

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231637501>

Uptake Measurements of Dibasic Esters by Water Droplets and Determination of Their Henry's Law Constants

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY A · DECEMBER 2003

Impact Factor: 2.69 · DOI: 10.1021/jp0368132

CITATIONS

10

READS

24

3 AUTHORS, INCLUDING:



Stéphane Le Calvé

French National Centre for Scientific Research

90 PUBLICATIONS 994 CITATIONS

SEE PROFILE

Uptake Measurements of Dibasic Esters by Water Droplets and Determination of Their Henry's Law Constants

Yasmine Katrib, Stéphane Le Calvé,* and Philippe Mirabel

Centre de Géochimie de la Surface/CNRS and Université Louis Pasteur, 1 rue Blessig, F-67084 Strasbourg Cedex, France

Received: September 19, 2003

The uptake of dimethyl malonate and dimethyl succinate on aqueous surfaces was measured between 266 and 279 K, using the droplet train technique coupled with mass spectrometric detection. The uptake coefficients γ were found to be independent of the aqueous phase composition and of the gas–liquid contact times. In addition, the uptake coefficients and the derived mass accommodation coefficients α show a negative temperature dependence in the temperature ranges studied. The mass accommodations decrease from 7.8×10^{-2} to 5.0×10^{-2} and from 4.5×10^{-2} to 2.3×10^{-2} for dimethyl malonate and succinate, respectively. These results are used to discuss the incorporation of oxygenated volatile organic compounds (VOCs) into the liquid using the nucleation theory. Henry's law constants of both compounds were directly measured between 283 and 298 K using a dynamic equilibrium system. Their values exponentially decrease when temperature increases, from $(2.60 \pm 0.30) \times 10^4$ to $(0.40 \pm 0.05) \times 10^4$ and from $(1.20 \pm 0.10) \times 10^4$ to $(0.30 \pm 0.03) \times 10^4$ for dimethyl malonate and succinate, respectively (in units of M atm^{-1}). The partitioning of both dibasic esters between gas and aqueous phases and the corresponding atmospheric lifetimes have then been derived.

Introduction

Dibasic esters are oxygenated organic compounds of the diester type with the general formula $\text{CH}_3\text{OC}(\text{O})(\text{CH}_2)_n\text{C}(\text{O})\text{OCH}_3$ where n is an integer. Dibasic esters are usually a mixture of methyl esters of short chain aliphatic acids and are used to replace established solvents with high volatility such as acetone or methylene chloride. They are already used as rubber and resin cleaning agents and as solvents for inks, plasticizers, hand cleaners, textile lubricants, paint strippers, and so forth. Dibasic esters are recyclable by vacuum distillation and evaporate slowly. Their use may reduce the evaporative emissions of volatile organic compounds (VOCs) in the atmosphere.

Although exhibiting low toxicity, dibasic esters 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 VOCs can undergo photochemical transformations initiated by OH radicals or can be taken up by cloud droplets. This last process may represent a very efficient loss process if the dibasic esters have high Henry's law coefficients ($\geq 10^3 \text{ M atm}^{-1}$). By analogy with the case of acetates, reactions with the NO_3 radical¹ or with ozone² as well as photolysis³ can be considered as slow loss processes for the dibasic esters. These compounds should not be adsorbed on atmospheric particles due to their relatively high vapor pressure estimated between 0.5 and 1 Torr at 298 K.

The kinetics of OH reaction with dimethyl succinate ($n = 2$) and two other dibasic esters have previously been investigated.^{4,5} Cavalli et al. also identified and quantified the products generated by the atmospheric oxidation of dimethyl succinate in the presence of NO_x .⁵ They identified succinic formic anhydride, monomethyl succinate, carbon monoxide, dimethyl

oxaloacetate, and methoxy formylperoxynitrate. The yields of these products were (0.34 ± 0.07) , (0.45 ± 0.11) , (0.31 ± 0.06) , (0.18 ± 0.04) , and (0.03 ± 0.01) , respectively.

Dibasic esters and their oxidation products are potentially very soluble in cloud droplets where they can react with several radicals such as OH, NO_3 , or SO_4^- .⁶ Uptake coefficients and Henry's law coefficients are needed in order to estimate the efficiency of their uptake by water droplets in order to more completely assess their impact on air quality.

In this work, we report uptake coefficients of dimethyl malonate and dimethyl succinate by water droplets over the temperatures range 266–279 K. We also directly determined their Henry law constants for temperatures ranging from 283 to 298 K. To our knowledge, all these measurements are the first to be reported for these compounds.

Experimental Section

Uptake Measurements. The uptake rate of a trace gas by a liquid is a multistep process that can be related to fundamental properties of the gas, of the interface, or of the condensed phase such as the mass accommodation coefficient α , the solubility, or the 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 Φ_{net} of a trace gas into a surface is expressed in terms of a measured uptake coefficient γ 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, γ 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.

* To whom correspondence should be addressed. E-mail: slecalve@illite.u-strasbg.fr.

