Tellus (1992), *44B*, 533–544

Phase-partitioning and chemical reactions of low molecular weight organic compounds in fog

By M. C. FACCHINI, S. FUZZI, and J. A. LIND*, *Istituto FISBAT-CNR, Via de' Castagnoli 1, 40126 Bologna, Italy*, H. FIERLINGER-OBERLINNINGER, M. KALINA, H. PUXBAUM and W. WINIWARTER, *Institut für Analytische Chemie, Technische Universität Wien, Getreidemarkt 9/151, A-1060 Wien, Austria*, B. G. ARENDS, *Netherland Energy Research Foundation, P.O. Box 1, 1755 ZG Petten, The Netherlands*, W. WOBROCK and W. JAESCHKE, *Zentrum für Umweltforschung, Johann Wolfgang Goethe Universität, Robert-Mayer-Strasse 7–9, D-6000 Frankfurt a.M., Germany*, A. BERNER and C. KRUISZ, *Institut für Experimentalphysik, Universität Wien, Strudlhofgasse 4, A-1090 Wien, Austria*

(Manuscript received 28 November 1991; in final form 1 June 1992)

ABSTRACT

Concurrent gas and fog water measurements of formic, acetic and pyruvic acids and formaldehyde carried out during the Po Valley Fog Experiment 1989 are presented. The reaction between HCHO and S(IV) in fog water solution to form HMSA was studied. The effect of HMSA formation was found to increase HCHO solubility in fog water up to 100 times. 95% on average of HCHO is present as HMSA in fog water samples with pH > 4.5. At lower pH values, HMSA formation is limited by the availability of S(IV) in solution. A common feature of HCOOH, CH_3COOH and HCHO gas/liquid distribution is represented by the large departures from theoretical predictions when fog water pH is in the region where a large fraction of these compounds is partitioned into the liquid phase. A limitation in mass transport across the air/droplet interface is a likely explanation for this behaviour.

1. Introduction

Among several thousand different gaseous organic compounds that have been detected in the atmosphere, the number of species which are water soluble is limited to those having low molecular weight and high polarity. For this reason, low molecular weight carbonyl compounds and carboxylic acids represent a major fraction of the total organic carbon in cloud and fog water and in precipitation (Graedel and Weschler, 1981; Likens et al., 1983). In particular, we have observed high concentrations of carbonyl compounds (mainly HCHO and CH_3CHO) and carboxylic acids (HCOOH and CH_3COOH) in radiation fog water collected during several experimental projects carried out in the Po Valley, Northern Italy (Facchini et al., 1986; 1990; Fuzzi et al., 1988; 1990; Winiwarter et al., 1988).

In addition to gas phase photochemical production, carbonyl compounds are introduced into the atmosphere by a wide variety of combustion and industrial sources. HCHO is the most abundant gaseous carbonyl compound in the atmosphere (Graedel et al., 1986). HCOOH and CH_3COOH, the principal gaseous carboxylic acids in the atmosphere are produced by photochemical oxidation of natural and anthropogenic hydrocarbons (Jacob and Wofsy, 1988; Madronich et al., 1990), but are also directly emitted by anthropogenic sources (Kawamura et al., 1985; Talbot et al., 1988). Direct emission of organic acids into the atmosphere by vegetation and by decomposition of organic matter are also possible (Keene and Galloway 1986; 1988).

In the presence of water droplets, low molecular weight carbonyl compounds and carboxylic acids redistribute between the aqueous and gas phases

* Now at: NCAR, Atmospheric Chemistry Division, P.O. Box 3000, Boulder, Colorado, USA.

as a function of the respective Henry's law constants. The pH of the droplets strongly influences the phase distribution of the carboxylic acids, as a function of their acid dissociation constant. The solubility of carbonyl compounds, on the other hand, is a function of their hydration constant.

Aqueous phase chemical reactions involving these compounds are also important in the gas/liquid partitioning.

(a) Photochemical oxidation of hydrated formaldehyde by OH radical:

$$CH_2(OH)_2 + OH \xrightarrow{O_2} HCOOH + HO_2 + H_2O \quad (1)$$

which is in competition with photochemical destruction of $HCOO^-$, also by OH radical:

$$HCOO^- + OH \xrightarrow{O_2} CO_2 + HO_2 + H_2O \quad (2)$$

The production of HCOOH from (1) is favoured in acidic solution ($pH < pK_a$), since the produced HCOOH is rapidly transferred to the gas phase, preventing reaction (2) from occurring (Jacob, 1986).

(b) Formation of S(IV)-carbonyl adducts (Deister et al., 1986; Olson and Hoffmann, 1989):

$$RCHO_{(aq)} + S(IV) \leftrightarrow RCH(OH)SO_3^-. \quad (3)$$

The formation of hydroxyalkylsulfonates in solution influences the gas/liquid distribution of SO_2 and HCHO. Since S(IV) solubility is pH dependent, the equilibrium (3) is also pH dependent. The formation of S(IV)-carbonyl adducts may also prevent S(IV) oxidation (Munger et al., 1984; 1986).

In this paper, we present the results of a detailed study on the concentration, phase distribution and chemical reactions of the main low molecular weight carbonyl compounds and carboxylic acids during an extended period of fog in the Po Valley. The importance of these species in the Po Valley fogs has already been evidenced in previous studies (Winiwarter et al., 1988; Facchini et al., 1990). The present study was carried out as part of the Po Valley Fog Experiment 1989 (Fuzzi et al., 1992). During this large experiment, aimed at the study of the physical and chemical processes occurring in fog, we had the opportunity not only to measure concurrently the gas and liquid phase concentration of the organic species of interest, but also to have available a wide range of additional information needed to characterize the atmospheric system under investigation from the meteorological, chemical and microphysical points of view (Fuzzi et al., 1992).

