

# Kinetics of Mass Transfer of Carbonyl Fluoride, Trifluoroacetyl Fluoride, and Trifluoroacetyl Chloride at the Air/Water Interface

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Received: April 18, 1994; In Final Form: August 8, 1994<sup>®</sup>

The heterogeneous chemistry, on aqueous surfaces, of a series of acid halides,  $\text{COF}_2$ ,  $\text{CF}_3\text{COF}$ , and  $\text{CF}_3\text{COCl}$ , was studied. The technique used consists of a low-pressure flow tube reactor in which a stream of monodisperse droplets interacts with the gaseous acid halide. The experiments, which were performed as a function of the initial pH of the droplets, temperature, and gas/liquid interaction time, yield low uptake coefficients in the range  $5 \times 10^{-4}$  to  $5 \times 10^{-3}$  and allow estimation of the product  $H\sqrt{k}$ , where  $H$  is the Henry's law constant and  $k$  is the hydrolysis rate constant. The values reported here are 60, 60, and 350  $\text{M}\cdot\text{atm}^{-1} \text{ s}^{-1/2}$  for  $\text{CF}_3\text{COCl}$ ,  $\text{CF}_3\text{COF}$ , and  $\text{COF}_2$ , respectively, at 273 K. Separate values of  $H$  and  $k$  are also reported. The results show slightly different behavior between the chloride and the fluorides as a function of temperature. This study shows Henry's law and hydrolysis rate constants large enough that heterogeneous reactions on aqueous surfaces will limit the residence time of these species in the atmosphere.

## Introduction

Chlorofluorocarbons (so called CFC's) which have very long lifetimes in the atmosphere (up to 500 years) do not react in the troposphere but are transported to the stratosphere, where, under solar irradiation, they release chlorine atoms, which, in turn, can destroy ozone molecules. This potential ability of CFC's to attack stratospheric ozone leads to the projected use of the much more reactive hydrofluorocarbons (HFC's) and hydrochlorofluorocarbons (HCFC's). It has been shown that OH radicals attack these latter species in a very efficient way,<sup>1</sup> leading to a lifetime range of 1.5–60 years. However, this reaction leads to the formation of secondary oxidation products in the form of halogenated carbonyl compounds (RCOX). The fate of these oxidation products is not entirely known at the present time, but their homogeneous gas phase removal does not seem to play a major role, since the lifetime of such carbonyls, with respect to such processes, is expected to be long (many years).<sup>1,2</sup>

These products can react with condensed "atmospheric" water, leading to another pathway for the removal of these halogenated species through heterogeneous "rain-out"<sup>3</sup> by water droplets or sea surfaces. Such a process is governed by the rate of transfer of material between the gas and the aqueous phases, the solubility in the liquid phase (Henry's law constant), and the rate of hydrolysis. In this context, the rate of mass transfer between gas and aqueous phases has to be known to describe completely the fate of these acid halides and to understand their partitioning between gas and aqueous phases. The rate of heterogeneous mass transfer can also be used to estimate the ozone depletion potential of these oxidation products.

We present here the results of an experimental determination of uptake coefficients for carbonyl fluoride, trifluoroacetyl chloride, and trifluoroacetyl fluoride. These uptake coefficients are a measure of the effective rate of mass transfer between gas and aqueous phases.

## Experimental Section

The details of this technique have been described previously<sup>4,5</sup> and will be presented only briefly here. The experimental apparatus is a low-pressure flow tube reactor which consists of five successive chambers: a droplet-generating chamber, a buffer chamber containing an electromagnetic shutter which controls access to the next chamber, the interaction chamber where trace gases and droplets interact, another buffer chamber, and the droplet collection chamber. The stream of droplets and the flow of trace gases and carrier gas are coaxial.

The droplets are generated using the vibrating orifice method.<sup>6</sup> Filtered water is forced through a calibrated orifice, formed in a stainless steel plate sealed to a piezoelectric ceramic (QUARTZ et SILICE) connected to a frequency generator. When the generator is turned on, the vibrations control the disintegration of the water jet, and for particular frequencies, a monodisperse stream of droplets is produced.

After leaving the generation chamber, the droplets enter the first buffer zone, in which a thermocouple permits control of the inside temperature. When the electromagnetic shutter is open, the stream enters the interaction chamber, where the  $\text{N}_2$  carrier gas containing the trace gas flows. The interaction tubes are 0.75 cm in radius and 7.5–21.5 cm in length. Combining the different droplet velocities with the different lengths provides interaction times between 4 and 16 ms. The train of droplets leaves the interaction chamber through a 3 mm diameter diaphragm and enters a second buffer zone, where argon is injected to sweep out the droplets. In the last chamber, these droplets are collected in a Pyrex flask and immediately frozen in liquid nitrogen to preserve them from possible contamination.

