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Atmospheric loss processes of dimethyl and diethyl carbonate

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Abstract

A combined study of the OH gas phase reaction and uptake on aqueous surface of two carbonates, dimethyl and diethyl carbonate has been carried out to determine the atmospheric lifetimes of these compounds. Rate coefficients have been measured for gas phase reactions of OH radicals with dimethyl and diethyl carbonate. The experiments were carried out using pulsed laser photolysis - laser induced fluorescence over the temperature range 263-372 K and the kinetic data were used to derive the following Arrhenius expressions (in units of $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$): for dimethyl carbonate, $k_1 = (0.83 \pm 0.27) \times 10^{-12} \exp[-(247 \pm 98)/T]$ and for diethyl carbonate, $k_2 = (0.46 \pm 0.15) \times 10^{-12} \exp[(503 \pm 203)/T]$. At 298 K, the rate coefficients obtained (in units of $10^{-12} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$) are: $k_1 = (0.35 \pm 0.04)$ and $k_2 = (2.31 \pm 0.29)$. The results are discussed in terms of structure-activity relationships.

The uptake coefficients of both carbonates on aqueous surfaces were measured as a function of temperature and composition of the liquid phase, using the droplet train technique coupled to a mass spectrometric detection. Dimethyl and diethyl carbonate show very similar results. For both carbonates, the measured uptake kinetics were found to be independent of the aqueous phase composition (pure water, NaOH solutions) but dependent on gas-liquid contact time which characterises a surface saturation effect. The uptake coefficient values show a slight negative temperature dependence for both carbonates. These values vary from 1.4×10^{-2} to 0.6×10^{-2} in the temperature range of 265-279 K for dimethyl carbonate, from 2.4×10^{-2} to 0.9×10^{-2} in the temperature range of 270-279 K for diethyl carbonate. From the kinetic data, the following Henry's law constants were derived between 279 and 265 K : dimethyl carbonate, $H_1 = 20\text{-}106 \text{ M atm}^{-1}$; and diethyl carbonate, $H_2 = 30\text{-}98 \text{ M atm}^{-1}$. The

reported data show that the OH reaction is the major atmospheric loss process of these two carbonates with lifetimes of 33 and 5 days, respectively, while the wet deposition is a negligible process.

Key Words: OH radicals, rate coefficients, uptake measurements, dimethyl carbonate, diethyl carbonate.

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Introduction

Organic carbonates have been suggested as fuel additives because their use may reduce the vapour pressure of fuels and in turn reduce their emissions to the atmosphere by evaporation. If pure dimethyl carbonate freezes at 1°C, at a concentration of 3-4 % in gasoline, it remains in solution without becoming cloudy or hazy below -40 °C allowing it to be used as a fuel additive in winter. Organic carbonates have also a good blending octane (Pacheco *et al.*, 1997) and very high oxygen contents, in contrast to ethers (Bilde *et al.*, 1997), which can reduce significantly CO emissions from motor vehicles.

In addition to these primary emission sources, organic carbonates can be generated in the atmosphere during the oxidation of diethers. For instance, the oxidation of dimethoxy methane (CH₃OCH₂OCH₃) leads to about 25 % of dimethyl carbonate (CH₃OC(O)OCH₃) (Wenger *et al.*, 1999).

Although having low toxicity, carbonates may play a significant role in photochemical pollution by contributing to the formation of tropospheric ozone and other photooxidants. When released into the atmosphere, these oxygenated volatile organic compounds (VOCs) can undergo photochemical transformations initiated by OH radicals or be taken up by clouds, which also represent a net sink during precipitation events. By analogy with acetates, reactions with the NO₃ radical (Langer *et al.*, 1993), and with ozone (Atkinson *et al.*, 1984), as well as photolysis (Calvert *et al.*, 1966) can be considered as slow loss processes for the carbonates. Therefore, kinetic and mechanistic information on the major tropospheric gas-phase and multi-phase oxidation of organic carbonates is needed, in order to assess their impact on air quality.

In this work, we report absolute rate coefficient data for the OH radical reactions with dimethyl carbonate (k_1) and diethyl carbonate (k_2) over the temperature range 263-372 K :



This work provides the second determination of k_1 (Bilde *et al.*, 1997) and the first one for k_2 . Since carbonates are polar, it is expected that they interact with atmospheric liquid water and

in this context, we have determined the uptake coefficients of both carbonates by the aqueous phase. To our knowledge, these measurements are the first to be reported.

