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Organic acids in different size classes of atmospheric particulate material

By J. LUDWIG and O. KLEMM, *Institute of Hydrology, University of Bayreuth, P.O. Box 101251, D-8580 Bayreuth, FRG*

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ABSTRACT

During fall and winter 1986/87, aerosol samples were collected with a 5-stage impactor in an urban, a suburban, and a rural area in Central Europe. The weak acid content of aerosol particles was characterized by buffer capacity titrations, and organic acids were determined by HPLC. C_4–C_6 dicarboxylic acids were found to be the main constituents of aerosol organic acids, with the highest concentrations occurring during a winter-time smog period. Size distributions of single species showed a maximum in the accumulation mode, indicating that these compounds have gaseous precursors. It is suggested that these precursors are of anthropogenic origin.

1. Introduction

A better understanding of the processes related to acid deposition requires knowledge of all acidic species in the troposphere. In recent years, several investigations have shown that organic acids are constituents of rain and snow (Lunde et al., 1977; Barcelona et al., 1980; Norton et al., 1983; Guiang et al., 1984; Chapman et al., 1986). They may represent a significant portion of the acidity in precipitation, especially in remote areas where acetic and formic acids contribute up to 64% of the free acidity (Keene et al., 1983). These acids are also present in the gas phase in considerable concentrations (Talbot, 1987).

Because of the high amounts of strong acids in more industrialized regions, the relative contribution of organic acids to the free acidity is low (Galloway et al., 1976). Additionally, other organic acids, like phthalic acid and several dicarboxylic acids, may be present (Kawamura and Kaplan, 1983).

In contrast, relatively little information is available about organic acids in aerosol particles (Schuetzle et al., 1973; Grosjean et al., 1978; van Vaeck and van Cauwenberghe, 1985), although these acids can form an important part of the ether-extractable fraction (Ketseridis et al., 1976; Hahn, 1980) as well as of the total acidity (Ferek et al., 1983) of aerosol particles.

Occurrence of these acids has been observed, especially during photochemical or particulate smog episodes (Schuetzle et al., 1973; Grosjean et al., 1978). Different studies have shown several possible chemical formation mechanisms, such as reactions of HO_2 radicals with aldehydes, Criegee intermediates with H_2O vapour (Calvert et al., 1985), or photochemical reactions of hydrocarbons, NO_x, ozone, and free radicals (Grosjean et al., 1978). Thus, secondary origins of organic acids are indicated.

As all processes of an aerosol particle reacting with its environment (formation, transport, reactions, deposition) are dependent on its size, we focus our interest on the distribution of organic acids in the size spectra of atmospheric particulate material.

2. Materials and methods

2.1. *Sampling sites*

Samples were taken at three locations in Northern Bavaria (Central Europe) — urban (Bayreuth, BT), suburban (Rotmain, RM) and rural (Wülfersreuth, WF) sites — during several periods between September and November 1986 (RM, WF) and in January 1987 (RM, BT). The rural site is on a west-facing slope of the Fichtelgebirge mountains and the air pollution there originates mainly from industrial regions to the west (Verhoeven et al., 1987). In the city of Bayreuth, most of the pollution arises from coal and wood-fired domestic heating. January measurements include a smog episode with high concentrations of total particulate matter (TPM).

2.2. *Sampling of aerosols*

A model LP 1150 AERAS 5-stage low pressure impactor (Fa. Hauke, Vienna, Austria) was used to sample aerosol particles, separating the particles into the following aerodynamic equivalent diameter (Dp) ranges (with $\Delta \log \mathrm{Dp}$ being constant for each stage):

stage 1: 0.15–0.45 μm;
stage 2: 0.45–1.35 μm;
stage 3: 1.35–4.05 μm;
stage 4: 4.05–12.20 μm;
stage 5: >12.20 μm (Berner, personal communication 1986).