2. Experimental part

Organic acids (formic, acetic and pyruvic) were collected in the gas phase with an automated version of the scrubbing system proposed by Cofer et al. (1985) with a teflon prefilter of 5 μm pores on a time basis of 30 minutes. During fog episodes, droplets were excluded from the scrubber by means of a PTFE funnel (70 mm o.d.) and a U-shaped 10 mm i.d. PTFE tube of 200 mm length. The same kind of inlet has been shown to provide exclusion of particles larger than 5 μm (Rosenberg et al., 1988). Smaller particles contain only negligible amounts of formic or acetic acid (Andreae et al., 1987; Keene et al., 1989). Sampling rate was 5.1 l/min, and the inlet was used both in fog and non-fog periods. Chemical analysis of gas phase samples was performed by ion chromatography (IC) using a Dionex AS4A column, eluent 1 mM $Na_2B_4O_7$, immediately after sampling to avoid microbial decomposition. Gas phase detection limits (DL) were determined as 3 times the standard deviation of the system blanks, which were obtained by repeatedly filling the scrubber with 3 ml of deionized water, spraying for 1 minute and analysing this absorption solution. In this way, the overall gas phase DL (sampling and chemical analysis) was calculated as 7, 16, and 2 nmol/m^3 for formic, acetic, and pyruvic acid respectively.

Formaldehyde was the only carbonyl compound measured in the gas phase, using the continuous scrubbing fluorometric technique developed by Lazrus et al. (1988). Detection limit (DL) for formaldehyde gas phase determination, calculated as three times the noise signal, was 15 nmol m^{-3}; time resolution was 1 min.

SO_2 was also determined in the gas phase, in two-minute time steps, by means of a prototype continuous scrubbing chemiluminescence instrument described in Fuzzi et al. (1992). DL of this instrument was 2 nmol m^{-3}.

All the above gas-phase measurements were carried out at ground level.

Fog water samplings were performed at four different heights (ground, 10, 25 and 50 m) using the 50 m tower available at the field station of S. Pietro Capofiume, where the experiment took place (Fuzzi et al., 1992). The fog water collectors were two single stage impactors of different design (Winkler, 1986; Berner, 1988; Schell et al., 1992). The time basis of fog sampling was 1 hour.

Organic acids were determined in fog water samples with the same IC method reported above. Liquid phase (analytical) DL were 0.09, 0.05 and 0.02 μmol l^{-1} for formic, acetic and pyruvic acid respectively.

Four carbonyl compounds were determined in fog water samples: formaldehyde (DL = 0.5 μmol l^{-1}), acetaldehyde (DL = 0.3 μmol l^{-1}), acrolein (DL = 0.1 μmol l^{-1}) and acetone (DL = 1.0 μmol l^{-1}), using a modified DNPH-HPLC procedure (Facchini et al., 1990). The fraction of carbonyl compounds not bound to S(IV) was determined in the samples by HPLC after derivatization with dinitrophenyl-hydrazine (DNPH). A second sample aliquot was analyzed using the same procedure after the addition of NaOH to raise the pH to 13. In these pH conditions the carbonyl-S(IV) adducts are no longer stable and total carbonyl concentration can therefore be measured. Adduct concentration was determined by difference.

pH of fog water samples was measured in a thermostated flow system using a pH microelectrode, as reported in Fuzzi et al. (1992).

A Particulate Volume Monitor PVM-100 was used to determine fog liquid water content (LWC) (Fuzzi et al., 1992).

In the calculations throughout the paper, the cubic meter is defined at 278 °K and 1013 hPa.

3. Experimental results

The concentrations of formic, acetic and pyruvic acids and of formaldehyde and sulfur dioxide were measured in the gas phase throughout the experiment; in the presence of fog, the same species (plus acetaldehyde, acrolein and acetone) were determined also in fog water samples.

The concentration trend of ground level total (gas + liquid) HCOOH and CH_3COOH over the entire duration of the experiment is reported in Fig. 1 in 1-h time steps. The pyruvic acid concentration trend is not reported since this compound was present in very low concentration: the median total concentration value is below DL (Table 1).

The concentration trend of total HCHO and S(IV) over the same period is reported in Fig. 2. Liquid phase HCHO is reported showing the separate contributions of free HCHO and S(IV)-bound HCHO (HMSA). It should be noted that liquid phase S(IV) was not measured during the experiment and its concentration is approximated in the figure by HMSA concentration. The reported liquid phase S(IV) concentration should therefore be viewed as a lower limit for the actual S(IV) concentration.

For a direct comparison of the concentration values of the different species in- and out-of-fog periods, the data are reported in the figures as the sum of gas phase concentration plus (when fog is present) the liquid phase concentration. In fact, over the period of the experiment fog occurrence was more than 35% of the total time. To obtain the liquid phase equivalent air concentration of the species reported in the figures, the fog water concentrations were normalized to the fog liquid water content measured during the experiment (Arends et al., 1992):

$$c_{(\mathrm{air})}\,[\mathrm{nmol\,m^{-3}}] = c_{(\mathrm{fog})}\,[\mu\mathrm{mol\,l^{-1}}] \cdot \mathrm{LWC}\,[\mathrm{ml\,m^{-3}}] \qquad (4)$$

A statistical summary of the data shown in Figs. 1 and 2 is reported in Table 1; pyruvic acid is also included in the table. Also, in Table 2, we report a

Table 1. *Statistical summary of the total concentration (gas + liquid) of the low molecular weight organic compounds examined in the paper; S(IV) total concentration is also reported*

	Concentration (nmol m^{-3})				
Compound	min	25 per-centile	50 per-centile	75 per-centile	max
formaldehyde	DL	42	59	100	468
formic acid	DL	11	21	44	247
acetic acid	DL	16	27	60	175
pyruvic acid	DL	DL	DL	2	9
sulfur (IV)	4	10	26	40	282

DL values are reported in the text.