Experimental Section

OH experiments

The technique of pulsed laser photolysis - laser induced fluorescence (PLP-LIF) used in the OH experiments has been described in detail previously (Mellouki *et al.*, 1994, Mellouki *et al.*, 1995), and is only briefly discussed here. OH radicals were produced by photolysis of H₂O₂ at $\lambda = 248$ nm (KrF excimer laser). The concentration of OH radicals was monitored at various reaction times ranging from *ca.* 10 μ s to 10 ms by pulsed laser induced fluorescence (LIF). A Nd:YAG pumped frequency doubled dye laser was used to probe the OH radical at $\lambda = 282$ nm, the subsequent fluorescence was detected by a photomultiplier, fitted with a 309 nm narrow bandpass filter. The output pulse from the photomultiplier was integrated for a preset period by a gated charge integrator. Typically the fluorescence signal resulting from 100 probe laser shots was measured for 10 to 15 different delay times and averaged to generate OH concentration-time profiles over at least three lifetimes. Carbonate/H₂O₂ mixtures in helium diluent were flowed slowly through the cell, so that each photolysis/probe sequence interrogated a fresh gas mixture and reaction products did not build up in the cell.

All experiments were carried out under pseudo-first-order conditions with [carbonate] \gg [OH]₀, the initial concentration of OH being lower than 2×10^{11} molecule cm⁻³. The temporal profiles of the OH concentration, therefore, followed the pseudo-first-order rate law:

$$[\text{OH}]_t = [\text{OH}]_0 e^{-k'_i t} \quad \text{where } k'_i = k_i [\text{carbonate}_i] + k'_0 \quad (\text{I})$$

where carbonate_i refers to the carbonate in reaction *i* (*i* = 1, 2) and *k_i* is the rate coefficient for the reaction of OH with the carbonate (*i*). The decay rate, *k'₀*, is the first-order decay of OH in the absence of the carbonate. The value of *k'₀* is essentially the sum of the pseudo first order rate constant for OH with H₂O₂, and the rate constant for diffusion of OH out of the detection zone. The concentration of OH at various reaction times (delay between the photolysis and probe pulses) was determined by measuring the LIF signals at those delay times. Weighted

least-squares analyses were used to fit the data to the above equation and extract the values of k_i' . The second-order rate coefficients (k_i) were obtained from the measured values of k_i' at various carbonate concentrations.

Helium (UHP certified to > 99.9995 %) from Alphagas, was used without purification. A 50 wt. % H_2O_2 solution was obtained from Prolabo, and was further concentrated by bubbling helium through for several days prior to use it in order to remove water, and was then constantly flushed with He during the course of the experiments. During a kinetic experiment, the gas flow was admitted into the reaction cell by passing a small flow of helium through a glass bubbler containing H_2O_2 . Dimethyl carbonate (> 99 %) and diethyl carbonate (99 %) were respectively obtained from Fluka and BDH. They were further purified by repeated freeze-pump-thaw cycles and fractional distillation before use.

For the kinetic measurements, the carbonates were premixed with helium in a 10 L glass light-tight bulb to form a (0.7 – 4.0) % mixture at a total pressure of around 750 Torr. All the gases flowed into the reactor through Teflon tubing. The gas mixture containing the carbonate, photolytic precursor (H_2O_2) and the bath gas were flowed through the cell with a linear velocity ranging between 1 and 3 cm s^{-1} . The concentrations of the carbonates were calculated from their mass flow rates, temperature and pressure in the reaction cell. All flow rates were measured with mass flowmeters calibrated by measuring the rate of pressure increase in a known volume. The pressure in the cell was measured with a capacitance manometer located at the cell entrance.

Uptake experiments

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, interface and the condensed phase such as the mass accommodation coefficient (α), solubility and 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. This allows the calculation of the net flux Φ_{net} that crosses the interface:

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

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

Uptake rates were measured using, the droplet train technique already described elsewhere (Magi *et al.*, 1997, Schweitzer *et al.*, 1998). We will therefore provide only a brief summary of its principle of operation. The uptake coefficient was determined by measuring the decrease of the gas phase concentration of the trace species, due to their exposure to a monodisperse train of droplets. These latter were generated by a vibrating orifice (100 μm diameter) leading to droplet diameters of about 200 μm . The apparatus, where the contact between both phases takes place, is a vertically aligned flowtube. Its length can be varied up to 20 cm, in order to change the gas/liquid interaction time (0 - 20 ms) or the surface exposed by the droplet train (0 - 0.2 cm^2). Since the uptake process is directly related to the total surface S exposed by the droplets, any change ΔS in this surface results in a change of the trace gas density Δn at the exit ports of the flowtube. The uptake coefficient was calculated by considering the kinetic gas theory and the integrated signal during the transit time due to changes in the exposed surface (Worsnop *et al.*, 1989):

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

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 overall uptake coefficient γ was derived from the measurement of the fractional changes in concentration $\ln[n/(n-\Delta n)]$ as a function of $\langle c \rangle \Delta S / 4F_g$. This parameter can be measured as a function of the total pressure, gas/liquid contact time or composition of the liquid used to produce the droplets. These last measurements are necessary to decouple the overall process into individual steps. An important aspect of this technique is the careful control of the partial pressure of water in the flowtube since it controls the surface temperature of the droplets through evaporative cooling (Worsnop *et al.*, 1989). Therefore, the carrier gas (helium) was always saturated, at a given temperature, with water vapour before entering the flow tube.