Teflon foils were used as impaction surfaces as they provided low blank values and were easy to handle. Particles with diameters <0.15 μm were collected on a backup-filter (Whatman GM-A No. 1851865). The impactor was operated at a constant flow rate of 26 m^3 h^{-1}. To provide a sufficient amount of material for analysis, sampling periods varied from 4 to 48 h, according to the extent of air pollution. Due to effects of inlet design, bounce-off, and blow-off phenomena, reduced collection efficiency has to be considered mainly for large particles (Klockow, 1982). From comparison with measurements of a nearby monitoring station of the Bayerisches Landesamt für Umweltschutz with a filter sampling device (Filterinstrument: FH 62.I, Fa. Frieseke & Hoepfner), a total efficiency (for our sampling system) of 24–40% was calculated. A sampling efficiency in this order of magnitude has also been reported for other impactors, which were run with similar impaction surfaces (Walsh et al., 1978; Lawson, 1980).

2.3. *Analytical procedure*

Collected samples were leached twice (30 min per leaching) in an ultrasonic bath with 10 ml of double distilled water. Preliminary studies showed that this procedure yields 98% of the water-soluble fraction part of the collected aerosol particles. The extracts were mixed, filtered (Sartorius 11106 — blanks below detection limit), and stored in a refrigerator until analysis.

Analysis of weak acids was carried out with a HPLC (model: Gilson Abimed, column: Interaction ORH-801 (at 35°C), pressure: ≈ 10 MPa, eluent: H_2SO_4 (pH 2.1), flow rate: 0.54 ml min^{-1}, detection: UV at $\lambda = 210$ nm). Acids were identified by comparing their retention time with those of standard solutions. In Table 1, the acids employed as reference substances and their detection limits are listed. The sensitivity of the UV-detector is highly dependent on the structure and functional groups of the organic acids, leading to high detection limits for the long-chain aliphatic acids. Oxalic acid, the most polar of the investigated acids, had the lowest retention time and could not be sufficiently separated from the nitrate peak. All other acids that we used as reference species eluted after the nitrate peak.

To determine if all weak acids present in solution were analysed, the results were compared with data from a titration technique

Table 1. *Detection limits of organic acids (HPLC)*

	Detection limit (mol l^{-1})
acetic acid	2.7×10^{-4}
formic acid	3.6×10^{-4}
propionic acid	4.0×10^{-4}
lactic acid	3.1×10^{-7}
butyric acid	5.7×10^{-4}
isobutyric acid	2.9×10^{-4}
valeric acid	1.0×10^{-2}
isovaleric acid	6.7×10^{-3}
oxalic acid	7.4×10^{-7}
malonic acid	1.1×10^{-4}
succinic acid	2.0×10^{-4}
fumaric acid	1.4×10^{-8}
maleic acid	1.6×10^{-7}
oxaloacetic acid	1.2×10^{-6}
malic acid	1.4×10^{-6}
tartaric acid	3.3×10^{-5}
methyl-succinic acid	2.4×10^{-4}
glutaric acid	2.1×10^{-4}
2-oxoglutaric acid	1.3×10^{-6}
adipic acid	2.8×10^{-4}

(Hantschel and Klemm, 1987). The slope of the titration curve,

$$\beta(\Delta\mathrm{pH}) = \frac{\Delta c_{\mathrm{tit}}}{\Delta\mathrm{pH}} \qquad (1)$$

Δc_{tit}: amount of added base (or acid) per sample volume

is, for low values of ΔpH, considered to be identical with the buffer capacity

$$\beta(\mathrm{pH}) = \frac{\mathrm{d}c_{\mathrm{tit}}}{\mathrm{dpH}} \qquad (2)$$

(cf. Stumm and Morgan, 1981).

If concentration c_a and dissociation constant K_a are known for one of the weak acids present, its contribution to the buffer capacity $\beta(\mathrm{pH})$ can be computed from eq. (3):

$$\beta_{\mathrm{w.a.},i}(\mathrm{pH}) = 2.303 \times \frac{c_{a,i} \times K_{a,i} \times [\mathrm{H_3O^+}]}{(K_{a,i} + [\mathrm{H_3O^+}])^2}, \qquad (3)$$

$\beta_{\mathrm{w.a.},i}$: buffer capacity due to ith weak acid,
$K_{a,i}$: dissociation constant of ith weak acid,
c_a: concentration of ith weak acid.