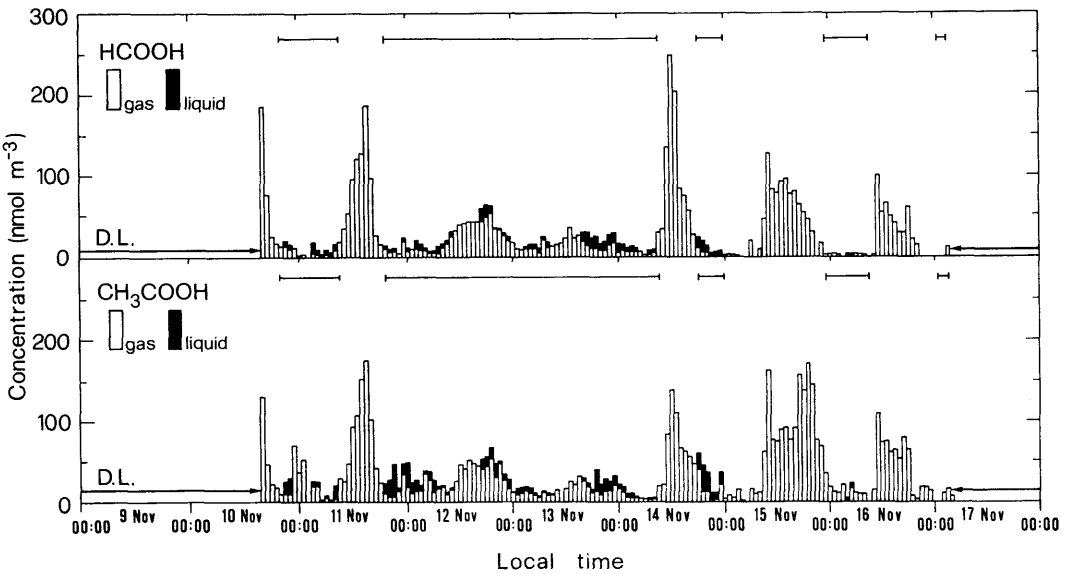

Fig. 1. Temporal trend (hourly data) of organic acid phase distribution during the Po Valley Fog Experiment 1989. Fog periods are indicated by the upper horizontal bars. The lack of gas phase and/or liquid phase (during fog periods) results indicates missing data. The reported DL is that of the gas phase measurements.

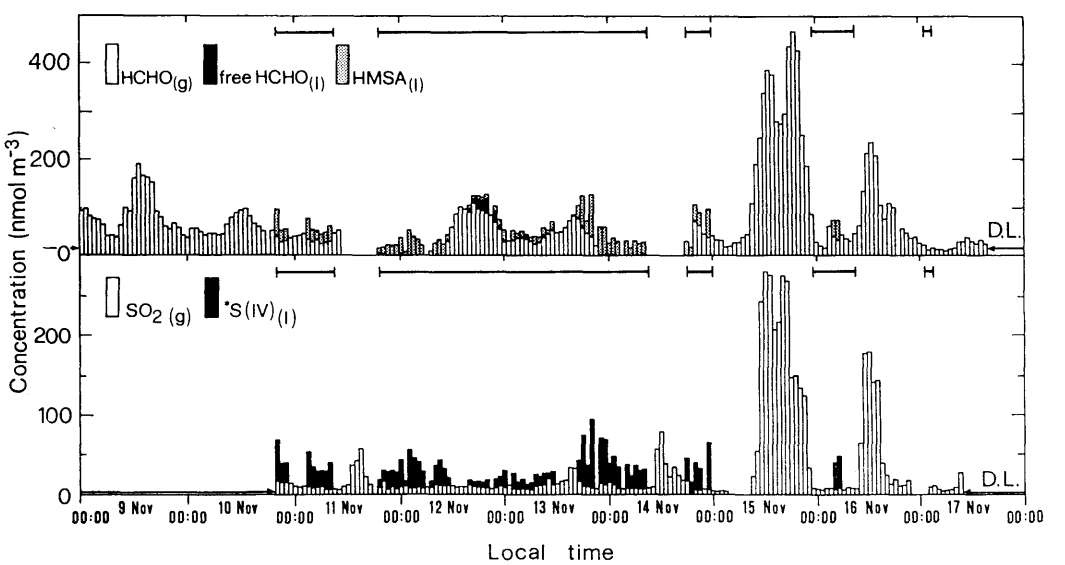

Fig. 2. As in Fig. 1, but for HCHO and S(IV). The contributions of free HCHO and HMSA to the total liquid phase HCHO concentration are reported separately. *Liquid phase S(IV) was not measured and is approximated by HMSA concentration.

Table 2. *Statistical summary of the concentration in fog water of the low molecular weight organic compounds examined in the paper*

Compound	Concentration (nmol m^{-3})				
	min	25 per-centile	50 per-centile	75 per-centile	max
formaldehyde (free)	DL	4.7	10.0	21.2	220.9
formaldehyde (total)	29.0	80.6	125.4	215.8	843.8
acetaldehyde (free)*	DL	4.8	11.8	30.2	328.3
formic acid	0.8	26.0	39.1	52.7	150.3
acetic acid	6.6	24.5	39.1	59.4	229.1
pyruvic acid	DL	1.6	3.5	7.1	30.8

Acrolein and acetone concentrations are not reported since they are consistently below DL. DL values are reported in the text.* Acetaldehyde is entirely present in the free form.

statistical summary of liquid phase concentrations of the different organic compounds. Some preliminary evidence appears from the above figures and from the tables.

(i) Among the 3 organic species considered, HCHO is undoubtedly the most abundant (median concentration more than double that of organic acids), while S(IV) total concentration is similar to that of organic acids.

(ii) All reported organic species exhibit a diurnal trend with maximum concentration values during the central hours of the day. Sometimes a 2nd peak is observed in the late afternoon. The midday maximum is common to that of other gaseous species (SO_2, NH_3, HNO_3; see Fuzzi et al., 1992). Vertical mixing and horizontal transport may be responsible for this diurnal trend (Wobrock et al., 1992), but chemical reactions are also possible.

(iii) The onset of fog results in a general decrease in concentrations of all organic species. The establishment of a temperature inversion, characteristic of the fog formation period (Wobrock et al., 1992) separates the lower levels of the atmosphere from the air aloft. Under these conditions, transport becomes a less important factor, and the compounds lost at the ground or scavenged by wet aerosol cannot be replaced by vertical mixing processes. The formation of fog droplets then causes a further enhancement of deposition of the species incorporated in the liquid phase. Fog therefore represents a sink for these soluble organic species.

(iv) The liquid phase concentration, in the presence of fog, represents a considerable fraction of the total concentration of HCOOH, CH_3COOH and HCHO. HCHO is present in the liquid phase almost entirely bound to S(IV) in the form of HMSA. In addition, the liquid phase concentration of HMSA accounts for up to 90% of the total S(IV) concentration (gas + liquid).