To measure uptake rates, we used the droplet train technique which has already been described elsewhere,^{7,8} and therefore, we will only provide a brief summary of its principles of operation. The uptake coefficient is determined by measuring the decrease of the gas-phase concentration of the trace species, due to its exposure to a monodisperse train of droplets. These latter are generated by a vibrating orifice (70 μm diameter), leading to droplet diameters of about 140 μm . The apparatus, where the contact between both phases takes place, is a vertically aligned flow tube. The interaction time between the gas and the droplets can be changed from 0 to 20 ms either by moving the inner injector (up to 20 cm) or by changing the surface exposed by the droplet train (0–0.2 cm^2). In this latter case, the change in surface of the droplet is achieved by changing the frequency of the vibrating orifice. 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 flow tube. By considering the kinetic gas theory, the overall uptake coefficient γ_{meas} can then be obtained by measuring the fractional change of the dibasic ester concentration in the gas phase as a function of the total droplet surface area, at a given temperature:⁹

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

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

The uptake coefficient γ_{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, which was in the range 15–25 Torr. 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 flow tube, since it controls the surface temperature of the droplets through evaporative cooling.⁹ Therefore, the carrier gas (helium) is always saturated with water vapor, at a given temperature, before entering the flow tube.

The gas stream coming out of the flow tube was analyzed using a differentially pumped mass quadrupole spectrometer Pfeiffer Vacuum QMS with an ionization energy of 60 eV. The signal was averaged over 1 s in order to increase the signal-to-noise ratio. Dimethyl malonate and succinate were respectively monitored at 101 amu ($\text{CH}_3\text{OC}(\text{O})\text{CH}_2\text{C}(\text{O})^+$) and 115 amu ($\text{CH}_3\text{OC}(\text{O})\text{C}_2\text{H}_4\text{C}(\text{O})^+$). In addition, H_2O and an inert tracer SF_6 were respectively monitored at 18 (H_2O^+) amu and 89 (SF_3^+) amu during the course of the experiments in order to detect any potential perturbations in gas-phase concentrations.

Henry's Law Constants. Henry's law constants for dimethyl malonate and dimethyl succinate were measured using a dynamic equilibrium system shown in Figure 1, which is similar to those used in recent studies.^{10–12}

Clean dry air (Alphagas, $\geq 99.99\%$) was passed through a microporous PTFE membrane tube (160 cm length \times 0.8 cm i.d., Sumitomo Corporation) at a highly controlled mass flow rate (0.2–0.4 L/min). The tube was immersed in about 0.6 L of a diluted aqueous solution containing approximately 1×10^{-3} M of the dibasic esters so that 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 which contains the diesters at equilibrium concentration was then diluted using additional dry clean air (0.5–1 L/min). The compound present in the gas phase was trapped using two cartridges connected in series and filled with an XAD2 resin

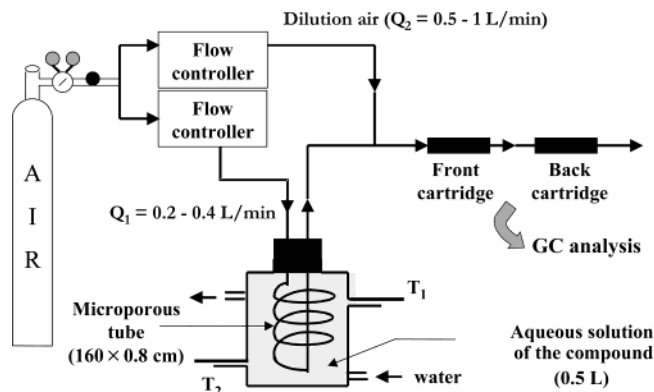


Figure 1. Scheme of the dynamic equilibrium system used to determine directly Henry's law constants as a function of the temperature (see text). The temperature is measured with two thermocouples T_1 and T_2 .

(Supelco) which was purified before use. At least 98% of dibasic ester was trapped in the first cartridge. For each experiment, up to 48 h was necessary to accumulate enough dibasic ester in the cartridges.

After sampling, the compound was extracted by passing 20 mL of methanol through the trap. Pure air was used to push methanol through the cartridge, ensuring that no methanol stayed inside. 1 μL of the solution obtained was then injected into a gas chromatograph (ThermoFinnigan 2000) equipped with a flame ionization detector (FID), a split–splitless injector in order to increase the sensitivity, and a 30 m long and 0.25 mm i.d. capillary column (PermaBond CW 20M). The column was kept at 40 $^\circ\text{C}$ for 2 min and was then brought to a final temperature of 140 $^\circ\text{C}$ at a rate of 20 $^\circ\text{C}/\text{min}$. Helium (UHP certified to $>99.9995\%$ from Alphagas) was used as carrier gas (1 mL/min) while air (Alphagas, $\geq 99.99\%$, 350 mL/min) and H_2 generated from a UHP hydrogen generator (Nitrox, UHP-60H) at a rate of 35 mL/min were used for the FID. The injector and detector were respectively maintained at 250 and 300 $^\circ\text{C}$ for all the analyses.

The gas-phase concentrations of dibasic esters were quantitatively determined from calibration curves. Known concentrations of dibasic ester were prepared in methanol, and 1 μL of this standard solution was then injected into the GC in order to plot a curve of concentration versus GC peak area. The calibration curves were linear in the concentration range used in this study, and the correlation coefficients were greater than 0.90.

Each aqueous solution was made from Milli-Q water (18 M Ω cm). Dimethyl malonate (98%) and dimethyl succinate (98%) were purchased from Aldrich and Fluka, respectively, and were used without further purification.

Results and Discussion

Representative plots of $\ln(n/(n - \Delta n))$ as a function of $\langle c \rangle \Delta S / 4F_g$ are shown in Figure 2 for the uptake of dimethyl malonate and succinate on pure water at 274 and 275 K, respectively. From eq 2, one can see that the slope of each curve gives the uptake coefficient γ_{meas} of the compound at the studied temperature. The same procedure was applied for the temperature ranges 266–278 K and 268–279 K for dimethyl malonate and succinate, respectively. The corresponding results are shown in Tables 1 and 2.