The extraction of kinetic information from the droplet train technique may be affected by the high speed of the droplets which favors convective transport into the droplets.

However, several facts demonstrate that, given the accuracy of the experiments, this effect does not represent a significant source of error. The time scale of the experiment was short (typically less than 20 ms) which do not allow a massive influence of convective transport. Using the description given by Pruppacher *et al.* (1978), some calculations have shown that this influence on the uptake process is less than 5% for times below 20 ms (George, 1993), in agreement with the results of Baboobal *et al.* (1981).

Aqueous solutions used to prepare the droplets were made from Milli-Q water (18 M Ω cm) and NaOH (BDH, \geq 99 %) when necessary. Dimethyl carbonate (\geq 99 %) and diethyl carbonate (99 %) were respectively obtained from Fluka and Aldrich.

The gas stream coming out of the flowtube was analysed using a differentially pumped mass quadrupole spectrometer Pfeiffer Vacuum QMS with an ionisation energy of 60 eV. The signal was averaged over a second in order to increase the signal to noise ratio. Dimethyl carbonate was monitored at 59 amu ($\text{CH}_3\text{C}(\text{O})\text{O}^+$) and diethyl carbonate at 63 ($\text{C}^+(\text{OH})_3$) and 91 ($\text{C}_2\text{H}_5\text{OC}^+(\text{OH})_2$) amu. In addition, H_2O and an inert tracer SF_6 were respectively monitored at 18 (H_2O^+) amu and 89 (S^+F_3) amu during the experiments in order to see any potential perturbations in gas phase concentrations.

Results and Discussion

OH reactions rate constants

Loss of the OH radical in the presence of the substrate was, as expected, found to be exponential in all cases and plots of $k_1'-k_0'$ versus carbonate concentration showed excellent linearity. Representative data of OH reactions with both carbonates are shown in Figure 1. Values of k_1 for dimethyl and diethyl carbonate over the temperature range 263-372 K were obtained from least-squares fits of the data and are listed in Table I. The quoted errors for k_1 include 2σ from the least-squares analysis and an estimated systematic error of 5% due to uncertainties in measured concentrations. Possible errors in the measured rate coefficients due to secondary reactions of OH with the radicals produced in reactions (1) and (2) were significantly reduced by using $[\text{carbonate}]/[\text{OH}]_0$ ratios in the range 10^2 - 10^4 .

As indicated in Table I, the determined rate coefficients were shown to be independent of carbonate concentration (from 0.5 to 49.5×10^{14} molecule cm^{-3}). The rate coefficients were also insensitive to variations in the flow velocity through the reactor ($v = 1 - 3$ cm s^{-1}), in the photolysis laser energy at 248 nm ($E = 1.5 - 6$ mJ) and in pressure ($P = 100 - 300$ Torr).

The temperature dependence of the rate coefficients k_1 and k_2 can be conveniently expressed in the conventional Arrhenius form ($k = Ae^{-E_a/RT}$) as shown in Figure 2. The conventional Arrhenius parameters derived for k_1 and k_2 are given in Table II along with data reported by Bilde *et al.* (1997) for k_1 who used the Flash Photolysis–Resonance Fluorescence technique. The results are in good agreement over the entire temperature range of this study.

However, a slight curvature is clearly observed for dimethyl carbonate. This curvature in the Arrhenius plot may arise from the fact that two different reaction channels occur in the temperature range (263-372 K). At higher temperature, the OH radical reactions proceed via H-atom abstraction from the C-H bonds similarly to the alkanes (Atkinson, 1994). At lower temperature, a second pathway forming a long-lived adduct by OH addition to the carbonyl group may be possible. Both pathways would lead to the formation of the same products. This was, for instance, suggested for OH reactions with aliphatic ketones (Wallington *et al.*, 1987, Wollenhaupt *et al.*, 2000). In the case of OH reaction with acetone, Wollenhaupt *et al.* (2000) suggest the possible formation of an association complex $[(\text{CH}_3)_2\text{COOH}]^\ddagger$ which can decompose at low temperatures by C-C bond fission to yield acetic acid ($\text{CH}_3\text{C}(\text{O})\text{OH}$) and CH_3 radicals as products. Even if the change in slope in our temperature range is less marked

than Wollenhaupt et al. (2000) found for acetone, both processes may occur. k_1 could then be written as the sum of two exponentials ($k_1 = A_1e^{-E_{a1}/RT} + A_2e^{-E_{a2}/RT}$). E_{a1}/R is assumed to be equal to 1070 which corresponds to the activation energy for the reaction of ethane with OH in the temperature range of 300-390 K (Donahue *et al.*, 1998). This assumption is justified by the fact that both compounds have only two individual $-CH_3$ groups which have positive temperature dependence (Atkinson, 1994). The plot of $k_1 = 5.9 \times 10^{-12} \exp(-1070/T) + 1.3 \times 10^{-14} \exp(795/T)$ is in excellent agreement with the experimental data as it is shown in figure 2.