(v) The gas phase concentrations of all species in the presence of fog are often near DL (see Figs. 1, 2), a fact giving rise to some difficulty in evaluating the phase partitioning equilibria (see below). On the contrary, the liquid phase concentrations are generally well above DL.

4. Discussion

4.1. Sources of organic acids and carbonyl compounds in the Po Valley

In order to obtain some insight into the sources of the carbonyl compounds and carboxylic acids detected during the experiment, we performed a correlation analysis of the total concentrations of the different compounds (Table 3). This correlation analysis (Pearson Product Moment Correlation) provides a normalized and scale-free

Table 3. *Correlation analysis of total (gas + liquid) concentration of the different compounds examined in this paper (69 observations)*

	S(IV)	HCHO	HCOOH	CH_3COOH	$CH_3C(O)COOH$
S(IV)	1				
HCHO	0.821	1			
HCOOH	0.614	0.589	1		
CH_3COOH	0.611	0.776	0.711	1	
$CH_3C(O)COOH$	0.003	−0.014	0.235	0.096	1

measure of the association between the variables. As explained above, in our calculations, total (gas + liquid) concentrations were used in order to cancel the effect of phase partitioning (discussed below in detail). Andreae et al. (1987) and Jacob and Wofsy (1988) suggested that the main pathway of HCOOH formation in the atmosphere is the oxidation of isoprene emitted by vegetation; in this case, a correlation between HCOOH and pyruvic acid is expected, with a typical concentration ratio of 20. In the Po Valley experiment, the low correlation coefficient (see Table 3) could indicate that there is no such connection, but they may also be due to large uncertainties in the pyruvic acid data. In any case, there is no clear evidence of the biogenic origin of formic acid. It should be remembered, however, that our field experiment was carried out during the dormant season when isopropene emission by vegetation is minimal. The good correlation of HCOOH and CH_3COOH with SO_2 indicates common anthropogenic sources.

It cannot be defined from the available data whether the organic acids are directly emitted by anthropogenic sources or whether they result from atmospheric reactions of primary pollutants. The good correlation between total S(IV) and HCHO and between HCHO and CH_3COOH also points to a common origin.

A possible chemical source of HCOOH in the liquid phase is provided by the two competitive reactions (1) and (2), which are strongly influenced by pH. We have investigated a possible HCOOH liquid phase production, following the same procedure suggested by Keene and Galloway (1988). Since HCOOH aqueous phase production increases at increasing $[H^+]$ (Jacob, 1986) and no pH-dependent mechanism is known which controls CH_3COOH total (gas + liquid) concentration (Jacob and Wofsy, 1988), an increase in the ratio $[HCOOH]_{total}/[CH_3COOH]_{total}$ at low pH can provide an indication of HCOOH liquid phase production. In our samples the trend of the above ratio as a function of fog water pH shows no evidence of HCOOH production within the fog droplets.

4.2. *Phase partitioning of organic acids*

The gas/liquid partitioning of a given specie is defined as a function of its Henry's law constant (K_H). In particular, the distribution of organic acids between the gas and aqueous phase is strongly dependent on the droplet pH, since these species undergo rapid acid-base equilibria in solution. A pseudo-Henry's law constant (K_H^*) is therefore defined to take into account this effect (Schwartz, 1984):

$$K_H^* = K_H \left(1 + \frac{K_a}{[H^+]}\right), \tag{5}$$

where K_a is the dissociation constant of the organic acids. The theoretical pseudo-Henry's law constant was calculated as a function of pH for both formic and acetic acids, and compared in Fig. 3 with an experimental constant calculated from the concurrent gas and liquid phase measurements (1-h time basis):

$$K^*_{H\,exper.} = \frac{[RCOOH_{(l)}]_{exper.}}{[RCOOH_{(g)}]_{exper.}} \tag{6}$$

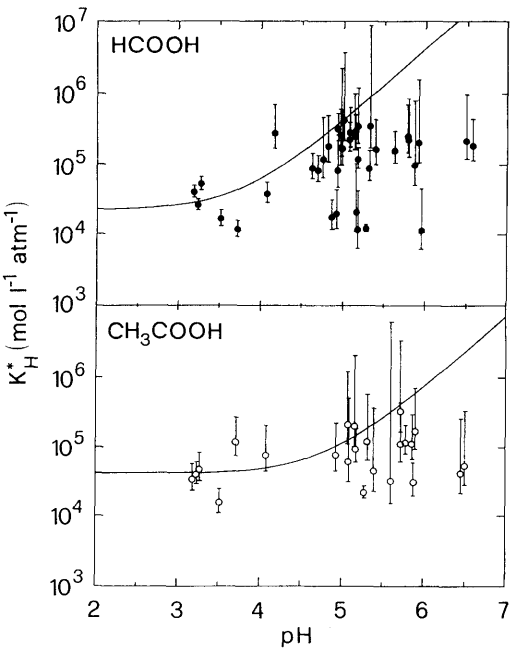

Fig. 3. Pseudo-Henry's law coefficient for organic acids as a function of fog water pH. The solid line represents the theoretical K_H^*, while the symbols represent the experimental results obtained from concurrent gas and liquid phase measurements (1-h time basis). The error bars account for sampling and analytical errors.

Calculations were performed as described in Winiwarter et al. (1988); an average temperature of 278 K was considered and temperature corrections for the equilibrium constants were applied accordingly. The error bars reported in Fig. 3 represent an overall estimate of sampling and analytical errors associated with the measurements (artifacts, values close to DL etc.). In the case of HCOOH, larger departures from equilibrium conditions are observed above pH 4.5, with $K^*_{H\ exper.}$ up to 100 times lower than theoretical K^*_H in the pH 6 region. This behaviour is less pronounced for CH_3COOH, but here too, deviations of up to 10–20 times are observed between theoretical and experimental K^*_H above pH 6. Similar results have already been reported by Winiwarter et al. (1988), although with a much more limited set of experimental data, mostly concerning HCOOH.