The uptake rate of a trace gas by a liquid is known to be a function of several processes which include gas-phase diffusion, mass accommodation, solubility, and reactivity in the liquid

TABLE 1: Uptake Coefficients and Mass Accommodation Coefficients of Dimethyl Malonate – Summary of Experimental Conditions

T (K)	$10^2 \times \gamma_{\text{meas}}$	$10^2 \times \gamma_{\text{diff}}$	$10^2 \times \alpha$
266.2	5.3 ± 0.6	22.0	6.9 ± 1.1
267.9	4.9 ± 0.6	21.2	6.4 ± 1.0
268.2	5.7 ± 0.6	21.4	7.8 ± 1.1
268.6 ¹	5.0 ± 0.9	21.0	6.6 ± 1.6
270.5	5.6 ± 0.3	20.6	7.7 ± 0.5
270.6 ¹	4.0 ± 0.5	20.5	5.3 ± 0.6
271.6	4.7 ± 1.0	20.2	6.1 ± 1.7
272.8	5.6 ± 0.9	21.6	7.5 ± 1.6
273.0	4.2 ± 0.6	19.9	4.9 ± 0.8
274.1 ¹	4.9 ± 0.5	19.5	6.6 ± 0.9
274.3	4.8 ± 0.2	19.1	6.4 ± 0.3
275.7	4.3 ± 0.3	18.8	5.5 ± 0.6
277.3	4.2 ± 0.3	18.2	5.5 ± 0.5
278.3	4.3 ± 0.3	17.7	5.7 ± 0.2

¹ Experiments carried out using 0.1 M NaOH solution.**TABLE 2: Uptake Coefficients and Mass Accommodation Coefficients of Dimethyl Succinate – Summary of Experimental Conditions.**

T (K)	$10^2 \times \gamma_{\text{meas}}$	$10^2 \times \gamma_{\text{diff}}$	$10^2 \times \alpha$
267.9	3.3 ± 0.7	22.4	3.9 ± 1.0
268.4 ¹	3.8 ± 0.8	23.3	4.5 ± 1.1
269.3	3.1 ± 0.5	23.7	3.5 ± 1.1
270.2 ¹	2.5 ± 0.9	22.7	2.8 ± 1.1
271.3	3.4 ± 0.3	22.3	4.0 ± 0.4
273.3	3.0 ± 1.2	22.5	3.4 ± 1.6
273.5	2.9 ± 0.5	20.1	3.4 ± 0.7
273.9	2.1 ± 0.4	21.3	2.3 ± 0.5
275.0	3.1 ± 0.2	20.3	3.7 ± 0.3
275.9 ¹	2.8 ± 0.1	19.8	3.2 ± 0.2
278.3	2.3 ± 0.5	18.8	2.7 ± 0.6
278.7	2.8 ± 0.2	18.5	3.3 ± 0.3
279.4	2.6 ± 0.5	17.6	3.0 ± 0.6

¹ Experiments carried out using 0.1 M NaOH solution.

phase. Each of these processes may introduce a resistance (γ_{diff} , α , γ_{sat} , and γ_{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 to¹³

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

In this equation, 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),⁹ H is the Henry's law constant, R is the perfect gas constant, T is the droplets' temperature, D_g and D_a are the gas and aqueous phase diffusion coefficients, respectively, t is the gas/liquid contact time, and k is the first-order rate constant for a given reaction in the liquid phase.

The hydrolysis reaction of dibasic esters might be catalyzed by OH anions. However, one can note from our results that the presence of NaOH has no influence on the observed uptake rates (see Tables 1 and 2). Indeed, hydrolysis is a very slow process characterized by a lifetime greater than several days while the gas/liquid interaction time in our experiments is very short. With the uptake coefficients being independent of the aqueous phase composition, it is therefore possible to neglect the resistance related to an eventual aqueous phase reaction. In the same way, the uptake coefficients are independent of the vapor/liquid