In contrast to k_1 which has a similar positive temperature dependence than the rate constant of OH reaction with ethane in the temperature range of 300-390 K, k_2 has a negative temperature dependence compared to the net positive dependence observed for the rate constant of OH reaction with n-butane. Therefore, at 400 K, OH + n-butane is faster than OH + DEC, but is slower at 250 K.

The obtained rate constant at 298 K can be compared with the calculated ones using the structure-activity relationship (SAR) (Atkinson, 1987, Kwok *et al.*, 1995). In this method, calculation of H-atom abstraction for C-H bonds is based on the estimation of $-CH_3$, $-CH_2-$ and $-CH<$ group rate constants, assuming that the group rate constants depend on the identity of substituents attached to the group. At 298 K, the group rate constants are given by: $k(CH_3-X) = k_{prim} F(X)$, $k(Y-CH_2-X) = k_{sec} F(X) F(Y)$, $k((Y)(Z)CH(X)) = k_{tert} F(X) F(Y) F(Z)$, where k_{prim} , k_{sec} , k_{tert} are the rate constants per CH_3- , $-CH_2-$, $>CH-$ groups and $F(X)$, $F(Y)$, $F(Z)$ are the substituent factors. k_1 and k_2 have been calculated using the following parameters at 298 K (Kwok *et al.*, 1995): $k_{prim} = 0.136 \times 10^{-12}$, $k_{sec} = 0.934 \times 10^{-12}$ (units of cm^3 molecule $^{-1} s^{-1}$), $F(-CH_3) = 1$, $F(-CH_2-) = 1.23$, $F(-OC(O)OR)$ is not defined but was assumed to be equal to $F(-OC(O)R) = 1.6$. The calculated values of k_1 and k_2 using these parameters were higher than the experimental ones (the calculated values are in parentheses): $k_1 = 0.35$ (0.44) and $k_2 = 2.3$ (3.3) (in $10^{-12} cm^3 molecule^{-1} s^{-1}$). A better agreement between the experimental and calculated rate constants is obtained with a new substituent factor for the $-OC(O)OR$ group: $F(-OC(O)OR) = 1.17$, derived from the experimental rate coefficient of OH reaction with dimethyl carbonate and diethyl carbonate.

Uptake experiments

As already mentioned, uptake coefficients are measured from the fractional changes in trace gas concentration due to a modification in the exposed droplets surface (equation III) which is function of diffusion rates in both phases, mass accommodation process, and solubility and reactivity in the liquid phase. To each of these processes, one can attribute a specific uptake coefficient and the overall uptake coefficient is calculated by summing up the individual resistances (defined as the inverse of the specific uptake coefficient) according to (Kolb *et al.*, 1994) :

$$\begin{aligned} \frac{1}{\gamma} &= \frac{1}{\gamma_{\text{diff}}} + \frac{1}{\alpha} + \frac{1}{\gamma_{\text{sat}} + \gamma_{\text{rxn}}} \\ &= \frac{\langle c \rangle d_{\text{eff}}}{8D_g} - \frac{1}{2} + \frac{1}{\alpha} + \frac{\langle c \rangle}{4\text{HRT}\sqrt{D_a}} \left(\frac{2}{\sqrt{\pi}} + \sqrt{k} \right)^{-1} \end{aligned} \quad (\text{IV})$$

where d_{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) (Worsnop *et al.*, 1989), 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 term $-1/2$ accounts for the distortion of the Boltzmann collision rate.

This relation clearly shows that the uptake coefficient is a function of different fundamental properties of the gas molecule such as its solubility, diffusion, etc. The treatment used to obtain equation (IV) is very similar to the one used for the calculation of deposition velocity on the ocean surface (Liss *et al.*, 1974).

The observed curvature in figure 3 characterises the existence of a surface saturation effect. This is confirmed by figure 4 which shows the inverse of uptake coefficient as a function of the gas/liquid contact time for dimethyl carbonate. It can be clearly seen that γ is time dependent, which means that saturation of the droplets' surface occurs in the temperature range studied here (265-279 K). The uptake coefficients were therefore determined by using the first straight data. The quoted errors for γ include then a large estimated error of 10 % and 2σ from the least-squares analysis.

