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Seasonal cycle and temperature dependence of pinene oxidation products, dicarboxylic acids and nitrophenols in fine and coarse air particulate matter

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Abstract. Filter samples of fine and coarse air particulate matter (PM) collected over a period of one year in central Europe (Mainz, Germany) were analyzed for water-soluble organic compounds (WSOCs), including the α- and β-pinene oxidation products pinic acid, pinonic acid and 3-methyl-1,2,3-butanetricarboxylic acid (3-MBTCA), as well as a variety of dicarboxylic acids and nitrophenols. Seasonal variations and other characteristic features in fine, coarse, and total PM (TSP) are discussed with regard to aerosol sources and sinks in comparison to data from other studies and regions. The ratios of adipic acid and phthalic acid to azelaic acid indicate that the investigated aerosol samples were mainly influenced by biogenic sources. A strong Arrhenius-type correlation was found between the 3-MBTCA concentration and inverse temperature ($R^2 = 0.79$, $n = 52$, E_a=126 ± 10 kJ mol^{-1}, temperature range 275–300 K). Model calculations suggest that the temperature dependence observed for 3-MBTCA can be explained by enhanced photochemical production due to an increase of hydroxyl radical (OH) concentration with increasing temperature, whereas the influence of gas-particle partitioning appears to play a minor role. The results indicate that the OH-initiated oxidation of pinonic acid is the rate-limiting step in the formation of 3-MBTCA, and that 3-MBTCA may be a suitable tracer for the chemical aging of biogenic secondary organic aerosol (SOA) by OH radicals. An Arrhenius-type temperature dependence was also observed for the concentration of pinic acid ($R^2 = 0.60$, $n = 56$, E_a=84 ± 9 kJ mol^{-1}); it can be tentatively explained by the temperature dependence of biogenic pinene emission as the rate-limiting step of pinic acid formation.

1 Introduction

Water-soluble organic compounds (WSOCs) are major components of atmospheric aerosols, accounting for up to ∼ 50% of the organic fraction of particulate matter. They can influence the optical properties and hygroscopicity of aerosol particles and their effects on climate. WSOCs originate from primary emissions like fossil fuel combustion and biomass burning as well as from secondary formation in the atmosphere, i.e., photooxidation of anthropogenic or biogenic precursors (Pöschl, 2005).

Organic acids are a prominent group of WSOCs and were found in urban, rural, marine and polar aerosols in various regions around the world as detailed below (Kawamura and Ikushima, 1993; Kawamura et al., 1996b; Kawamura and Usukura, 1993). This group includes monocarboxylic acids, dicarboxylic acids, oxocarboxylic acids and tricarboxylic acids. The total dicarboxylic acids account for 0.3–11% of WSOC (Pavuluri et al., 2010 and references therein) and oxalic acid, malonic acid and succinic acid (C_2-C_4) are the most abundant species in the dicarboxylic acid group (Kawamura and Ikushima, 1993). Dicarboxylic acids originate from a wide range of sources. Primary sources include motor exhaust (Kawamura and Kaplan, 1987), biomass combustion (Kundu et al., 2010; Lefer et al., 1994; Legrand

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and DeAngelis, 1996; Narukawa et al., 1999) and oceanic emissions (Mochida et al., 2003b). Secondary formation sources are the photooxidation of unsaturated fatty aids and cyclic alkenes (Hatakeyama et al., 1987; Kawamura et al., 1996a). The photooxidation of biogenic hydrocarbons is a major source of secondary organic aerosol (SOA) (Hoffmann et al., 1997), and SOA formation by oxidation of pinene and other terpenes has been studied extensively (Hallquist et al., 2009). Pinic acid as a dicarboxylic acid and pinonic acid as an oxocarboxylic acid are major products of the ozonolysis or OH-initiated oxidation of pinene (here and below pinene stands for both α- and β-pinene) (Atkinson and Arey, 2003; Hatakeyama et al., 1989, 1991; Yu et al., 1999a). Further reaction of the initial oxidation products of pinene leads to highly oxidized, acyclic, polar compounds (3-hydroxyglutaric acid and 3-methyl-1,2,3-butanetricarboxylic acid, 3-MBTCA) (Szmigielski et al., 2007; Kourtchev et al., 2009; Jaoui et al., 2005). 3-MBTCA is formed by OH-initiated oxidation of *cis*-pinonic acid (Szmigielski et al., 2007) and was first detected in aerosol samples from Amazonia and Belgium (Kubatova et al., 2000, 2002). Another prominent group of WSOCs are nitrophenols like 2-nitrophenol and 4-nitrophenol, which have been found in urban and rural aerosol, rainwater and snow samples. They originate from primary sources including motor vehicle exhaust (Nojima et al., 1983; Tremp et al., 1993), coal and wood combustion, as well as decomposition and hydrolysis reactions of herbicides and insecticides (Shafer and Schonherr, 1985). Moreover, they are formed by nitration of phenol and the transformation of benzaldehyde under photochemical smog conditions (Grosjean, 1985; Luttke and Levsen, 1997; Luttke et al., 1997). Road traffic is considered to be the main source of nitrophenols.