Perdue and Beck (1988) suggested that the mixing of droplets in equilibrium with the surrounding atmosphere may result in a bulk sample which is not in equilibrium with respect to the original conditions. Recently, Pandis and Seinfeld (1991) estimated that the above effects produces a bulk sample supersaturated with respect to the gas phase. In our samples, a subsaturation is however observed. Winiwarter et al. (1992) argued that the high variability of LWC in fog on a short time basis can account for an undersaturation effect of bulk fog water samples of up to a factor of 20. Nonetheless, this effect cannot entirely account for the large departures from Henry's law equilibrium observed in our samples. Other explanations are also possible to account for the observed departures from Henry's law equilibrium: outgassing of organic acids from the samples or effects due to temperature changes from the field to the laboratory. These effects can also cause variations in the pH of the samples introducing a further uncertainty into the evaluation of the actual Henry's law equilibrium. A similar deviation from Henry's law equilibrium is reported by Facchini et al. (1992) for the species $NH_{3(g)}/NH^+_{4(fog)}$ in the pH region below 4.5. A common feature of organic acids and ammonia emerges: large deviations from Henry's law are observed in both cases in the pH range where the equilibria are shifted toward the liquid phase (pH < 4.5 for ammonia, pH > 4.5 for organic acids). The above discussion is based on the assumption that equilibrium conditions between gas and liquid phase are expected for fog droplets, since the diffusional transport at the air-droplet interface and the mass transport across the interface itself is relatively fast (order of minutes) as compared to the fog sampling time (one hour) (Schwartz, 1986). However, Chang and Hill (1980) and Gill et al. (1983) hypothesized that an organic film on the surface of fog/cloud droplets would sensibly reduce the mass exchange across the air/droplet interface. Hydrophobic organic substances have recently been detected in polluted fogs (Capel et al., 1990; 1991). The presence of such species, capable of producing an organic film on the surface of fog droplets, is likely to occur also in the high pollution conditions of the Po Valley. This effect would produce the largest deviations from gas/liquid equilibrium in the pH region where a higher mass transfer across the gas/liquid interface is expected.

4.3. Phase partitioning and chemistry of HCHO

The HCHO gas/liquid partitioning is strongly influenced by HMSA formation (eq. (3)), which considerably enhances the solubility of both HCHO and SO_2 (Olson and Hoffmann, 1989). This is especially evident in our fog system, where a major fraction of HCHO in the liquid phase is bound as HMSA. CH_3CHO, the other carbonyl compound present in appreciable concentrations if fog water, is entirely in the free form (Table 2). This observation is in agreement with both previous experimental results (Facchini et al., 1990) and with the thermodynamic predictions of Betterton et al. (1988).

The effect of HMSA formation on HCHO solubility in fog water is shown in Fig. 4, where free and total $[HCHO_{(l)}]$ are reported as a function of HCHO partial pressure. The theoretical Henry's law prediction is also reported in the figure, calculated at 278 K, the average temperature during the experiment, from the equation of Dong and Dasgupta (1986):

$$[HCHO_{(l)}]_{free} = 10^{[(4538/T) - 11.34]} \cdot [HCHO_{(g)}]^{[(252.2/T) + 0.2088]} \quad (7)$$

While this expression also takes into account the hydration of HCHO in solution (Betterton and Hoffmann, 1988), the fraction of HCHO bound to S(IV) (eq. (3)) is not accounted for. According to

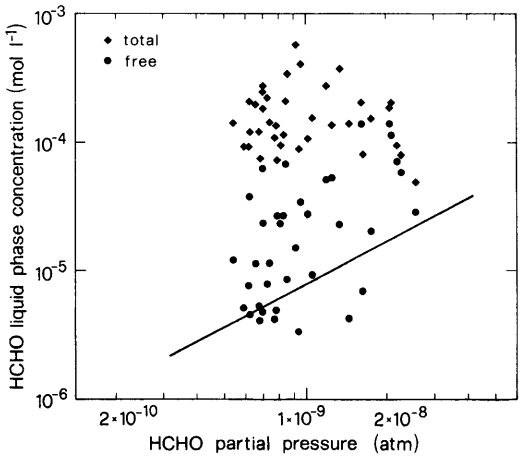

Fig. 4. Free and total HCHO liquid phase concentration as a function of the measured atmospheric partial pressure. The solid line represents the theoretical Henry's law prediction for free HCHO liquid concentration, calculated from Dong and Dasgupta (1986).

eq. (7), the liquid phase concentration of free HCHO is not pH dependent. The measured free $[HCHO_{(l)}]$ results are quite scattered and generally overestimate the Henry's law predictions (up to a factor of 10). From the figure it is also evident that HMSA formation causes the HCHO equilibrium concentration in fog water to increase up to a factor of 100.

In contrast to the equilibrium behaviour of free HCHO the fraction of HCHO that reacts with S(IV) to form HMSA is a function of fog water pH (Fig. 5). The ratio $[HMSA_{(l)}]/[HCHO_{(l)}]_{total}$ increases at increasing pH, approaching 0.95 for $pH > 4.5$. At pH values lower than 4.5 the percentage of HMSA present in fog water over the total available liquid HCHO rapidly decreases. It is possible that the decrease of $[HMSA_{(l)}]/[HCHO_{(l)}]_{total}$ at low pH depends on the unfavourable kinetics of HMSA formation in acid solution (Boyce and Hoffmann, 1984; Munger et al., 1984; 1986; Olson and Hoffmann, 1986),