On the other hand, uptake coefficients are independent of the aqueous phase composition. Indeed, we observed the same results when the uptake was studied over pure

water and a 0.1M NaOH solution. From this observation, we concluded that the uptake coefficient on liquid droplets are controlled by gas diffusion γ_{diff} , mass accommodation α and aqueous phase saturation, i.e. equation V can be simplified to:

$$\frac{1}{\gamma} = \frac{\langle c \rangle d_{\text{eff}}}{8D_g} - \frac{1}{2} + \frac{1}{\alpha} + \frac{\langle c \rangle \sqrt{\pi t}}{8HRT \sqrt{D_a}} \quad (\text{V})$$

Equation V may also be written as:

$$\frac{1}{\gamma} - \frac{1}{\gamma_{\text{diff}}} = \frac{1}{\alpha} + \frac{\langle c \rangle \sqrt{\pi t}}{8HRT \sqrt{D_a}} = \frac{1}{\gamma_{\text{corr}}} \quad (\text{VI})$$

The gas phase diffusion coefficients (D_g) are not known and therefore had to be estimated, as already mentioned, by the method presented by 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:

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

where $P_{\text{H}_2\text{O}}$ and P_{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 (see Table III for numerical values).

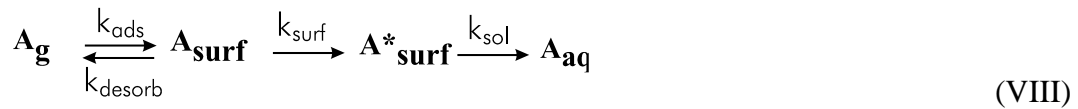
The raw data ($1/\gamma$) were corrected for gas phase diffusion according to equation VI recommended by Kolb *et al.* (1994). The Fuchs–Sutugin equation (Fuchs *et al.*, 1971) is certainly the most widely employed for the description of mass transport in the Knudsen transition regime ($0.1 < \text{Kn} < 1$), which is our case. However, its derivation is less simple and the observed deviation, compared to Kolb's equation, is less than 5% for our experimental conditions (even less than 3% for some experiments) (Kolb *et al.*, 1998). The error due to this approximation can be included in the given error of $2\sigma \pm 10\%$.

In this work, carbonate concentrations varied typically between 10 and 100 ppmv. Both carbonates show very similar results. For dimethyl carbonate and diethyl carbonate, the

uptake coefficients γ decrease respectively from 1.4×10^{-2} to 0.6×10^{-2} between 265 and 279 K and from 2.4×10^{-2} to 0.9×10^{-2} M atm⁻¹ between 270 and 279 K, for the different aqueous solutions (Figure 5). The raw uptake coefficients γ and the corrected ones γ_{corr} are listed in Table IV and Table V for both carbonates in function of the experimental conditions.

By plotting $1/\gamma$ versus $t^{1/2}$, the Henry's law constant H and the mass accommodation α can be respectively extracted from the slope and the intercept according to equation (V). Mass accommodation coefficients α have been determined for dimethyl carbonate and for diethyl carbonate. Their values decrease from 0.2 to 0.01 between 265 and 279 K for both carbonates for the different aqueous solutions as shown in Figure 6. As shown in Figure 4, the intercepts are very small (i.e., the mass accommodation coefficients are in fact very large) and therefore introduces large errors bars. It must also be underlined that the errors stated above are just statistical errors, which do not account for other error sources such as the uncertainties in the values of the gas phase diffusion coefficient. As we have seen above, the latter is estimated by the Reid *et al.* (1987) method (equation VII), which generally leads to an average error of 9% when compared to experimental values. However, in some occasions the error can reach 30%.

Interfacial transport is characterised by the mass accommodation coefficient α . To explain the negative temperature dependence of α , Nathanson *et al.* (1996) developed a model suggesting that the gas uptake proceeds via growth of critical clusters containing N^* molecules. The incoming gas molecule strikes the surface and becomes a loosely bound surface specie (A_{surf}) which participates in the nucleation process. If such a molecule becomes part of a critical sized cluster, it will invariably be incorporated into the bulk liquid via aggregation growth. This process can be represented as:



where g, surf and aq represent the gaseous, surface and liquid state of the studied specie. A^*_{surf} represents the specie within a critical cluster.

It is possible to express the mass accommodation α as follows:

$$\frac{\alpha}{1-\alpha} = \frac{k_{\text{sol}}}{k_{\text{desorb}}} = \frac{\exp\left(\frac{-\Delta G^*}{RT}\right)}{\exp\left(\frac{-\Delta G_{\text{vap}}}{RT}\right)} = \exp\left(\frac{-\Delta G_{\text{obs}}}{RT}\right) \quad (\text{IX})$$

where ΔG^* and ΔG_{vap} are the free energies of the vapour and the critical cluster compared to the free energy of surface state. The values for ΔH_{obs} and ΔS_{obs} can be obtained by plotting $\ln(\alpha/(1-\alpha))$ as a function of $1/T$. The slope of such a plot is $-\Delta H_{\text{obs}}/R$ and the intercept is $\Delta S_{\text{obs}}/R$. The obtained values on water are reported in Table VI.