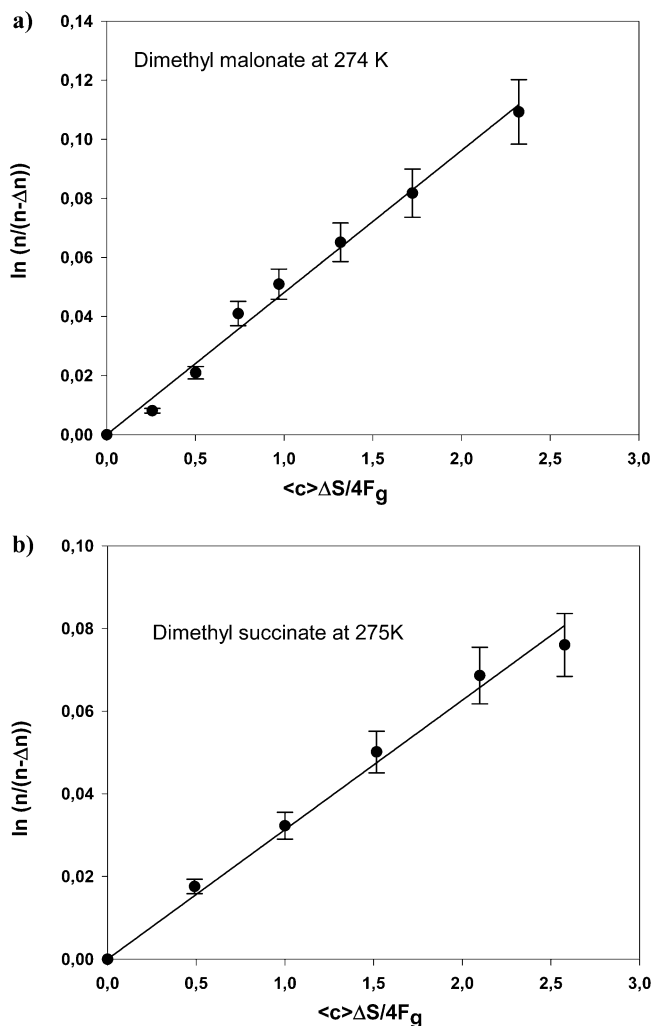


Figure 2. Typical plots of $\ln(n/(n - \Delta n))$ versus $\langle c \rangle \Delta S / 4F_g$ for (a) dimethyl malonate and (b) dimethyl succinate on pure water at 274 and 275 K, respectively. According to eq 2, the slope is the uptake coefficient γ . The error bars are given at the $2\sigma \pm 5\%$ level.

contact time, which means that the resistance related to aqueous phase saturation can also be neglected. With these observations, it is possible to conclude that, under our experimental conditions, the uptake rate of dimethyl malonate and succinate on water droplets is controlled solely by gas diffusion (γ_{diff}) and mass accommodation (α). Therefore, the uptake coefficient may be described according to

$$\frac{1}{\gamma_{\text{meas}}} = \frac{1}{\gamma_{\text{diff}}} + \frac{1}{\alpha} = \frac{\langle c \rangle d_{\text{eff}}}{8D_g} - \frac{1}{2} + \frac{1}{\alpha} \quad (4)$$

where the term $-1/2$ accounts for the distortion of the Boltzmann collision rate.⁹ The gas-phase diffusion coefficients (D_g) needed have been estimated by the method of Reid et al.¹⁴

Equation 4 may also be rewritten as follows:

$$\frac{1}{\gamma_{\text{meas}}} - \frac{1}{\gamma_{\text{diff}}} = \frac{1}{\alpha} \quad (5)$$

in which the raw data ($1/\gamma_{\text{meas}}$) are corrected for gas-phase diffusion. Therefore, eq 5 allows the direct determination of the mass accommodation coefficient α . Note that, under our experimental conditions, the correction to $1/\gamma_{\text{meas}}$ due to gas diffusion is less than 10%.

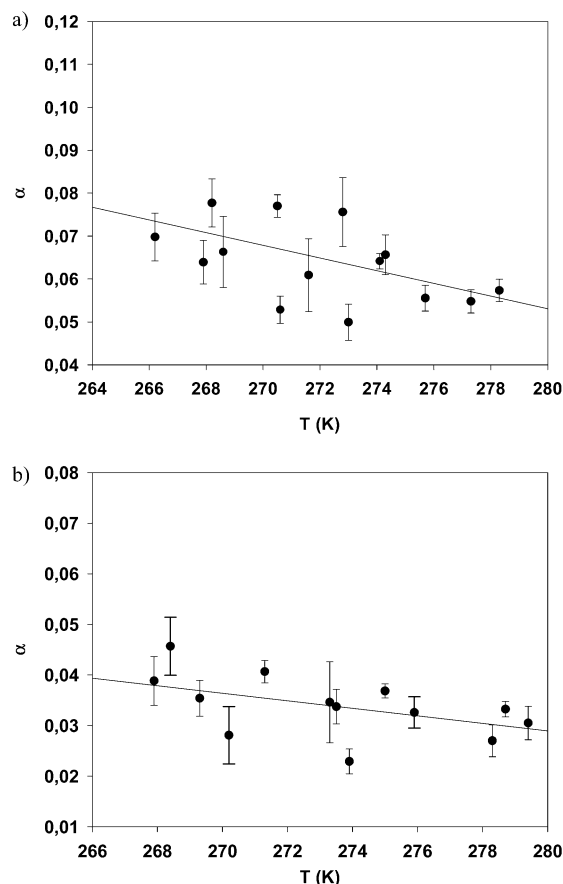


Figure 3. Plot of the mass accommodation α of (a) dimethyl malonate and (b) dimethyl succinate versus temperature. The error bars are given at the $2\sigma \pm 5\%$ level.

Tables 1 and 2 summarize the values of γ_{meas} , γ_{diff} , and α as a function of temperature. The quoted errors for γ_{meas} and α were derived from the least-squares analysis and the estimated systematic error of 5%. As expected, the mass accommodation values, α , obtained decrease from 0.077 to 0.050 for dimethyl malonate when the temperature increases from 266 to 278 K and from 0.045 to 0.023 for dimethyl succinate when the temperature increases from 268 to 279 K (Figure 3). This negative temperature dependence of α is a general feature for the mass accommodation process of soluble nonreacting gases.^{15–19}

To explain the negative temperature dependence of α characterizing the interfacial transport, Davidovits et al.^{15,16} developed a model suggesting that the gas uptake proceeds via the growth of critical clusters containing N^* molecules. They proposed the following equation:

$$\frac{\alpha}{1 - \alpha} = \exp\left(\frac{-\Delta G_{\text{meas}}^*}{RT}\right) \quad (6)$$

where the parameter ΔG_{meas}^* is the Gibbs free energy barrier between the vapor phase and the critical cluster. The values for ΔH_{meas} and ΔS_{meas} can be obtained by plotting $\ln(\alpha/(1 - \alpha))$ versus $1/T$; the slope of such a plot is $-\Delta H_{\text{meas}}/R$, and the intercept provides $\Delta S_{\text{meas}}/R$ (Figure 4). The obtained values for dimethyl malonate are $\Delta H_{\text{meas}} = (-3.1 \pm 3.0)$ kcal mol⁻¹ and $\Delta S_{\text{meas}} = (-16.8 \pm 11.2)$ cal mol⁻¹ K⁻¹, and those for dimethyl succinate are $\Delta H_{\text{meas}} = (-3.4 \pm 2.9)$ kcal mol⁻¹ and $\Delta S_{\text{meas}} = (-19.0 \pm 10.5)$ cal mol⁻¹ K⁻¹.