The pressures inside the different chambers are measured by three pressure sensors (EUROSENSOR), and electronically controlled valves insure the uniformity of pressure across the apparatus. Our working pressures are typically in the range 20–25 Torr, with pressure differences between the chambers never exceeding 0.1 Torr.

In both buffer chambers, a counterflow enables the length of interaction between trace gas and droplets to be fixed. It involves injecting an inert gas ( $\text{N}_2$  or Ar) near the diaphragms through which droplets enter and exit the interaction chamber.

<sup>®</sup> Abstract published in *Advance ACS Abstracts*, September 15, 1994.

It has been shown in previous experiments<sup>4</sup> and in preliminary runs for these halogenated species that the quantity of trace gases taken up by the droplets is independent of the concentration of these trace gases injected in the flow tube (in preliminary runs, we generally vary these concentrations by a factor of 3–10 depending upon the substance). These observations are indirect verifications of the efficiency of the counterflow system, since they show that the mass of trace gas that may be swept out of the interaction chamber to the collection chamber by the droplet train does not significantly affect the total mass taken up by the droplets and therefore the measured uptake rates. Otherwise, an increase of the uptake rate should have been observed as the quantity of gas injected in the flow tube was increased.

An important aspect of this technique is the control of the water vapor pressure in the reactor, since it controls the surface temperature of the droplets.<sup>7</sup> In our experiments the gas phase was saturated with water vapor in such a way that the temperature was varied between 273 and 294 K.

The gas phase concentration in the interaction chamber is measured by means of liquid chromatography after dissolution in water of a known volume of gas. Care was taken to have complete dissolution of the acid halides; in fact, the dissolution time was varied between 1 and 24 h without any changes. All the chemicals used in this study were obtained from Fluorochem Limited and were used without any further purification.

After each experiment, which lasted about 5–10 min, the small flask was isolated and separated from the reactor. The fraction of trace gas incorporated in the liquid phase was then determined by means of ion chromatography using a Waters IC-Pack A HR column with an IC-Pack guard column. For the acid halides of interest (COF<sub>2</sub>, CF<sub>3</sub>COX with X = F or Cl) we analyzed the presence of the halides X in the solution by conductimetry using a borate/gluconate eluant, and the presence of the acid CF<sub>3</sub>COOH by UV detection using an octanesulfonic acid sodium salt eluant (2.5 mM). These two techniques gave the same results for the amount of trace gas incorporated in our experiments within 7%, which corresponds roughly to the accuracy of the chromatographic system. Furthermore, the conductimetric method is close to its detection limit while the UV method is still very sensitive.

The uptake coefficient  $\gamma_{\text{obs}}$ , which reflects the different factors affecting the uptake of a gaseous species,<sup>4,7</sup> can be expressed by