Using the classical nucleation theory, it is possible to link the thermodynamic parameters ΔH_{obs} and ΔS_{obs} to the critical cluster size N^* , representing the minimum value for efficient incorporation (Nathanson *et al.*, 1996):

$$\Delta H_{\text{obs}} = -10 \times (N^* - 1) + 7,53 \times (N^{*2/3} - 1) - 0,1 \times 10 \quad (\text{kcal M}^{-1}) \quad (\text{X})$$

$$\Delta S_{\text{obs}} = -13 \times (N^* - 1) - 19 \times (N^* - 1) + 9,21 \times (N^{*2/3} - 1) - 0,1 \times 13 \quad (\text{cal M}^{-1} \text{ K}^{-1}) \quad (\text{XI})$$

The N^* values calculated for dimethyl and diethyl carbonate are respectively 4.4 and 5.6. The fact that those values are not integer might be due to the influence of the orientation of the molecule at the interface, related to the impact angle. Our results are in very good agreement with the theoretical N^* values and the experimental results given by Nathanson *et al.* (1996) or by our group as it is shown in figures 7a and 7b.

In this model, the facility of incorporation of a molecule in the condensed phase depends on its capacity to participate to the nucleation phenomenon. This capacity should be directly related to the specific structure of the molecule. It has been demonstrated that the critical cluster size will be smaller when the capacity to make hydrogen bonds is important as it is well known for alcohols or carboxylic acids. In contrast to these families, the N^* values for organic carbonates determined in this work are much larger in correlation with their low capacities to make hydrogen bonds. The chemical structures of dimethyl and diethyl carbonate are similar, at least for the functional group, and this is probably why very few differences are observed in the N^* values. According to the model, once a critical cluster is formed around the hydrophilic part (-OC(O)O-) of the carbonate, the cluster continues to grow irreversibly.

The deduced Henry's law constants are plotted as a function of temperature in Figure 8 for both carbonates. For dimethyl carbonate and diethyl carbonate, the measured H values

decrease respectively from 106 to 20 M atm⁻¹ between 265 and 279 K and from 98 to 30 M atm⁻¹ between 270 and 279 K, for the different aqueous solutions. It is important to underline again that any small errors (experimental errors or systematic errors due, for example, to incorrect estimates of the diffusion coefficients in both phases) will in turn modify the calculated Henry's law constant. Unfortunately, these Henry's law constants could not be calculated using a predictive method (Meylan *et al.*, 1991) because the authors do not take into account the carbonate structure.

Our experimental data can be expressed as a function of the temperature according to the expression:

$$\log H = A + \frac{B}{T} \quad (\text{XII})$$

The obtained fitted data in figure 8 are A= -8.0 ± 3.8, B= 2600 ± 1000 for dimethyl carbonate and A= -10.2 ± 2.9, B= 3280 ± 800 for diethyl carbonate.

The Henry's law constants for both carbonates can be extrapolated at 298 K from the above expression leading to: H₁ (298 K) = 5.3 ± 1.7 M atm⁻¹ (dimethyl carbonate) and H₂ (298 K) = 6.3 ± 1.5 M atm⁻¹ (diethyl carbonate). These values for carbonates (ROC(O)OR) are smaller than those of the corresponding ketones (RC(O)R): H (298 K) = 30 M atm⁻¹ (acetone) (Staudinger *et al.*, 1996) and H (298 K) = 20 M atm⁻¹ (3-pentanone) (Janini *et al.*, 1986). On the other hand, the Henry's law constants for carbonates are similar to those of the corresponding esters (RC(O)OR): H (298 K) = 8.7 M atm⁻¹ (methyl acetate) (Buttery *et al.*, 1969) and H (298 K) = 4.6 M atm⁻¹ (ethyl propionate) (Hine *et al.*, 1975).

Atmospheric implications

The atmospheric implications of this work can be obtained from the comparison of the lifetimes (τ) of these organic carbonates in the troposphere with respect to their gas-phase removal by OH radicals and removal by liquid water in clouds.

In the gas-phase, as mentioned previously, the photolysis (Calvert *et al.*, 1966) of these carbonates as well as their reactions with the NO₃ radical (Langer *et al.*, 1993) or ozone (Atkinson *et al.*, 1984) are slow processes. The rate coefficient data obtained in the present study can then be used to estimate the tropospheric lifetimes of dimethyl and diethyl carbonate with respect to reaction with OH radicals ($\tau_{\text{OH}} = 1/k_{\text{OH}}[\text{OH}]$). Assuming as usual an average OH concentration of 1×10⁶ molecule cm⁻³, tropospheric lifetimes of 33 days and 5 days in the gas-phase are calculated for dimethyl carbonate and diethyl carbonate respectively. The atmospheric oxidation of dimethyl carbonate initiated by OH radicals leads

mainly to the formation of $\text{CH}_3\text{OC}(\text{O})\text{OC}(\text{O})\text{H}$ as primary product and $\text{HC}(\text{O})\text{OC}(\text{O})\text{OC}(\text{O})\text{H}$ as secondary product (Bilde *et al.*, 1997).