The buffer capacity due to strong acids in aqueous solutions is only dependent on the pH:

$$\beta_{\mathrm{s.a.}}(\mathrm{pH}) = 2.303 \times \left(\frac{K_w}{[\mathrm{H_3O^+}]} + [\mathrm{H_3O^+}]\right). \qquad (4)$$

If, in a certain range of pH, the titrated buffer capacity $\beta(\Delta\mathrm{pH})$ accounts for more than the sum of that computed from analytical results, $\beta_{\mathrm{s.a.}} + \sum_i \beta_{\mathrm{w.a.},i}(\mathrm{pH})$, one or more additional weak acids are present. Their concentration can be calculated (Hantschel and Klemm, 1987) from $\beta_{\mathrm{unknown}}(\mathrm{pH})$, which is the difference between titrated and computed buffer capacities:

$$\beta_{\mathrm{unknown}}(\mathrm{pH}) = \beta(\Delta\mathrm{pH}) - \left(\beta_{\mathrm{s.a.}}(\mathrm{pH}) + \sum_i \beta_{\mathrm{w.a.},i}(\mathrm{pH})\right). \qquad (5)$$

To give a measure for the aerosol-phase acid content in air, we calculated the buffer capacities $\beta^a(\mathrm{pH})$ in the dimension equiv. m^{-3} with

$$\beta^a(\mathrm{pH}) = \beta(\mathrm{pH}) \times \frac{\text{volume of dilution water}}{\text{volume of air sample}}. \qquad (6)$$

For titration, an aliquot of the sample was deaerated with purified N_2 to remove CO_2. If necessary, the samples were acidified down to pH 3.6–3.7 with HCl (0.01 mol l^{-1}) and subsequently titrated to pH 8.4 with 5×10^{-4} mol l^{-1} NaOH. Preliminary tests showed that the recovery for volatile species such as acetic acid is in the range of 98%. More details are given by Hantschel and Klemm (1987). To compute buffering of HSO_4^-, NH_4^+, and Al^{3+}, their concentrations were determined (NH_4^+: photometry (Frevert, 1983); Al^{3+}: AAS (VARIAN AA 20); SO_4^{2-}: Ion-chromatography (GILSON ABIMED, column: HAMILTON RPR-X 100)) and $\beta_{\mathrm{w.a.},i}$ were calculated using eq. (3). β_{Al} was calculated assuming the following reactions (Bartels and Block, 1985)

$$Al^{3+} + H_2O \rightleftharpoons Al(OH)^{2+} + H^+ \quad (\mathrm{p}K_a = 4.9) \qquad (7)$$

$$Al(OH)^{2+} + H_2O \rightleftharpoons Al(OH)_2^+ + H^+ \quad (\mathrm{p}K_a = 5.3) \qquad (8)$$

$$Al(OH)_2^+ + H_2O \rightleftharpoons Al(OH)_3 + H^+ \quad (\mathrm{p}K_a = 5.9). \qquad (9)$$

3. Results

In the samples from RM (September–November) and WF, no weak acids were found with HPLC. Results of the buffer capacity titrations (see, for example, Fig. 1) confirmed that no weak acids in concentrations >0.2 nequiv. m^{-3} were present in these samples. However weak organic acids were present in January urban, and suburban small (stages 1 and 2) particles and could be partly identified. All of the identified acids were dicarboxylic acids. Figs. 2 and 3 show the ionchromatogram and the β^a plots of a sample with high organic acid content. Both methods demonstrate that further unidentified acids were present: in the range of pH 4.8–6.0, the identified acids explain the measured buffering capacity very well (Fig. 3). Maxima of $\beta^a_{\mathrm{unknown}}$ occur at pH 4.2 and pH >6.5. While buffering at pH >6.5 could be partly explained by slow reactions of Al-species (Parnell, 1981), thus deprotonating at higher pH-values than predicted by eqs. (3) and (7)–(9), the maximum at pH 4.2 indicates that there is at least one acid with a pK_a value of about 4.2 present, which might be identical with one of the unknown acids, org1 or org2, in the ionchromatogram.