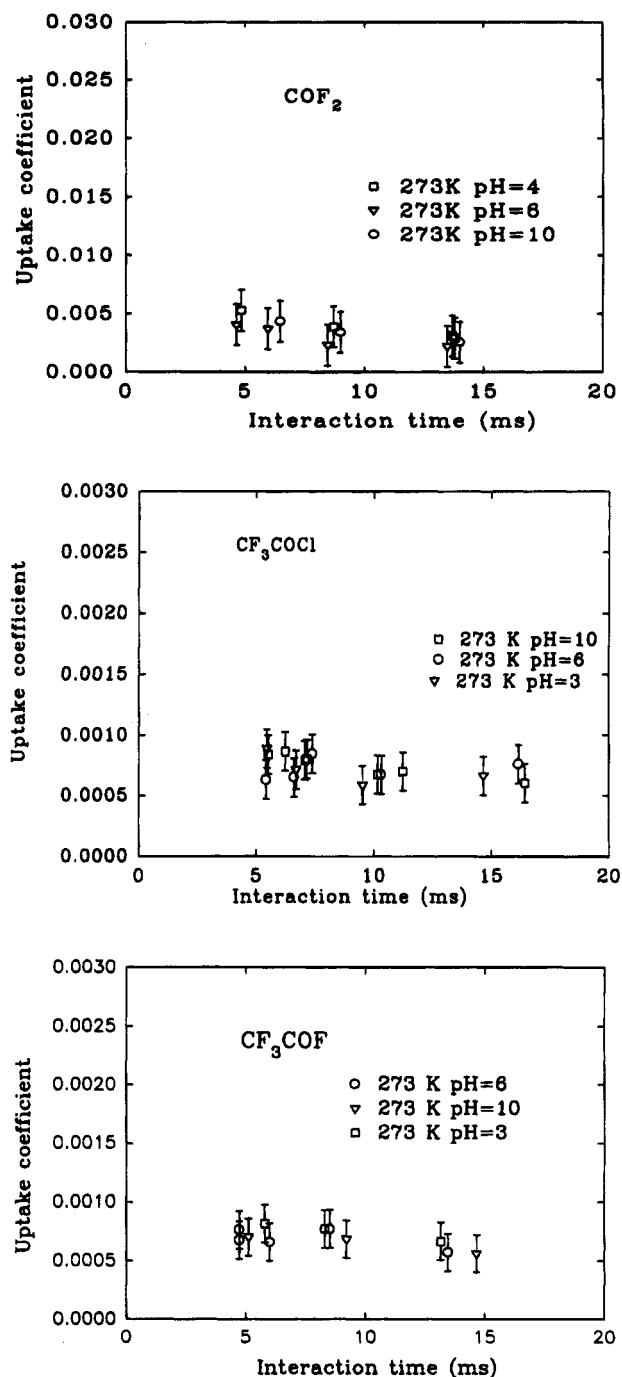
$$\gamma_{\text{obs}} = \frac{F_g \Delta n}{\frac{1}{4} \bar{c} N S_d n} \quad (1)$$

where  $n$  is the trace gas concentration,  $\Delta n$  is the change of the gas phase concentration due to the contact with the droplets,  $F_g$  is the volume rate of flow (cm<sup>3</sup>·s<sup>-1</sup>),  $\bar{c}$  is the trace gas thermal velocity (cm·s<sup>-1</sup>), and  $N S_d$  is the total area (cm<sup>2</sup>) exposed by the  $N$  droplets present in the interaction zone. In this apparatus, the train of droplets and the gas flow pass coaxially through the flow tube, leading to the possible existence of a concentration gradient along the length of the interaction chamber. Integrating the uptake over the length of the flow tube gives<sup>4,7</sup>

$$\gamma_{\text{obs}} = \frac{F_g}{\frac{1}{4} \bar{c} N S_d} \ln \left( \frac{n^{\text{in}}}{n^{\text{in}} - n^{\text{abs}}} \right) \quad (2)$$

where  $n^{\text{in}}$  is the inlet gas phase concentration and  $n^{\text{abs}}$  is the quantity absorbed by the droplets.

This uptake coefficient reflects a convolution of all the processes which may influence the rate of mass transfer between



**Figure 1.** Measured uptake coefficients for COF<sub>2</sub>, CF<sub>3</sub>COF, and CF<sub>3</sub>COCl as a function of interaction time and pH.

the aqueous and gaseous phases. In the next section, we discuss the different steps present in the incorporation of these acid halides.

## Results

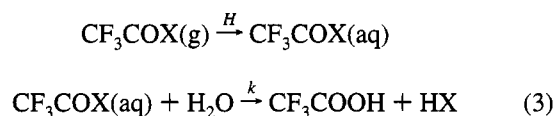
Experiments were performed for the three compounds of interest (COF<sub>2</sub>, CF<sub>3</sub>COCl, and CF<sub>3</sub>COF) in which the dependency of the uptake coefficient on the interaction time and the initial pH of the droplets was studied for a temperature of 273 K. The interaction time was varied between 4 and 16 ms, and the pH, between 3 and 10, leading to uptake coefficients in the range  $5 \times 10^{-4}$  to  $5 \times 10^{-3}$ . Figure 1 shows the results obtained for these compounds. No significant variation was obtained when the initial pH of the droplets was changed for all three compounds whereas a small time dependency was observed.

**TABLE 1: Aqueous Phase Diffusion Coefficients Estimated from the Wilke and Chang Semiempirical Method<sup>11</sup>**

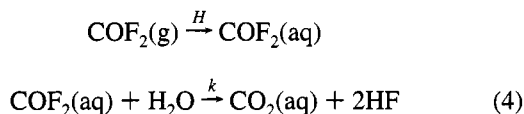
temp (K)	$D_{\text{aq}} (10^5 \text{ cm}^2\text{s}^{-1})$		
	$\text{COF}_2$	$\text{CF}_3\text{COF}$	$\text{CF}_3\text{COCl}$
273	0.8	0.6	0.5
284	1.2	0.8	0.8
294	1.6	1.1	1.0

The latter variation is more important in the case of carbonyl fluoride compared to the other two acid halides.