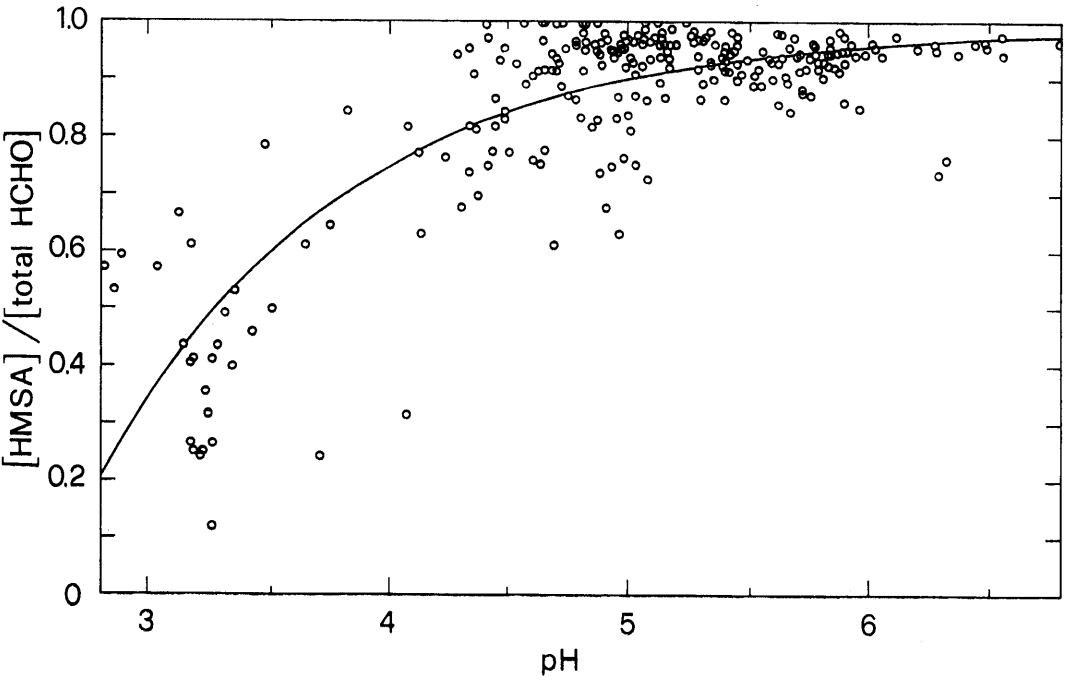

Fig. 5. Fraction of liquid phase HCHO bound as HMSA, as a function of fog water pH. The solid line represents the best fit (exponential function) of the experimental data.

although this behaviour can also be explained by equilibrium considerations.

From the available experimental data it is possible to calculate an "expected" liquid phase HMSA concentration (Olson and Hoffmann, 1989) for each sample:

$$[HMSA_{(l)}]_{expected} = p_{HCHO} \cdot K_{H_{HCHO}} \cdot p_{SO_2} \cdot K_{H_{SO_2}} \cdot \frac{K_{a1}}{[H^+]} K_{HMSA} \quad (8)$$

where:

p_{HCHO} = measured HCHO atmospheric partial pressure
p_{SO_2} = measured SO_2 atmospheric partial pressure
$K_{H_{HCHO}}$ = Henry's law constant for HCHO (from eq. (7))
$K_{H_{SO_2}}$ = Henry's law constant for SO_2
K_{a1} = first acid dissociation constant of SO_2 in solution
$[H^+]$ = hydrogen ion concentration in solution (from pH measurements)
K_{HMSA} = equilibrium constant of reaction (7) (Deister et al., 1986).

$[HMSA_{(l)}]_{expected}$ as defined in eq. (8) is a function of both HCHO and SO_2 gas/liquid distribution equilibria, the latter being pH dependent. Therefore, the overall gas/liquid partitioning of HCHO (dissolution + HMSA formation):

$$\begin{array}{lll} \text{liquid} & HCHO + S(IV) \rightleftarrows HMSA & \\ \text{-------} & \uparrow\downarrow \text{---} \downarrow\uparrow & \text{-------} \\ \text{gas} & HCHO \quad SO_2 & \end{array} \quad (9)$$

is also pH dependent. Considering that SO_2 solubility decreases at decreasing pH (Schwartz, 1984) S(IV) availability in solution can be the limiting factor on HMSA formation, thus explaining the decreasing value of the ratio $[HMSA_{(l)}]/[HCHO_{(l)}]_{total}$ in the low pH region (Fig. 5).

A convenient way to examine the consistency of our measurements in different pH conditions with theoretical HCHO gas/liquid partitioning equilibria, is to plot the ratio $[HMSA_{(l)}]_{measured}/[HMSA_{(l)}]_{expected}$, which should ideally be equal to 1, as a function of fog droplet pH (Fig. 6). The trend of the above ratio exhibits a behaviour similar to that reported for organic acids (Fig. 3)

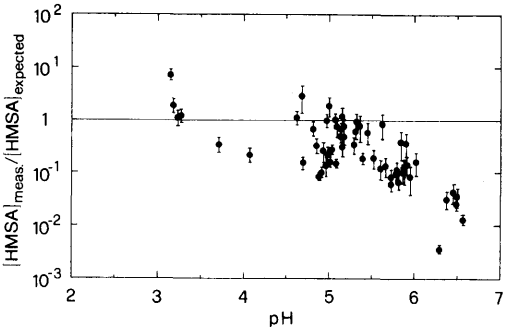

Fig. 6. The ratio between measured and expected (calculated from eq. (8)) HMSA concentration, as a function of fog water pH. The error bars account for sampling and analytical errors.

and ammonia (Facchini et al., 1992): the larger departures from equilibrium predictions are observed in the pH region above 5, where the overall equilibrium (9) shifts toward the liquid phase.

5. Conclusion

The concentration of gaseous HCHO, HCOOH and CH_3COOH measured during the Po Valley Fog Experiment 1989 were high compared with other data reported in literature for different areas in Europe (Carlier et al., 1986; Puxbaum et al., 1988; Hartmann et al., 1989). From indirect observations, we conclude that these species in the Po Valley mainly originate from anthropogenic sources, either as primary pollutants or produced by photochemical oxidation reactions. No evidence was found of HCOOH production in the aqueous phase.

In the presence of fog, these polar low molecular weight compounds are dissolved within the droplets.

Large departures from gas/liquid equilibrium conditions were observed for all species that were investigated in this study. Non-equilibrium conditions due to limited mass transfer across the gas/droplet interface in the presence of an organic coating on the droplet surface can be suspected. In fact, the larger deviations are observed in the pH region where the gas/liquid equilibrium shifts toward the liquid phase and thus higher

mass transport across the fog droplet surface is expected. Indeed, the presence of an organic film on the surface of fog droplets is likely in the pollution conditions of the Po Valley, but the subject certainly requires further investigation. Other possible causes of the observed deviations were investigated (sampling artifacts and analytical errors, non-representativity of the bulk fog water sample with respect to the original atmospheric droplet system), but neither of them seems to be sufficient to account for the observed experimental evidence. The reaction of HCHO in solution with S(IV) to form HMSA enhances HCHO solubility by up to two orders of magnitude. Apart from kinetic considerations, HMSA concentration at low pH seems to be controlled in our fog system by the low SO_2 solubility, which is strongly pH dependent. Appreciable CH_3CHO concentrations were measured in fog water, but this compound does not react with S(IV) in solution in our experimental conditions.