Concerning the removal process by the aqueous phase, we need to know if the mass transfer limits the efficiency of this process. For this, the time-scale of the occurring processes, i.e. diffusion in the gas phase and mass accommodation process, have to be calculated.

The diffusion limitation is calculated from:

$$\frac{1}{\gamma_{\text{diff}}} = \frac{\langle c \rangle d_{\text{drop}}}{8 D_{\text{g}}} - \frac{1}{2} \quad (\text{XIII})$$

where d_{drop} is the diameter of droplets (1-50 μm) contained in tropospheric clouds (Kolb *et al.*, 1994) and D_{g} is the diffusion coefficient of carbonate in air, calculated from equation VII.

The corresponding gas diffusion time-scale τ_{diff} can be estimated from the values of γ_{diff} :

$$\tau_{\text{diff}} = \frac{1}{\frac{1}{4} \langle c \rangle A_{\text{c}} \gamma_{\text{diff}}} \quad (\text{XIV})$$

where A_{c} is the condensed phase surface to gas volume ratio (cm^2/cm^3), taken as 5.0×10^{-4} for the tropospheric clouds (Kolb *et al.*, 1994). Using this equation, the diffusion time-scale τ_{diff} of both carbonates at 298 K for $d_{\text{drop}} = 50 \mu\text{m}$ are : 53 s (dimethyl carbonate) and 65 s (diethyl carbonate).

Mass accommodation can also limit the rate of gas uptake. The accommodation time-scale τ_{accom} can be estimated from the mass accommodation coefficient α as:

$$\tau_{\text{accom}} = \frac{1}{\frac{1}{4} \langle c \rangle A_{\text{c}} \alpha} \quad (\text{XV})$$

The values of α decrease from 0.14 to 0.01 between 265 and 279 K for both carbonates. Taking a minimum value of α of 1×10^{-2} at 279 K, the calculated accommodation time scale is 31 s and 35 s for dimethyl and diethyl carbonate, respectively. In regard to the tropospheric lifetimes of both carbonates in gas phase, the gas diffusion and mass accommodation are really fast process. Therefore, the uptake of these compounds by atmospheric droplets will not be limited by gas diffusion or mass accommodation.

One can then assume that organic carbonates in the gas phase will quickly reach their thermodynamic equilibrium with organic carbonates in the liquid phase. Under these

conditions, the fraction $X_{A, \text{aq}}$ of a non reactive compound, A, dissolved in typical cloudwater droplets, is given by (Seinfeld *et al.*, 1998):

$$X_{A, \text{aq}} = \frac{H_A RT L_{\text{wc}}}{1 + H_A RT L_{\text{wc}}} \quad (\text{XVI})$$

In this equation, the following units should be used: H_A , the Henry Law coefficient in $\text{mol L}^{-1} \text{atm}^{-1}$; the ideal gas constant, $R = 0.08205 \text{ L mol}^{-1} \text{ K}^{-1}$; and the dimensionless liquid water content of the cloud, $L_{\text{wc}} = 4.2 \times 10^{-7}$. L_{wc} is related to the condensed phase surface to gas volume ratio (cm^2/cm^3), A_c , by the following equation (Kolb *et al.*, 1994):

$$A_c = \frac{6 L_{\text{wc}}}{d_{\text{drop}}} \quad (\text{XVII})$$

By using equation (XVII) and assuming that organic carbonates do not react in the aqueous phase, the fraction of dimethyl and diethyl carbonate in the atmospheric aqueous phase is about 5×10^{-5} and 6×10^{-5} , respectively at 298 K.

The small fractions of dissolved carbonates calculated above implies that wet deposition is not an efficient process for the removal of organic carbonates from the atmosphere. It is possible to estimate the removal rate of organic carbonates by assuming a first-order loss mechanism. In absence of reaction and assuming a fast equilibrium between gas and liquid atmospheric phase, the first-order removal constant by wet deposition, k_{wd} , is given by (Brimblecombe *et al.*, 1985):

$$k_{\text{wd}} = \frac{R_r E \exp(-z/Z_X)}{Z_X \left(\frac{1}{H_A RT} + L_{\text{wc}} \right)} \quad (\text{XVIII})$$

where R_r is the assumed annual rainfall rate (1 m/year), E is an enhancement factor due to droplet evaporation (assumed to be 1.33), z is a characteristic height for clouds (assumed to be 3.5 km), Z_X is the scale height for the species (assumed to be 2.2 km (Brimblecombe *et al.*, 1985)). The annual rainfall varies considerably from one environment to another, but the assumptions made here enable to estimate the time scale of this removal process. Based on

these assumptions, the wet deposition lifetime is about 55 years for both carbonates. This is not a realistic lifetime, however, it shows that this process is insignificant.