The unidentified acid org2 was found in all

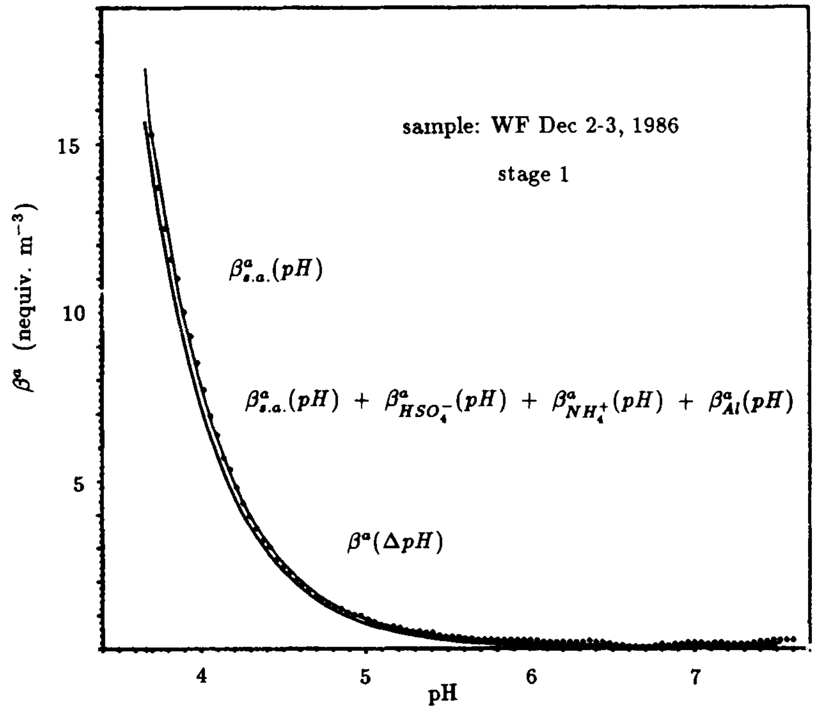

Fig. 1. Buffer capacity plot of a sample with no HPLC-detectable organic acid content. The absence of differences between the measured $\beta^a(\Delta pH)$ points and the buffer capacity calculated from ion analysis (upper line) shows that there is no buffering due to weak organic acids. Lower line: calculated buffer capacity due to strong acids.

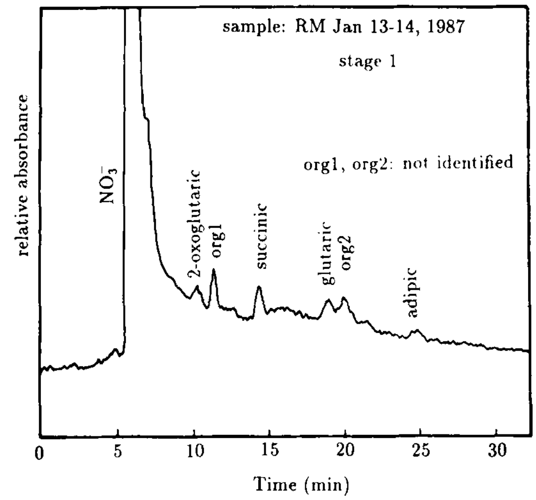

Fig. 2. Ion chromatogram for a sample with high organic acid content.

samples in which any organic acid could be determined. Succinic and glutaric acid are also main constituents (Table 2). They were also found by Grosjean et al. (1978) and Ferek et al. (1983) to be important organic acids in aerosol particles. The reported concentrations for glutaric and adipic acids of $c = 1.5$–3.5 nmol m^{-3} (Grosjean et al., 1978) and $c = 10$ nmol m^{-3} (Schuetzle et al., 1973) are in good agreement with our data of max. 4–10 nmol m^{-3} (corrected for sampling efficiency: 25 nmol m^{-3}), which were measured during a smog episode. We could find organic acids only in particles with diameters $Dp < 1.35$ μm, with two exceptions in the size class 1.35–4.05 μm. Fig. 4 shows the mass distribution of succinic acid with an extended maximum in the accumulation mode. Particles of this mode result mainly from gas-to-particle conversion processes (Prospero et al., 1983). Short-term variations may give valuable indi-