Using the classical nucleation theory, it is possible to link the thermodynamic parameters ΔH_{meas} and ΔS_{meas} to the critical

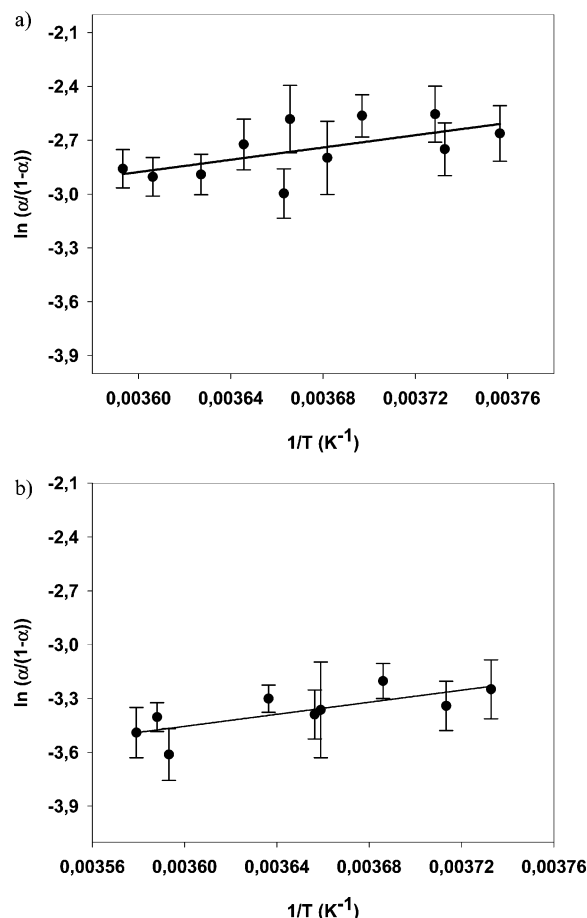


Figure 4. Plot of $\ln(\alpha/(1 - \alpha))$ versus $1/T$ (a) for dimethyl malonate and (b) for dimethyl succinate. The slope of such a plot is $-\Delta H_{\text{meas}}/R$, and the intercept is $\Delta S_{\text{meas}}/R$. The error bars are given at the $2\sigma \pm 5\%$ level.

cluster size N^* , representing the minimum value of N leading to efficient incorporation in the liquid:^{15,16}

$$\Delta H_{\text{meas}} = -10(N^* - 1) + 7.53(N^{*2/3} - 1) - 0.1 \times 10 \text{ (kcal M}^{-1}) \quad (7)$$

$$\Delta S_{\text{meas}} = -13(N^* - 1) - 19(N^* - 1) + 9.21(N^{*2/3} - 1) - 0.1 \times 13 \text{ (cal M}^{-1} \text{ K}^{-1}) \quad (8)$$

Using these two equations, the calculated N^* values are 1.6 and 1.7 for dimethyl malonate and succinate, respectively. Note that these noninteger values represent an average number of molecules in a critical cluster or aggregates in the interfacial region. Since the chemical structures of dimethyl malonate and succinate are very similar, only small differences are observed for the N^* values.

Our results (ΔH_{meas} , ΔS_{meas} , N^*) are in very good agreement with the theoretical values calculated using eqs 7 and 8 and the experimental results given, for example, by Kolb et al.²⁰ or by our group,^{18,19} as is shown in Figure 5.

We have shown, using the droplet train technique, that these compounds do not saturate the water droplets, which means that their solubility in water is quite large. However, in the absence of saturation, the droplet train technique does not allow the determination of Henry's law constants. To estimate the partitioning of dimethyl malonate and succinate between air and water droplets in the atmosphere, we have therefore used a

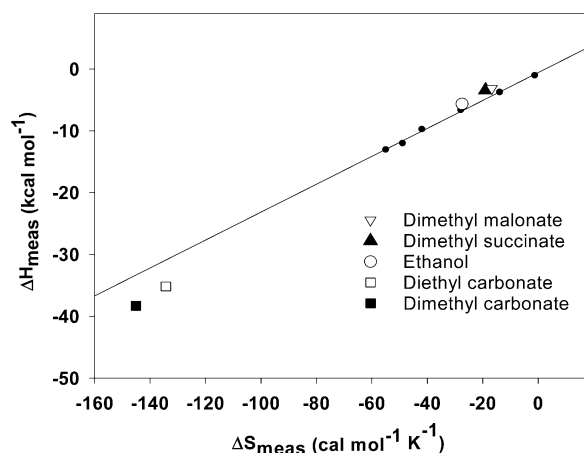


Figure 5. Plot of ΔH_{meas} versus ΔS_{meas} . The data represented by black circles correspond to the values of ΔH_{meas} and ΔS_{meas} calculated with N^* values by applying eqs 7 and 8. Our experimental results are represented as well.