Nitrophenols are usually analyzed by gas chromatography coupled with a mass spectrometer (GC/MS), with an electron capture detector (GC-ECD), or with a nitrogen phosphorous detector (GC-NPD) (Herterich, 1991; Leuenberger et al., 1985; Luttke et al., 1997). Belloli et al. (1999) used high performance liquid chromatography coupled with a diode array detector (HPLC-DAD) for nitrophenol detection. Most studies of carboxylic acids used GC/MS after derivatization, i.e., conversion of the acids into methyl- or butylesters (Kawamura and Ikushima, 1993). Römpp et al. (2006) and Warnke et al. (2006) applied high performance liquid chromatography coupled with a mass spectrometer (HPLC/MS) for the analysis of organic acids in aerosol samples.

In this study, we apply HPLC/MS for the analysis of nitrophenols as well as carboxylic acids (aliphatic C_5-C_{16} dicarboxylic acids, phthalic, pinic and pinonic acid, 3-MBTCA) in a large set of fine and coarse aerosol particle samples collected over a period of one year in central Europe (Mainz, Germany, June 2006 to May 2007).

2 Methods

2.1 Collection of filter samples

Aerosol samples were collected on glass fiber filters (Pall Corporation, Type A/A, 102-mm diameter) over a period of one year in Mainz, Germany (130 m a.s.l., June 2006–May 2007). The sampling station was positioned on a mast at the top of the Max Planck Institute for Chemistry (MPIC, ∼5 m above the flat roof of the 3-story building) on the campus of the University of Mainz (49°59′31.36″ N and 8°14′15.22″ E). The air masses sampled at MPIC represent a mix of urban and rural continental boundary layer air in central Europe (Fröhlich-Nowoisky et al., 2009). A high-volume dichotomous sampler (Solomon et al., 1983) was used to separate and collect coarse and fine aerosol particles on a pair of glass fiber filters. The sampler was operated with a rotary vane pump (Becker VT 4.25) at a total flow rate of approximately 300 $\mathrm{L\,min^{-1}}$, corresponding to a nominal cut-off diameter of ∼3µm. Coarse particles with aerodynamic diameters larger than the cut-off were collected through a virtual impactor operated in line with the inlet (∼27 $\mathrm{L\,min^{-1}}$), and fine particles with aerodynamic diameters smaller than the cut-off were collected from the main gas flow perpendicular to the inlet (∼270 $\mathrm{L\,min^{-1}}$).

The sampling period was generally ∼7 d, corresponding to a sampled air volume of approximately 3000 $\mathrm{m^3}$. A few samples were collected over shorter periods (1–5 d, ∼ $400-2000\,\mathrm{m^3}$). A list of all investigated air filter samples (57 coarse and 58 fine particle samples) and of the corresponding sampling times and volumes is given in the online supplement (Tables S1 and S2).

For the investigation of seasonal trends, the air samples were grouped into summer (June, July and August, JJA) (coarse: 18; fine: 18), autumn (September, October and November, SON) (coarse: 14; fine: 14), winter (December, January and February, DJF) (coarse: 12; fine: 13) and spring (March, April and May, MAM) (coarse: 13; fine: 13). Before use, all glass fiber filters were decontaminated by baking at 500 °C over night. Loaded filters were packed in aluminum foil (also prebaked at 500 °C), and stored in a freezer at −80 °C until WSOC extraction (Fröhlich-Nowoisky et al., 2009).