To explain these observations, we have to take into account all subprocesses involved in the incorporation of the gaseous compounds. In regard to previously published data,<sup>8,9</sup> the rate-limiting process may be the solubility or the rate of hydrolysis. The small time decrease of the uptake coefficient reflects a convolution of saturation of the droplet surfaces due to low solubility and low hydrolysis rate. The trifluoroacetyl halides react with water to form trifluoroacetic acid according to the following equations:



where  $H$  is the Henry's law constant and  $k$  is the hydrolysis rate constant. Carbonyl fluoride reacts with water according to eq 4:



The overall kinetics of the uptake of the acid halides is determined by a combination of the establishment of the gas/liquid equilibrium (described by the Henry's law constant) and of the hydrolysis (first-order rate constant  $k$ ).<sup>8</sup> In fact, the existence of a time dependency is a consequence of saturation at the surface of the droplets.<sup>4,7</sup> The steady state solution between surface saturation and chemical reaction can be described by the following equation:<sup>7,10</sup>

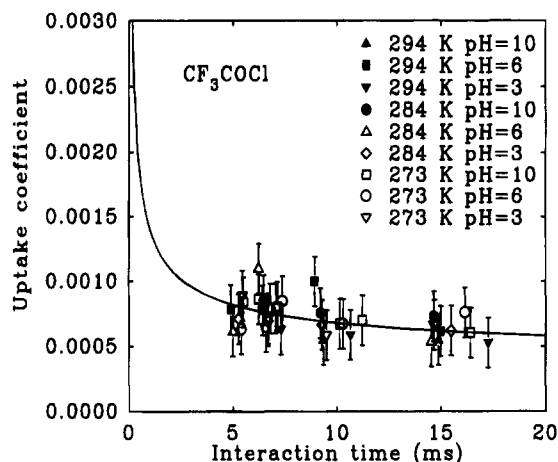
$$\frac{1}{\gamma_{\text{obs}}} = \frac{1}{\alpha} + \frac{\bar{c}}{4HRT\sqrt{D_{\text{aq}}}\left(\frac{1}{\sqrt{t}} + \sqrt{k}\right)} \quad (5)$$

where  $\alpha$  is the mass accommodation coefficient,  $R$  is the gas constant,  $D_{\text{aq}}$  is the aqueous phase diffusion coefficient (calculated by the Wilke and Chang formula;<sup>11</sup> see Table 1), and  $t$  is the interaction time. Equation 5 was obtained by considering that the different processes affecting the uptake rate can be decoupled. However, Jayne *et al.*<sup>10</sup> have shown that this calculation is similar to the rigorous treatment of Danckwerts.<sup>12</sup>

For sufficiently long contact time  $t$ , the uptake may be adequately described by the following steady state expression:

$$\frac{1}{\gamma_{\text{obs}}} = \frac{\bar{c}}{4HRT\sqrt{kD_{\text{aq}}}} \quad (6)$$

In deriving eq 6, we have assumed that  $\alpha \gg \gamma_{\text{obs}}$ . This assumption may be deduced from the time behavior of the uptake rate of  $\text{COF}_2$  (see below) but also from the behavior of a series of similar halogenated compounds which exhibit large values of the mass accommodation coefficients.<sup>8,13</sup> The magnitude of the measured uptake coefficients for the three gases



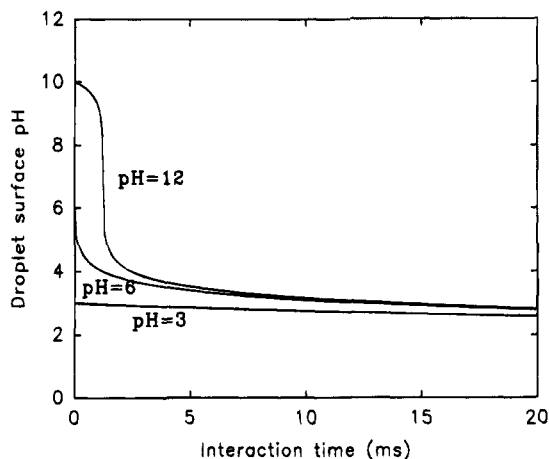
**Figure 2.** Variation of the uptake coefficient with temperature for  $\text{CF}_3\text{COCl}$  (the solid line is drawn from eq 8 for a temperature of 273 K).