In the above calculation, it has been supposed that the organic carbonates did not react in the aqueous phase. In fact, they can be very slowly hydrolysed to form alcohols (methanol or ethanol in our case) and CO₂ (Crandall, 1987). The amount of organic carbonates able to be dissolved will be then slightly greater and the wet deposition lifetime will be a little smaller than the above value. But the wet deposition will remain negligible.

These carbonates can also react in the atmospheric aqueous phase with radicals such as OH, NO₃, SO₄⁻. In this case, atmospheric lifetime due to reactive heterogeneous loss is expressed as (Kolb *et al.*, 1994):

$$\tau = \frac{1}{L_{WC} f_C HRT k^{1/2}} \left(k^{1/2} + \tau_D^{1/2} \right) \quad (\text{XIX})$$

where the term f_C is the frequency of occurrence of the heterogeneous phase ($f_C = 0.15$ in the troposphere), k is the reaction rate of the dissolved gas in the condensed phase ($k = k_{OH} [OH] + k_{NO_3} [NO_3] + k_{SO_4^-} [SO_4^-]$) and τ_D is the time required for diffusive mixing within the condensed phase defined by:

$$\tau_D^{1/2} = \frac{d_{\text{drop}}}{6D_1^{1/2}} \quad (\text{XX})$$

where D_1 is the condensed phase diffusion coefficient.

Rate constants of carbonates reaction with those radicals were measured by Parraudin *et al.* (2001). At room temperature, the rate constants are (in units of $M^{-1} s^{-1}$): $k(\text{DMC}+\text{OH}) = (5.1 \pm 2.2) \times 10^7$, $k(\text{DMC}+\text{SO}_4^-) = 1.3 \times 10^5$, $k(\text{DMC}+\text{NO}_3) = 1.5 \times 10^4$, $k(\text{DEC}+\text{OH}) = (7.9 \pm 3.2) \times 10^8$, $k(\text{DEC}+\text{SO}_4^-) = 5.4 \times 10^6$, $k(\text{DEC}+\text{NO}_3) = 8.4 \times 10^4$. Assuming average concentrations of $[OH]_{\text{aq}} = 5 \times 10^{-13}$ M, $[SO_4^-]_{\text{aq}} = 5 \times 10^{-13}$ M and $[NO_3]_{\text{aq}} = 1 \times 10^{-12}$ M in atmospheric aqueous phase (Ervens *et al.*, 2001), tropospheric lifetimes are 175 and 8.9 years respectively for dimethyl and diethyl carbonates. We can then conclude aqueous phase reactions are negligible for both carbonates.

Therefore, this work shows that gas phase reaction is the major atmospheric loss process for dimethyl and diethyl carbonates and that these compounds will not be found, or will exist in very small amount, in wet precipitations.

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Figure Captions

Figure 1: Plots of $(k'_i - k'_0)$ vs. carbonate concentration at 298 K. The lines represent the linear least-squares fit.

Figure 2: Plots of k_1 and k_2 vs. $1/T$ for the reaction of OH radicals with dimethyl and diethyl carbonate. The solid lines represent the Arrhenius parameter least-squares fits to the individual data points for each organic carbonate and the dashed line corresponds to the plot of $k_1 = 5.9 \times 10^{-12} \exp(-1070/T) + 1.3 \times 10^{-14} \exp(795/T)$. The error bars of the individual points are 2σ and do not include estimated systematic errors.

Figure 3: Typical plots of $\ln(n/n-\Delta n)$ versus $\langle c \rangle \Delta S / 4Fg$ for dimethyl carbonate (at 277.2K) on pure water. According to equation (IV), the slopes of such plots are a measure of the uptake coefficient γ which were determined with the first straight data. The quoted errors for γ include then a large estimated error of 10 % and 2σ from the least-squares analysis.

Figure 4: Plot of the inverse of uptake coefficients $1/\gamma$ as a function of the gas / liquid contact time for dimethyl carbonate (at 277.2K) on pure water showing that γ was a function of time within our experimental conditions. According to the equation (V), the Henry's law constants were derived from the slope. The intercept is the inverse of the mass accommodation coefficient. The error bars are given at the 2σ level.

Figure 5: Plot of the uptake coefficients γ as a function of temperature on water and 0.1 M NaOH solution for dimethyl carbonate (figure 5a) and diethyl carbonate (figure 5b). The error bars are given at the 2σ level.

Figure 6: Plot of the Henry's law constant H ($M \text{ atm}^{-1}$) versus the temperature for dimethyl carbonate (figure 6a) and diethyl carbonate (figure 6b). The error bars are given at the 2σ level.

Figure 7: Plot of ΔH versus ΔS . The error bars are given at the 1σ level.

Figure 8: Plot of the mass accommodation α versus the temperature for dimethyl carbonate (figure 8a) and diethyl carbonate (figure 8b). The error bars are given at the 2σ level.