TABLE 3: Henry's Law Constants as a Function of the Temperature for Dimethyl Malonate Determined Using the Dynamic Equilibrium System (see Figure 6)

T (K)	$10^{-4} \times H$ (M atm $^{-1}$)
283.1	2.6 ± 0.3
285.1	2.1 ± 0.23
286.0	1.7 ± 0.18
287.1	1.9 ± 0.2
288.1	1.7 ± 0.3
289.1	1.2 ± 0.2
290.1	0.8 ± 0.09
291.1	0.7 ± 0.08
292.6	0.9 ± 0.1
293.1	0.9 ± 0.1
295.1	0.5 ± 0.06
298.1	0.4 ± 0.05

TABLE 4: Henry's Law Constants as a Function of the Temperature for Dimethyl Succinate Determined Using the Dynamic Equilibrium System (see Figure 6)

T (K)	$10^{-4} \times H$ (M atm $^{-1}$)
283.15	1.2 ± 0.1
284.15	1.1 ± 0.1
286.05	1.2 ± 0.1
287.15	0.9 ± 0.09
288.15	1.0 ± 0.1
289.15	0.8 ± 0.8
290.15	0.6 ± 0.05
292.15	0.5 ± 0.05
292.65	0.5 ± 0.05
295.15	0.4 ± 0.03
298.15	0.3 ± 0.03

technique that was developed by Dasgupta and Dong²¹ which allows direct determination of Henry's law constants.

The Henry's law constants H (M atm $^{-1}$) were determined according to the following equation:

$$H = \frac{[X]}{P_X} \quad (9)$$

where $[X]$ is the aqueous concentration of the studied compounds (M) and P_X is its partial pressure (atm).

The Henry's law constants which were determined for dimethyl malonate and succinate in the temperature range 283–298 K are given in Tables 3 and 4 with quoted errors obtained by addition of 2σ statistical errors and 5% systematic uncertainties. These later account mainly for the uncertainties associated with the volume of methanol used for the extractions.

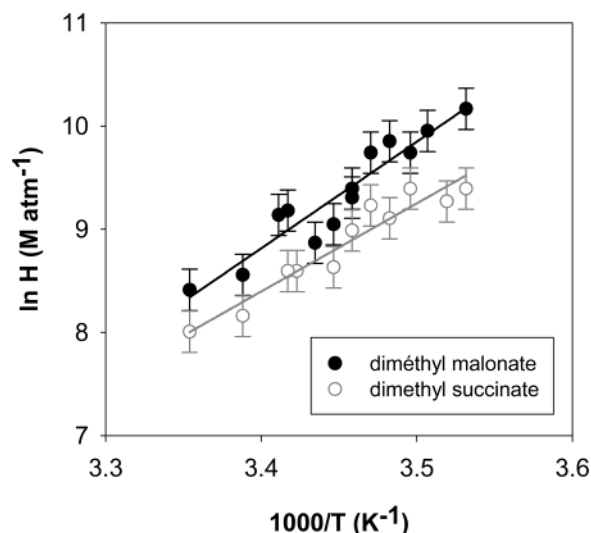


Figure 6. Plot of $\ln H$ (M atm $^{-1}$) versus the inverse of the temperature for dimethyl malonate and dimethyl succinate in the temperature range 283–298 K. The error bars are given at the $2\sigma \pm 5\%$ level.

As expected, the values of H obtained for dimethyl malonate and succinate are of the same order of magnitude, that is, $(4.0 \pm 0.5) \times 10^3$ for dimethyl malonate and $(3.0 \pm 0.3) \times 10^3$ for dimethyl succinate at 298 K. For the same temperature, the Henry's law constants of these two dibasic esters are surprisingly much higher than those corresponding to the acetate or propionate having only one ester function: $H = 8.7$ or 7.8 for methyl acetate^{22,23} and $H = 5.8$ M atm $^{-1}$ for methyl propionate²² at 298 K.

The high values of H explain why no saturation effects were observed while studying the incorporation kinetics of these dibasic esters into the water droplets using the droplet train technique. Equilibrium is not reached under the conditions used in our droplets train experiments, since the saturation term is smaller than 0.06 and then effectively negligible compared to the diffusion and accommodation terms, which are greater than 3 (see eq 3).

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

$$H = H^\circ \exp\left(\frac{\Delta H_{\text{solv}}}{R} \left(\frac{1}{T} - \frac{1}{T^\circ}\right)\right) \quad (10)$$

where ΔH_{solv} is the solvation enthalpy (J mol $^{-1}$) and H° refers to the standard conditions ($T^\circ = 298.15$ K).

We have therefore determined experimentally the values of ΔH_{solv} for dimethyl malonate and succinate by representing $\ln H$ as a function of $1/T$ (see Figure 6), with the slope being ΔH_{solv} . The values of ΔH_{solv} are represented in Figure 7 as a function of ΔH_{meas} and were derived from uptake studies (see nucleation theory above),^{18,19,24} for a series of compounds including the two studied dibasic esters.

It is very interesting to notice that an apparent negative linear relationship exists between these two enthalpies. This does not mean that they are directly related but that they might be governed by the same physical chemistry properties. The nucleation model^{15,16} we used to try to understand the phenomenon that takes place at the gas/liquid interface during the incorporation process shows that 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

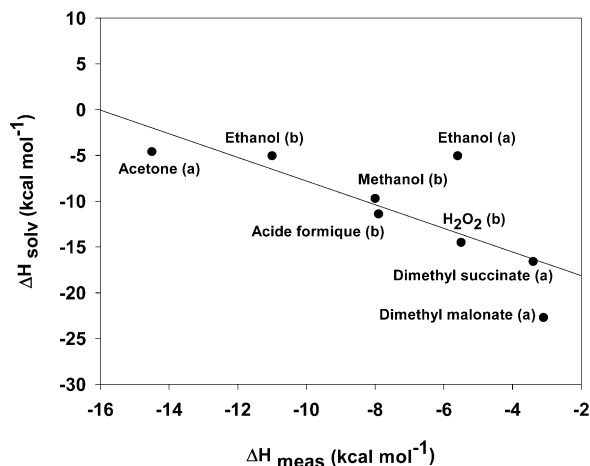


Figure 7. Plot of ΔH_{solv} as a function of ΔH_{meas} for different oxygenated compounds: (a) our results and (b) those of Nathanson et al.²⁴

molecule. It has been demonstrated that the critical cluster size will be smaller with increasing capacity to form hydrogen bonds. The ΔH_{solv} values should be related to the same properties, which is not surprising.