of interest can then be used to extract, from eq 6, the values of the product  $H\sqrt{k}$ . The values obtained at 273 K by this treatment are 60, 60, and 350  $\text{M}\cdot\text{atm}^{-1}\cdot\text{s}^{-1/2}$  for  $\text{CF}_3\text{COF}$ ,  $\text{CF}_3\text{COCl}$ , and  $\text{COF}_2$ , respectively. However, it has already been noted<sup>13</sup> that these values have to be considered as upper limits to the actual values, since the (small) time dependency observed in Figure 1 was not taken into account.

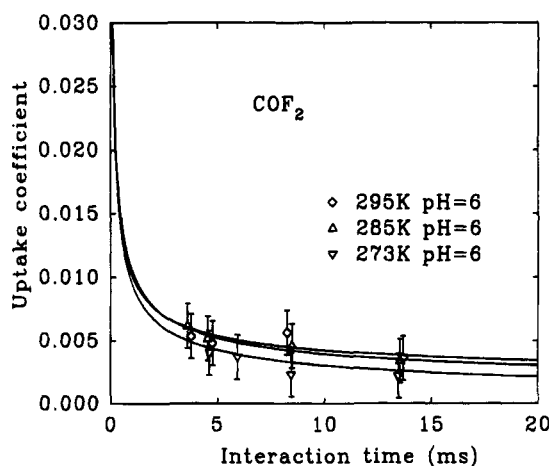
We also performed experiments in which the pH and the temperature were varied for  $\text{CF}_3\text{COCl}$ . It can be seen from Figure 2 that no clear variation of the uptake rate and then of the product  $H(k)^{1/2}$  was observed when the pH was changed, which is in disagreement with the measured acid- and base-catalyzed hydrolysis of some other chlorides or fluorides.<sup>13,14</sup> In these two studies, the technique employed enables direct monitoring of the hydrolysis of the acid halides by either a pH-stat<sup>14</sup> or a stopped flow technique.<sup>13</sup> In both cases, a strong increase of the hydrolysis rate was observed in acid ( $\text{pH} < 4$ ) or alkaline ( $\text{pH} > 7$ ) solutions, but this was not observed in our estimated values. To explain this apparent disagreement, one has to consider that the dissolution of the acid halides followed by their hydrolysis to products undergoing acid-base dissociation will change the droplet surface pH. Assuming that the gaseous species are always in equilibrium with the surface of the liquid droplets and assuming that the hydrolysis follows first-order kinetics, it becomes possible to estimate the pH at the surface of the droplets<sup>4,7</sup> as a function of the initial pH in the bulk:

$$[\text{H}^+] = \left[ -([\text{OH}^-]_0 - [\text{H}^+]_0 - 2kHP_X t) \pm \sqrt{([\text{OH}^-]_0 - [\text{H}^+]_0 - 2kHP_X t)^2 + 4 \times 10^{-14}} \right] / 2 \quad (7)$$

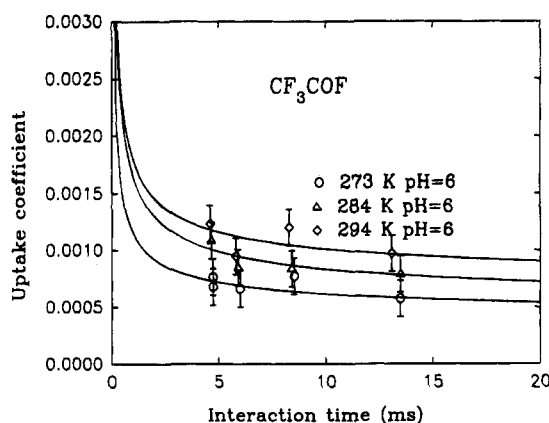
where  $P_X$  is the partial pressure of the acid halide considered ( $5 \times 10^{-5}$  atm in this simulation) and where the subscript "0" refers to the initial state in the bulk. Figure 3 shows the evolution of the droplet surface pH as a function of contact time for the different initial pH values used in our experiments for  $\text{CF}_3\text{COCl}$ . It is clear that the dissolution of the chloride acidifies the surface of the droplets even for an initial  $\text{pH} = 10$ . The pH values, after a few milliseconds exposure to the gas phase are always very low and of the same order of magnitude, whatever the initial pH used in this study. This point explains the lack of an observed pH dependence of the hydrolysis rate constants in our experiments. It should be noted that the hydrolysis rate constant given here may give an upper limit to the actual value at  $\text{pH} = 7$  in pure water because of the acid-catalyzed hydrolysis.