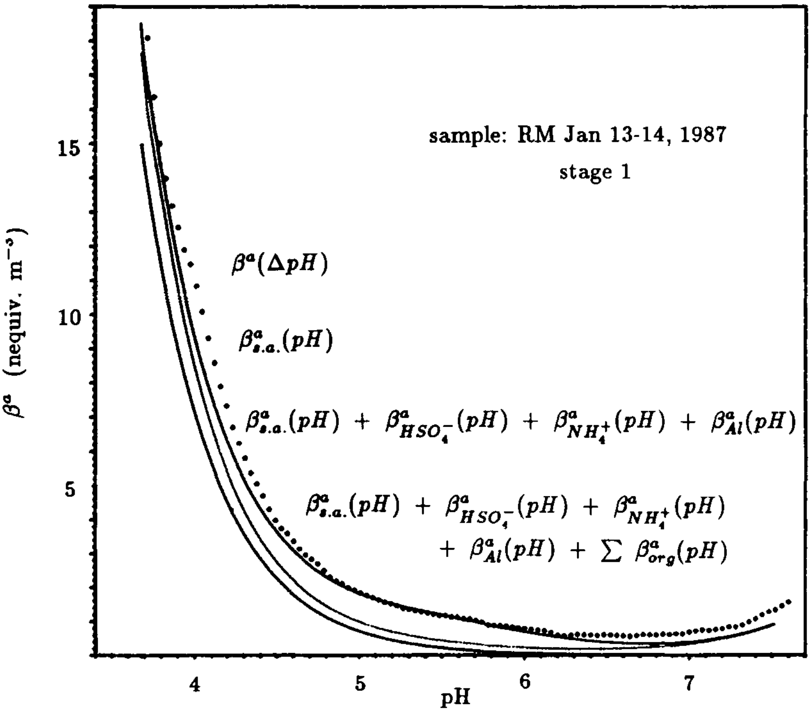

Fig. 3. Buffer capacity plot of a sample with high organic acid content. Lowest line: calculated buffer capacity due to strong acids. Second line: buffer capacity due to strong acids and analysed inorganic ions. The third line includes the buffer capacity of the organic acids analysed by HPLC. Differences between the values of the measured $\beta^a(\Delta pH)$ points and the third line show that there is at least one more weak acid present in considerable concentrations.

Table 2. *Maximum concentrations of organic acids and relative frequency in samples with detectable organic acids*

	Relative frequency (%)	c_{max} (nmol m^{-3})
org2	100.0	—
succinic acid	45.5	8.612
org3	36.4	—
glutaric acid	30.3	4.336
2-oxoglutaric acid	18.2	0.975
org1	18.2	—
adipic acid	12.1	10.140

cations to principle formation mechanisms. For the unknown acid org2, it was possible to determine its concentration continuously for two days (Fig. 5). This compoonent shows no clear diurnal variation and behaves approximately in the same way as the TPM. Slight maxima can be recognized in the afternoon.

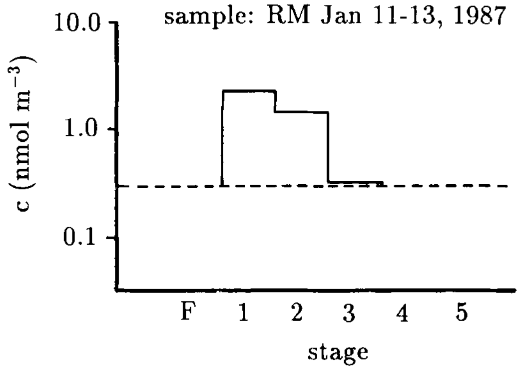

Fig. 4. Size distribution of succinic acid in the suburban sampling site (F: backup filter).