Atmospheric Implications

The atmospheric implications of this work can be inferred from a comparison of the average lifetimes τ of dimethyl malonate and dimethyl succinate in the troposphere with respect to gas-phase removal by OH or other radicals, by photolysis, or removal by liquid water contained in clouds. The estimated vapor pressure of dimethyl malonate and dimethyl succinate is around 0.5–1 Torr; it is, therefore, suspected that these compounds are present in the gas phase in the atmosphere.

In the gas phase, the photolysis³ of esters and also their reactions with the NO₃ radical¹ or ozone² are known to be slow processes. The estimated tropospheric lifetimes τ_{OH} of dimethyl malonate and succinate with respect to reactions with OH radicals can be calculated using the following equation:

$$\tau_{\text{OH}} = \left(\frac{1}{k_{\text{OH}}[\text{OH}]} \right) \quad (11)$$

where k_{OH} is the rate coefficient of gas oxidation by OH radicals and [OH] is the radical concentration in the troposphere.

At 298 K, the rate coefficient of OH reaction toward dimethyl malonate can be estimated to be 9.5×10^{-13} from the SAR method²⁵ while that corresponding to the reaction with dimethyl succinate can be estimated as 1.65×10^{-12} , which is the average of two existing values in the literature^{4,5} (in units of cm³ molecule⁻¹ s⁻¹). Assuming an average OH concentration of 10^6 molecule cm⁻³, tropospheric lifetimes of 12 and 7 days in the gas phase are estimated for dimethyl malonate and succinate, respectively.

In tropospheric clouds the mass accommodation coefficient is a rate determining parameter for gas/droplet mass transport if α is less than 10^{-2} .¹³ For larger values of α , which is the case here, the rate of uptake can be limited by gas-phase diffusion or by constraints imposed by Henry's law solubility, possibly modified by aqueous chemistry.

Gas-phase diffusion (γ_{diff}) can limit the rate of gas uptake, and this limitation is calculated as

$$\frac{1}{\gamma_{\text{diff}}} = \frac{\langle c \rangle d_{\text{drop}}}{8D_g} - \frac{1}{2} \quad (12)$$

where d_{drop} is the diameter of droplets (1–50 μm) contained in tropospheric clouds¹³ and D_g is the diffusion coefficient of dimethyl malonate and succinate in air.

The corresponding gas diffusion time scale τ_{diff} can be estimated from the values of γ_{diff} , calculated as

$$\tau_{\text{diff}} = \frac{1}{^{1/4}\langle c \rangle A_c \gamma_{\text{diff}}} \quad (13)$$

where A_c is the condensed phase surface to gas volume ratio (cm²/cm³). Using this equation, the calculated tropospheric lifetimes for $d_{\text{drop}} = 50 \mu\text{m}$ and $A_c = 5 \times 10^{-4}$ at 298 K are 67 and 72 s for dimethyl malonate and succinate, respectively.

Mass accommodation (α) can also limit the rate of gas uptake. The corresponding accommodation time scale τ_{accom} can be estimated as

$$\tau_{\text{accom}} = \frac{1}{^{1/4}\langle c \rangle A_c \alpha} \quad (14)$$

Taking the minimum values of α for each compound, the calculated accommodation time scale is 10 and 14 s for dimethyl malonate and succinate, respectively. In regard to these lifetimes, gas diffusion and mass accommodation appear to be really fast processes. Therefore, the uptake of these compounds by atmospheric droplets will not be limited by mass accommodation or gas diffusion.

At the thermodynamic equilibrium, the fraction of a nonre-active compound dissolved in typical cloud water droplets, X_{aq} , is given by²⁶

$$X_{\text{aq}} = \frac{HRTL_{\text{wc}}}{1 + HRTL_{\text{wc}}} \quad (15)$$

where R is the ideal gas constant, which is equal to 0.082 05 L atm mol⁻¹ K⁻¹, and L_{wc} is the dimensionless liquid water content of the cloud (4.2×10^{-7}). L_{wc} is related to the condensed phase surface to gas volume ratio (cm²/cm³) A_c by the following equation:¹³

$$A_c = \frac{6L_{\text{wc}}}{d} \quad (16)$$

By using this last equation and assuming that dibasic esters do not react in the aqueous phase, the fractions of dimethyl malonate and succinate in the atmospheric aqueous phase are approximately 4×10^{-2} and 3×10^{-2} , respectively, at 298 K. At 283 K, which corresponds to the average temperature in tropospheric clouds, these fractions increase to 0.20 and 0.11.