**Figure 3.** Evolution of the droplet surface pH as a function of the interaction time and the initial pH. A partial pressure of  $5 \times 10^{-5}$  atm is used for  $\text{CF}_3\text{COCl}$ .

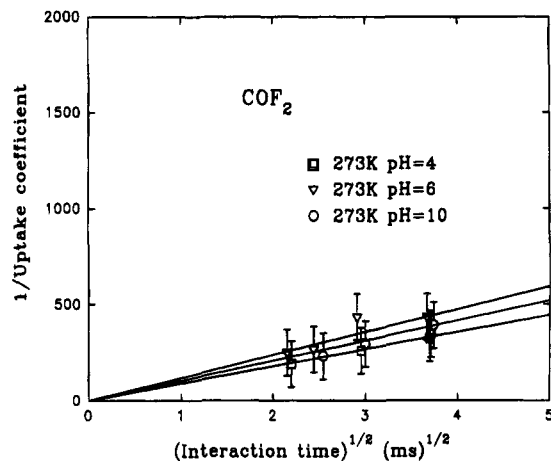


**Figure 4.** Variation of the uptake coefficient with temperature for  $\text{COF}_2$ .



**Figure 5.** Variation of the uptake coefficient with temperature for  $\text{CF}_3\text{COF}$ .

In additional experiments, we have studied the effect of temperature on the uptake rate for the three gases. We have performed measurements in which the temperature was changed between 273 and 294 K (Figures 2, 4, and 5). In these studies, we have observed a slight increase of the uptake rate with temperature for the two fluorides (Figures 4 and 5), and we believe that this behavior may reflect an increase of the hydrolysis rate with temperature. This corresponds to the expected variation of these constants with temperature, a behavior already observed by Bunton and Fendler<sup>14</sup> for the hydrolysis of acetyl fluoride. For  $\text{CF}_3\text{COCl}$ , we did not observe,



**Figure 6.** Plot of the inverse of the uptake coefficient versus  $t^{1/2}$  for  $\text{COF}_2$ .

within our experimental sensitivity, any significant changes of  $\gamma_{\text{obs}}$  with temperature. This means that the dependence of  $k$  on temperature is somewhat less than for the two fluorides. Such small temperature dependency for chlorides was already observed in another study on an analogous compound,  $\text{CCl}_3\text{COCl}$ ,<sup>13</sup> in which we studied the hydrolysis rate of  $\text{CCl}_3\text{COCl}$  as a function of temperature using two different techniques: a stopped flow apparatus and the droplet train technique. These two methods showed, in good agreement, a small dependence of  $k$  with temperature. This conclusion should also apply for  $\text{CF}_3\text{COCl}$  even though its hydrolysis rate temperature dependence is not yet completely resolved. However, with regard to our results it seems that the chloride and fluoride do not vary with temperature in the same manner.

Although the data presented in Figure 1 are rather scattered, it is tempting to determine the order of magnitude of  $H$  and  $k$  separately. The small time dependency observed in Figure 1 may be the consequence of saturation at the interface of the droplet.<sup>4,7</sup> According to eq 5, we have plotted in Figure 6  $\gamma_{\text{obs}}^{-1}$  versus  $t^{1/2}$  for  $\text{COF}_2$  for the different pH values studied. This plot exhibits a linear dependency at 273 K with a negligible intercept, meaning that the mass accommodation coefficient is much larger than the uptake coefficient measured in our experiments; i.e.,  $\gamma_{\text{obs}} \ll \alpha$ . This behavior also means that the effect of the hydrolysis rate (in eq 5) is negligible for the case of carbonyl fluoride at this temperature; i.e.,  $k < 1 \text{ s}^{-1}$ , the limit at which the dependency of  $1/\gamma_{\text{obs}}$  versus  $t^{1/2}$  will no longer be linear. The results of the fit of this equation to our data for  $\text{COF}_2$  lead to an average value of  $35 \text{ M}\cdot\text{atm}^{-1}$  for  $H$  and an upper limit of  $1 \text{ s}^{-1}$  for  $k$ .