6. Acknowledgements

The invaluable contribution of A. Correggiari, S. Miserocchi, D. Correggiari, C. Foschini and L. Tarozzi during the field work is gratefully acknowledged. G. Helas (MPI-Mainz) provided the mist chamber for sampling gaseous organic acids. Funds for this experiment were provided by: CNR-Progetto Strategico Deposizioni Atmosferiche Acide, Commission of the European Communities (Project EV4V-0084-C), Bundesministerium für Forschung und Technologie (Project 07EU773), Ministry of Economic Affairs of the Netherlands, Austrian Fonds zur Förderung der Wissenschaftlichen Forschung (Project P7656TEC). The station of S. Pietro Capofiume is managed by Assessorato Agricoltura, Regione Emilia Romagna. The Po Valley Fog Experiment 1989 was carried out within the project EUROTRAC, subproject GCE (Ground-based Cloud Experiment).

REFERENCES

Andreae, M. O., Talbot, R. W. and Li, S. M. 1987. Atmospheric measurements of pyruvic and formic acid. *J. Geophys. Res. 92D*, 6635–6641.

Arends, B. G., Kos, G. P. A., Wobrock, W., Schell, D., Noone, K. J., Fuzzi, S. and Pahl, S. 1992. Comparison of techniques for measurements of fog liquid water content. *Tellus 44B*, 604–611.

Berner, A. 1988. The collection of fog droplets by a jet impaction stage. *Sci. Total Environ. 73*, 217–228.

Betterton, E. A. and Hoffmann, M. R. 1988. Henry's law constants of some environmentally important aldehydes. *Environ. Sci. Technol. 22*, 1415–1418.

Betterton, E. A., Erel, Y. and Hoffmann, M. R. 1988. Aldehyde-bisulfite adducts: prediction of some of their thermodynamic and kinetic properties. *Environ. Sci. Technol. 22*, 92–99.

Boyce, S. D. and Hoffmann, M. R. 1984. Kinetics and mechanism of the formation of hydroxymethanesulfonic acid at low pH. *J. Phys. Chem. 88*, 4740–4746.

Capel, P. D., Gunde, R., Zürcher, F. and Giger, W. 1990. Carbon speciation and surface tension of fog. *Environ. Sci. Technol. 24*, 722–727.

Capel, P. D., Leuenberger, C. and Giger, W. 1991. Hydrophobic organic chemicals in urban fog. *Atmos. Environ. 25A*, 1335–1346.

Carlier, P., Hannachi, H. and Mouvier, G. 1986. The chemistry of carbonyl compounds in the atmosphere, a review. *Atmos. Environ. 20*, 2079–2099.

Chang, D. P. Y. and Hill, R. C. 1980. Retardation of aqueous droplet evaporation by air pollutants. *Atmos. Environ. 14*, 803–807.

Cofer III, W. R., Collins, V. G. and Talbot, R. W. 1985. Improved aqueous scrubber for collection of soluble atmospheric trace gases. *Environ. Sci. Technol. 19*, 557–560.

Deister, U., Neeb, R., Helas, G. and Warneck, P. 1986. Temperature dependence of the equilibrium $CH_2(OH)_2 + HSO_3^- = CH_2(OH)SO_3^- + H_2O$ in aqueous solution. *J. Phys. Chem. 90*, 3213–3217.

Dong, S. and Dasgupta, P. K. 1986. Solubility of gaseous formaldehyde in liquid water and generation of trace standard gaseous formaldehyde. *Environ. Sci. Technol. 20*, 637–640.

Facchini, M. C., Chiavari, G. and Fuzzi, S. 1986. An improved HPLC method for carbonyl compound speciation in the atmospheric liquid phase. *Chemosphere 15*, 667–674.

Facchini, M. C., Lind, J., Orsi, G. and Fuzzi, S. 1990. Chemistry of carbonyl compounds in the Po Valley fog water. *Sci. Total Environ. 91*, 79–86.

Facchini, M. C., Fuzzi, S., Kessel, M., Wobrock, W., Jaeschke, W., Arends, B. G., Möls, J. J., Berner, A., Solly, I., Kruisz, C., Reischl, G., Pahl, S., Hallberg, A., Ogren, J. A., Fierlinger-Oberlinninger, H., Marzorati, A. and Schell, D. 1992. The chemistry of sulfur and nitrogen species in a fog system: a multiphase approach. *Tellus 44B*, 505–521.

Fuzzi, S., Orsi, G., Nardini, G., Facchini, M. C.,

McLaren, S., McLaren, E. and Mariotti, M. 1988. Heterogeneous processes in the Po Valley radiation fog. *J. Geophys. Res. 93D*, 11141–11151.

Fuzzi, S., Cesari, G., Evangelisti, F., Facchini, M. C. and Orsi, G. 1990. An automatic station for fog water collection. *Atmos. Environ. 24A*, 2609–2614.

Fuzzi, S., Facchini, M. C., Orsi, G., Lind, J. A., Wobrock, W., Kessel, M., Maser, R., Jaeschke, W., Enderle, K. H., Arends, B. G., Berner, A., Solly, I., Kruisz, C., Reischl, G., Pahl, S., Kaminski, U., Winkler, P., Ogren, J. A., Noone, K. J., Hallberg, A., Fierlinger-Oberlinninger, H., Puxbaum, H., Marzorati, A., Hansson, H.-C., Wiedensohler, A., Svenningsson, I. B., Martinsson, B. G., Schell, D. and Georgii, H. W. 1992. The Po Valley fog experiment 1989: an overview. *Tellus 44B*, 448–468.

Gill, P. S., Graedel, T. E. and Weschler, C. J. 1983. Organic films on atmospheric aerosol particles, fog droplets, cloud droplets, raindrops and snowflakes. *Rev. Geophys. Space Phys. 21*, 903–920.

Graedel, T. E. and Weschler, C. J. 1981. Chemistry within aqueous atmospheric aerosols and raindrops. *Rev. Geophys. Space Phys. 19*, 505–539.

Graedel, T. E., Hawkins, D. T. and Claxton, L. D. 1986. *Atmospheric chemical compounds*. Orlando: Academic Press.