The quite large fractions of dissolved dimethyl malonate and succinate calculated above imply that wet deposition can be an efficient process for the removal of these dibasic esters from the atmosphere. It is possible to estimate the removal rate by assuming a first-order loss mechanism. In the absence of reaction in the aqueous phase and assuming a fast equilibrium between gas and liquid, the first-order removal constant by wet deposition, k_{wd} , is given by²⁷

$$k_{\text{wd}} = \frac{R_s E \exp(-z/Z_X)}{Z_X \left\{ \left(\frac{1}{HRT} \right) + L_{\text{wc}} \right\}} \quad (17)$$

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), and Z_X is the scale height for the species (assumed to be 2.2 km^{25}). The annual rainfall varies considerably from one environment to another, but the assumptions made here enable us to estimate an average time scale for this removal process at 283 K. On the basis of these assumptions, the wet deposition lifetime is about 6 and 11 days for dimethyl malonate and succinate, respectively. Moreover, the loss of dibasic esters by the heterogeneous process may be accelerated by reactions in the aqueous phase.

Comparing the lifetimes of dimethyl malonate and succinate in the troposphere with respect to gas-phase removal by OH radicals and removal by liquid water contained in the atmospheric clouds shows that there is a real competition between these two loss processes.

Acknowledgment. Financial support for this work by the French Ministry of Research through the PNCA program and by the Region Alsace is gratefully acknowledged. This is EDST contribution No. 2003.103-UMR7517.

References and Notes

- (1) Langer, S.; Ljungstrom, E.; Wangberg, I. *J. Chem. Soc., Faraday Trans.* **1993**, 89, 425.
- (2) Atkinson, R.; Carter, W. P. L. *Chem. Rev.* **1984**, 84, 437.
- (3) Calvert, J.; Pitts, J. N., Jr. *Photochemistry*; John Wiley and Sons: New York, 1966.
- (4) Aschmann, A. M.; Atkinson, R. *Int. J. Chem. Kinet.* **1998**, 30, 471.
- (5) Cavalli, F.; Barnes, I.; Becker, J. *Int. J. Chem. Kinet.* **2001**, 33, 431.
- (6) George, C.; El Rassy, H.; Chovelon, J. M. *Int. J. Chem. Kinet.* **2001**, 33, 539.
- (7) Magi, L.; Schweitzer, F.; Pallares, C.; Cherif, S.; Mirabel, P.; George, C. *J. Phys. Chem. A* **1997**, 101, 4943.
- (8) Schweitzer, F.; Mirabel, P.; George, C. *J. Phys. Chem. A* **1998**, 102, 3942.
- (9) Worsnop, D. R.; Zahniser, M. S.; Kolb, C. E.; Gardner, J. A.; Jayne, J. T.; Watson, L. R.; van Doren, J. M.; Davidovits, P. *J. Phys. Chem.* **1989**, 93, 1159.
- (10) Shepson, P. B.; Mackay, E.; Muthuramu, K. *Environ. Sci. Technol.* **1996**, 30, 3618.
- (11) Treves, K.; Shragina, L.; Rudich, Y. *Environ. Sci. Technol.* **2000**, 34, 1997.
- (12) Gautier, C.; Le Calvé, S.; Mirabel, P. *Atmos. Environ.* **2003**, 37, 2347.
- (13) Kolb, C. E.; Worsnop, D. R.; Zahniser, M. S.; Davidovits, P.; Hanson, D. R.; Ravishankara, A. R.; Keyser, L. F.; Leu, M. T.; Williams, L. R.; Molina, M. J.; Tolbert, M. A. Laboratory Studies of Atmospheric Heterogeneous Chemistry. In *Advanced Series in Physical Chemistry*; Barker, J. R., Ed.; World Scientific: Singapore, 1995; Vol. 3, p 771.
- (14) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The properties of gases and liquids*, 4th ed.; McGraw-Hill: New York, 1987.
- (15) Davidovits, P.; Jayne, J. T.; Duan, S. X.; Worsnop, D. R.; Zahniser, M. S.; Kolb, C. E. *J. Phys. Chem.* **1991**, 95, 6337.
- (16) Davidovits, P.; Hu, J. H.; Worsnop, D. R.; Zahniser, M. S.; Kolb, C. E. *Faraday Discuss.* **1995**, 65.
- (17) Schweitzer, F.; Magi, L.; Mirabel, P.; George, C. *J. Phys. Chem. A* **1998**, 102, 593.
- (18) Katrib, Y.; Mirabel, P.; Le Calvé, S.; Weck, G.; Kochanski, E. *J. Phys. Chem. B* **2002**, 106, 7237.
- (19) Katrib, Y.; Deiber, G.; Mirabel, P.; Le Calvé, S.; George, C.; Mellouki, A.; Le Bras, G. *J. Atmos. Chem.* **2002**, 43, 151.
- (20) Kolb, C. E.; Davidovits, P.; Jayne, J. T.; Shi, Q.; Worsnop, D. R. *Prog. React. Kinet. Mech.* **2002**, 27, 1.
- (21) Dasgupta, P. K.; Dong, S. *Atmos. Environ.* **1986**, 20, 565.
- (22) Buttery, R. G.; Ling, J. L.; Guadagni, D. G. *J. Agric. Food Chem.* **1969**, 17, 385.
- (23) Kieckbusch, T. G.; King, C. J. *J. Chromatogr. Sci.* **1979**, 17, 273.
- (24) Nathanson, G. M.; Davidovits, P.; Worsnop, D. R.; Kolb, C. E. *J. Phys. Chem.* **1996**, 100, 13007.
- (25) Kwok, E. S. C.; Atkinson, R. *Atmos. Environ.* **1995**, 29, 1685.
- (26) Seinfeld, J. H.; Pandis, S. N. *Atmospheric Chemistry and Physics*; New York, 1998.
- (27) Brimblecombe, P.; Dawson, G. A. *J. Atmos. Chem.* **1985**, 2, 95.