The behavior of the other two compounds is quite different (see Figures 7 and 8); i.e., the hydrolysis rate may affect the overall uptake rate whereas this was not the case for  $\text{COF}_2$ . However, we believe that the assumption that  $\gamma_{\text{obs}} \ll \alpha$  is still valid for  $\text{CF}_3\text{COCl}$  and  $\text{CF}_3\text{COF}$ , in agreement with previously published data,<sup>8</sup> leading to another form of eq 5:

$$\gamma_{\text{obs}} = \frac{4HRT\sqrt{D_{\text{aq}}}}{\bar{c}} \left( \frac{1}{\sqrt{t}} + \sqrt{k} \right) \quad (8)$$

The validity of this equation, which is only an approximation, was checked by plotting  $\gamma_{\text{obs}}$  versus  $t^{-1/2}$ . The solid lines in Figures 7 and 8 also represent the best fit of eq 8 to our data. The values obtained by this treatment at 284 K for  $H$  (in  $\text{M}\cdot\text{atm}^{-1}$ ) and  $k$  (in  $\text{s}^{-1}$ ) are respectively 3 and 150 for  $\text{CF}_3\text{COF}$ , and 2 and 220 for  $\text{CF}_3\text{COCl}$ . The reader should keep in mind that these values are subject to very large uncertainties

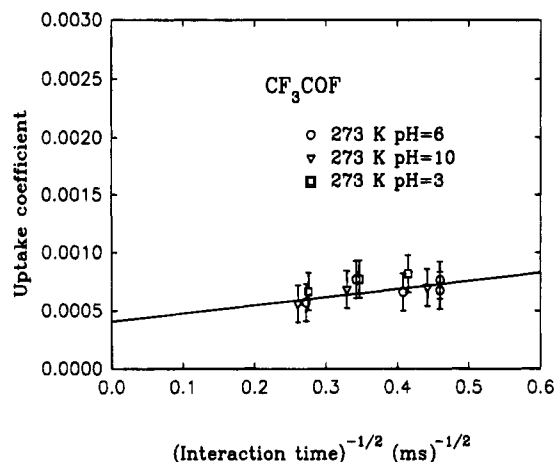


Figure 7. Plot of the uptake coefficient versus  $t^{-1/2}$  for  $\text{CF}_3\text{COF}$ .

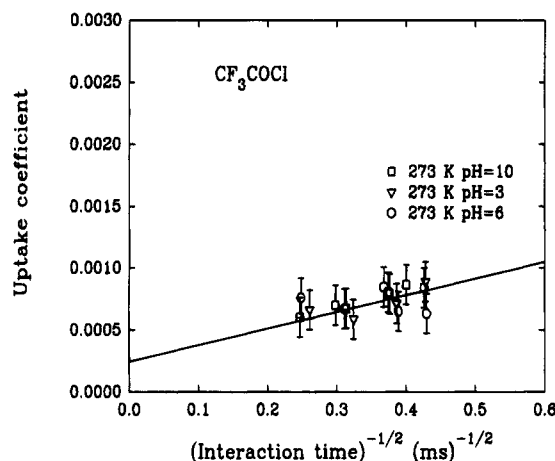


Figure 8. Plot of the uptake coefficient versus  $t^{-1/2}$  for  $\text{CF}_3\text{COCl}$ .

which are about a factor 2 for  $H$  and 3 for  $k$ . In particular, the products  $H\sqrt{k}$  based on these values are smaller than those obtained directly from eq 6. However, considering that the use of eq 6 leads to upper limits of  $H\sqrt{k}$  and that the determination of separate  $H$  and  $k$  values is subject to very large uncertainties, the comparison of the two sets of data is still favorable.

### Comparison with Other Results

The orders of magnitude of the uptake coefficients reported here are consistent with those reported by other laboratories; i.e., in all cases low uptake coefficients were observed.<sup>8,15-18</sup> However, all these results show uptake coefficients large enough that the estimated tropospheric lifetimes of the studied species are expected to be short.

De Bruyn *et al.*<sup>17,18</sup> have developed a new experimental technique which allows, in a similar way to the one presented here, deconvolution of the hydrolysis and solubility effects. The principle of their method is based on the reaction of the column of bubbles with water during contact times which can be varied between 0.1 and 2 s. Their estimates show a similar order of magnitude for  $H$  but greatly different values for  $k$ .

The reason for the large discrepancy between the two methods is not yet clear, since the two methods appear to be similar in principle and in treatment of the data except that the time scale used is different. The same group reported an upper limit for the product  $H\sqrt{k}$  of  $100 \text{ M}\cdot\text{atm}^{-1}\cdot\text{s}^{-1/2}$  using also a droplet train technique.<sup>8</sup> This limit is in agreement with the values reported in this paper.