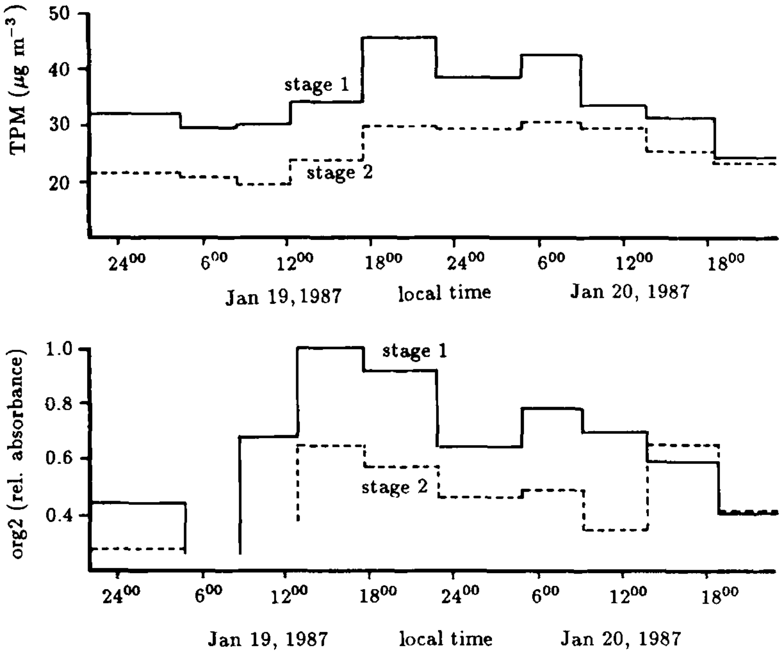

Fig. 5. Concentrations of TPM and the unknown acid org2 during a smog period in the city of Bayreuth. No acid org2 could be detected on the backup filter or on stages 4–5.

4. Discussion

The results indicate that the organic acid fraction of aerosol particles consists mainly of dicarboxylic acids. The vapour pressure of these acids is lower by a factor of between 10^2 and 10^4 than that of the corresponding monocarboxylic acids, particularly formic and acetic acid (Table 3), which dominate in the gas-phase (Talbot, 1987). The values are especially low at the low temperatures of our winter-time sampling period. There remains some doubt concerning the reasons for the absence of formic and acetic acid in our aerosol samples. They could have volatilized during sampling as a result of the considerable pressure drop in the impactor in stages 1 and 2. However, their high vapour pressures indicate that these acids should be mainly present in the gas phase, even before sampling.

Table 3. *Vapour pressure of selected organic acids (0°C) (after Schäfer and Lax, 1960)*

	p (Pa)
formic acid	$1.06 \times 10^{+3}$
acetic acid	$4.45 \times 10^{+2}$
propionic acid	$9.52 \times 10^{+1}$
butyric acid	$2.13 \times 10^{+1}$
isobutyric acid	$4.67 \times 10^{+1}$
oxalic acid	1.81×10^{-2}
malonic acid	1.97×10^{-2}
succinic acid	3.91×10^{-2}
glutaric acid	5.36×10^{-1}
adipic acid	$1.06 \times 10^{\pm 0}$

All acids we found were present in the particles of the accumulation mode. This behaviour was observed by Van Vaeck and Van Cauwenberghe (1985) for other acids too, and indicates that the acids in particulates have gaseous precursors.

Grosjean et al. (1978) described formation of dicarboxylic acids from irradiated cyclopentene-NO_x and cyclohexene-NO_x mixtures in smog chamber experiments. Cyclopentene and cyclohexene are constituents of gasoline and automobile exhaust and as such are present in urban air. Because maximum concentrations in our investigation are about 5–10 times higher than those of Grosjean et al. (1978), further sources should be taken into consideration. We suppose that oxidation of coal and wood in house heating could be a primary source of dicarboxylic acids or could supply a variety of gaseous precursors, e.g., aldehydes (Lipari et al., 1984), for secondary dicarboxylic acids.

As diurnal variations are not well marked, formation mechanisms seem not to be controlled directly by solar radiation. The data base is not sufficient to give conclusive indications about source strengths and atmospheric lifetimes of the acids found. For more detailed investigations of these processes, analytical procedures should be improved, for example by use of a conductivity detector in the HPLC analysis. Also, collecting particulate samples divided into two fractions (DP $<2\ \mu$m and DP $>2\ \mu$m) could allow one to measure organic acids either at lower concentrations or with a better time resolution without losing essential information.

5. Conclusions

During a smog episode, organic, mainly dicarboxylic, acids are found in atmospheric particulate material of an urban area at concentrations up to 25 μmol m^{-3} for single compounds. Size distributions of single acids in aerosols indicate that they have gaseous precursors, mainly from combustion processes. Further research is needed to understand formation mechanisms and the role of these acids in the chemistry of highly polluted air.

6. Acknowledgements

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