Hartmann, W. R., Andreae, M. O. and Helas, G. 1989. Measurements of organic acids over Central Germany. *Atmos. Environ. 23*, 1531–1533.

Jacob, D. J. 1986. The chemistry of OH in remote clouds and its role in the production of formic acid and peroxymonosulfate. *J. Geophys. Res. 91*, 9807–9826.

Jacob, D. J. and Wofsy, S. C. 1988. Photochemistry of biogenic emissions over the Amazon forest. *J. Geophys. Res. 93D*, 1477–1486.

Kawamura, K., Ng, L. L. and Kaplan, I. R. 1985. Determination of organic acids (C1–C10) in the atmosphere, motor exhaust, and engine oils. *Environ. Sci. Technol. 19*, 1082–1086.

Keene, W. C. and Galloway, J. N. 1986. Considerations regarding sources for formic and acetic acids in the troposphere. *J. Geophys. Res. 91D*, 14466–14474.

Keene, W. C. and Galloway, J. N. 1988. The biogeochemical cycling of formic and acetic acids through the troposphere: an overview of current understanding. *Tellus 40B*, 322–334.

Keene, W. C., Talbot, R. W., Andreae, M. O., Beecher, K., Berresheim, H., Castro, M., Farmer, J. C., Galloway, J. N., Hoffmann, M. R., Li Shai-Meng, Maben, J. R., Munger, W., Norton, R. B., Pszenny, A. A. P., Puxbaum, H., Westberg, H. and Winiwarter, W. 1989. An intercomparison of measurement systems for vapor and particulate phase concentrations of formic and acetic acids. *J. Geophys. Res. 94*, 6457–6471.

Lazrus, A. L., Fong, K. L. and Lind, J. A. 1988. Automated fluorometric determination of formaldehyde in air. *Analyt. Chem. 60*, 1074–1078.

Likens, G. E., Edgerton, E. S. and Galloway, J. N. 1983. The composition and deposition of organic carbon in precipitation. *Tellus 35B*, 16–24.

Madronich, S., Chatfield, R. B., Calvert, J. G., Moortgat, G. K., Veyret, B. and Lesclaux, R. 1990. A photochemical origin of acetic acid in the troposphere. *Geophys. Res. Lett. 17*, 2361–2364.

Munger, J. W., Jacob, D. J. and Hoffmann, M. R. 1984. The occurrence of bisulfite-aldehyde adducts in fog and cloud water. *J. Atmos. Chem. 1*, 335–350.

Munger, J. W., Tiller, C. T. and Hoffmann, M. R. 1986. Determination of hydroxymethanesulfonate in fog water. *Science 231*, 247–249.

Olson, T. M. and Hoffmann, M. R. 1986. On the kinetics of formaldehyde-S(IV) adduct formation in slightly acidic solution. *Atmos. Environ. 20*, 2277–2278.

Olson, T. M. and Hoffmann, M. R. 1989. Hydroxyalkylsulfonate formation: its role as a S(IV) reservoir in atmospheric water droplets. *Atmos. Environ. 23*, 985–997.

Pandis, S. N. and Seinfeld, J. H. 1991. Should bulk cloudwater samples obey Henry's law? *J. Geophys. Res. 96D*, 10791–10798.

Perdue, E. M. and Beck, K. C. 1988. Chemical consequences of mixing atmospheric droplets of varied pH. *J. Geophys. Res. 93D*, 691–698.

Puxbaum, H., Rosenberg, C., Gregori, M., Lanzerstorfer, C., Ober, E. and Winiwarter, W. 1988. Atmospheric concentrations of formic and acetic and related compounds in Eastern and Northern Austria. *Atmos. Environ. 22*, 2841–2850.

Rosenberg, C., Winiwarter, W., Gregori, M., Pech, G., Casensky, V. and Puxbaum, H. 1988. Determination of inorganic and organic volatile acids, NH_3, particulate SO_4^{2-}, NO_3^- and Cl^- in ambient air with an annular diffusion denuder system. *Fres. Z. Anal. Chem. 331*, 1–7.

Schell, D., Georgii, H. W., Maser, R., Jaeschke, W., Arends, B. G., Kos, G. P. A., Winkler, P., Schneider, T., Berner, A. and Kruisz, C. 1992. Intercomparison of fog water samplers. *Tellus 44B*, 612–631.

Schwartz, S. E. 1984. Gas-aqueous reactions of sulfur and nitrogen oxides in liquid water clouds. In: *SO_2, NO and NO_2 oxidation mechanisms: atmospheric considerations* (ed. J. G. Calvert). Butterworth: Boston, 173–208.

Schwartz, S. E. 1986. Mass-transport considerations pertinent to aqueous phase reactions of gases in liquid-water clouds. In: *Chemistry of multiphase atmospheric systems* (ed. W. Jaeschke). Heidelberg: Springer-Verlag, 415–471.

Talbot, R. W., Stein, K. M., Harriss, R. C. and Cofer III, W. R. 1988. Atmospheric geochemistry of formic and acetic acids at a mid-latitude temperate site. *J. Geophys. Res. 93D*, 1638–1652.

Winkler, P. 1986. Observation of fog water composition in Hamburg. In: *Atmospheric pollutants in forest areas* (ed. H. W. Georgii). Dordrecht: Reidel Publishing Company, 143–151.

Tellus B/44/5-7

Winiwarter, W., Puxbaum, H., Fuzzi, S., Facchini, M. C., Orsi, G., Beltz, N., Enderle, K. and Jaeschke, W. 1988. Organic acid gas and liquid-phase measurements in Po Valley fall-winter conditions in the presence of fog. *Tellus 40B*, 348–357.

Winiwarter, W., Brantner, B. and Puxbaum, H. 1992. Comment on: "Should bulk cloudwater or fogwater samples obey Henry's law". *J. Geophys. Res. 97*, 6075–6078.

Wobrock, W., Schell, D., Maser, R., Kessel, M., Jaeschke, W., Fuzzi, S., Facchini, M. C., Orsi, G., Marzorati, A., Winkler, P., Arends, B. G. and Bendix, J. 1992. Meteorological characteristics of the Po Valley fog. *Tellus 44B*, 469–488.