Unfortunately, there exist only a few measurements of hydrolysis kinetics of acetyl fluorides or chlorides. Furthermore,

these experiments were performed in solutions containing low concentrations of water in order to limit the rate of hydrolysis, which is otherwise too fast to be observed directly.

Exner *et al.*<sup>19</sup> measured the hydrolysis rate constant for  $\text{CF}_3\text{COF}$  in organic solvents containing less than 1 vol % water. They extrapolated their data linearly to pure water and obtained a value of  $11 \text{ s}^{-1}$  at 298 K, which has to be considered as a lower limit to the actual hydrolysis rate constant. More recently, Michel *et al.*,<sup>20</sup> using also a linear extrapolation to pure water, have shown that the previously reported rate constant for  $\text{CF}_3\text{COF}$  was greatly underestimated and a more accurate measurement leads to a value of  $120 \pm 50 \text{ s}^{-1}$  at 298 K, which is in good agreement with the value reported here. In fact, these values may still be underestimated, since some authors<sup>14,21</sup> conducted studies in which the effect of the amount of water in organic solutions was studied. Their results clearly show that the hydrolysis rate constant increases exponentially with the concentration of water.

In a separate study,<sup>13</sup> we also observed that the estimated  $k$  for  $\text{CCl}_3\text{COCl}$  was closely comparable to direct observations made using a stopped flow technique.<sup>14</sup> Ugi and Beck<sup>22</sup> followed the hydrolysis of various acid chlorides in 10.9 vol % water and 89.1 vol % acetone at 253 K, and they found a lower limit for  $\text{CCl}_3\text{COCl}$  of  $k > 10 \text{ s}^{-1}$ . Swain and Scott<sup>23</sup> studied the hydrolysis of acetyl chloride and fluoride in a 25 vol % water and 75 vol % acetone mixture at 298 K, and they found  $k = 0.86$  and  $0.00011 \text{ s}^{-1}$  for the chloride and fluoride, respectively. Their value of  $k$  for acetyl fluoride is considerably smaller than that measured by Bunton and Fendler<sup>14</sup> ( $0.023 \text{ s}^{-1}$  at 300 K). However, all these rates of hydrolysis are expected to be even faster in pure water in regard to the results of Hudson and Moss,<sup>21</sup> whose hydrolysis rate constant for acetyl chloride varied between 0.306 and  $292 \text{ s}^{-1}$  when the fraction of water (by volume) was increased from 19.6 to 75.6%. Trichloroacetyl chloride was observed to behave similarly in dioxane-water mixtures;<sup>14</sup>  $k$  increased from 2.78 to  $105.4 \text{ s}^{-1}$  when the water content was increased from 25 to 90.9%. In regard to all these observations, we believe that our estimates of the different hydrolysis rate constants are consistent with those constants are consistent with those reported in the literature, especially if we consider the exponential increase of  $k$  with the water content.

### Conclusion

With all these observations in mind, we believe that the estimated rate of hydrolysis and solubility will give interesting input data for modeling studies of the atmospheric lifetime and deposition of these halogenated compounds, which determine the atmospheric impact of these species. Kanakidou *et al.*<sup>24</sup> have performed simulations on the atmospheric lifetimes of  $\text{COF}_2$ ,  $\text{CF}_3\text{COF}$ , and  $\text{CF}_3\text{COCl}$  using the estimated Henry's law and hydrolysis rate constants reported here. Using MOGUNTIA, a 3-D climatological global model of the troposphere, they were able to show that the lifetime of these species, due to heterogeneous removal by cloud droplets, is less than 6 days. They concluded that this sink is the most efficient one for these acid halides, in agreement with the previous results reported by Rodriguez *et al.*<sup>25</sup> These very short lifetimes indicate that the fraction of these acid halides able to reach the stratosphere is likely to be negligible. These results suggest that in the case of the chlorine-containing  $\text{CF}_3\text{COCl}$  no significant contribution to the stratospheric chlorine concentration and hence to chemical ozone destruction catalytic cycles should exist.

**Acknowledgment.** The authors would like to thank Dr. J. Franklin and Dr. J. M. Libre for helpful discussions. The work

has been funded in whole by the Alternative Fluorocarbons Environmental Acceptability Study (A.F.E.A.S.) under Contract No. CTR92-36/P92-089 to the Université Louis Pasteur of Strasbourg.

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