it is also possible that direct formation occurs inside the droplets by oxidation of many water soluble organic precursors, present in hydrometeors ([Guillard et al., 2003](#)), or by dissolution of larger organic molecules linked to the cloud condensation nuclei (CCN) ([Hallquist et al., 2009](#)).

Several products were identified during the OH-oxidation of acetone in water and they were used to suggest a possible oxidation mechanism. The main reaction products (in terms of carbon yields) are methylglyoxal and hydroxyacetone that are also found during the acetone oxidation in the gas phase ([Atkinson, 1994](#)). [Monod et al. \(2005\)](#) have found that under in-cloud conditions, acetone photooxidation is 1.5 times faster compared to clear sky (gas) conditions. This can explain (at least in part) the cloud droplets' supersaturations (by a factor of three) of methylglyoxal and hydroxyacetone observed by [van Pinxteren et al. \(2005\)](#).

In the aqueous phase, due to the absence of NO<sub>x</sub> reactivity (towards nonaromatic compounds) the formation of organic hydroperoxides is possible and for the first time (to our knowledge) the formation of such compounds was directly observed. The formation of hydroperoxides in water droplets influences the reactivity ([Monod et al., 2007](#)) and particularly the oligomerization processes ([Hallquist et al., 2009](#)) occurring in the aqueous phase. Besides, methylglyoxal has been identified as a key species for the formation of oligomers within the aqueous phase ([Kalberer et al., 2004](#); [Altieri et al., 2008](#)). Therefore, the aqueous phase photooxidation of acetone can indirectly induce a source of oligomers through hydroperoxides and methylglyoxal formation. These oligomers are low volatile organic compounds, and thus can represent a new source of aerosol after droplet evaporation ([El Haddad et al., 2009](#)), and can also directly modify the cloud condensation nuclei properties.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.chemosphere.2010.07.032](https://doi.org/10.1016/j.chemosphere.2010.07.032).

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