2.2 Sample extraction and analysis (HPLC/MS)

A filter aliquot (typically 1/8 sector) was transferred into a 7 mL glass vial with a PTFE-coated cap and extracted with 2 mL of a water-methanol mixture (methanol volume fraction 10 %, water: chromatography grade, Merck, Darmstadt, Germany; methanol: LC-MS grade, Merck, Darmstadt, Germany). The sample vials were sonicated for 30 min in an ice bath. The extract solution was collected using an Eppendorf pipette with polyethylene (PE) tips. Subsequently, the filters were extracted for the second time following the same

Table 1. Molar masses, retention time and detection limits of the investigated organic compounds.

Compound	M[a] g mol^{-1}	RT[b] min	LOD[c] nmol L^{-1}	LOQ[d] nmol L^{-1}	ELOD_coarse[e] ng m^{-3}	ELOQ_coarse[f] ng m^{-3}	ELO_fine[g] ng m^{-3}	ELOQ_fine[h] ng m^{-3}
Glutaric Acid (C_5)	132	7.59	14.36	47.88	0.02	0.08	0.03	0.09
Adipic Acid (C_6)	146	9.01	3.01	10.03	0.01	0.02	0.01	0.02
Pimelic Acid (C_7)	160	10.35	2.69	8.96	0.01	0.02	0.01	0.02
Suberic Acid (C_8)	174	11.59	19.22	64.07	0.04	0.14	0.05	0.16
Azelaic Acid (C_9)	188	12.75	19.10	63.65	0.05	0.15	0.05	0.17
Sebacic Acid (C_{10})	202	13.87	1.83	6.09	0.005	0.02	0.01	0.02
Dodecanedioic Acid (C_{12})	230	15.84	1.68	5.60	0.005	0.02	0.01	0.02
Tridecanedioic Acid (C_{13})	244	17.17	1.74	5.80	0.01	0.02	0.01	0.02
Tetradecanedioic Acid (C_{14})	258	16.77	1.62	5.39	0.01	0.02	0.01	0.02
Hexadecanedioic Acid (C_{16})	286	19.54	1.29	4.30	0.005	0.02	0.01	0.02
Phthalic Acid (Ph)	166	10.72	2.85	9.50	0.01	0.02	0.01	0.02
3-Methyl-1,2,3-butanetricarboxylic acid (3-MBTCA)	204	9.45	0.59	1.98	0.002	0.01	0.002	0.01
Pinic Acid	186	11.04	1.90	6.35	0.004	0.01	0.005	0.02
Pinonic Acid (PA)	184	13.88	18.06	60.20	0.04	0.14	0.05	0.16
4-Nitrocatechol	155	12.30	20.10	67.00	0.04	0.13	0.04	0.15
2-Nitrophenol	138	14.18	17.28	57.61	0.03	0.10	0.03	0.11
4-Nitrophenol	138	14.86	11.58	38.60	0.02	0.07	0.02	0.08

[a] molar mass;
[b] retention time;
[c] limit of detection of the HPLC/MS method defined as 3-fold standard deviation of background signal;
[d] limit of quantification of the HPLC/MS method defined as 10-fold standard deviation of background signal;
[e] effective limit of detection for coarse particulate matter (7-day sample);
[f] effective limit of quantification for coarse particulate matter (7-day sample);
[g] effective limit of detection for fine particulate matter (7-day sample);
[h] effective limit of quantification for fine particulate matter (7-day sample).

procedure and the extract solutions were combined and used directly for HPLC/MS analysis (Römpp et al., 2006).

The applied HPLC/MS system consists of a thermostated auto-sampler (Series 200, Perkin Elmer, Norwalk, Connecticut, USA), a degasser and a quaternary pump (1100 Series, Agilent Technologies, Waldbronn, Germany), and a hybrid Qq-TOF mass spectrometer QSTAR (Applied Biosystems MDS SCIEX, Toronto, Canada) with an electrospray ion source (ESI). The ESI source was operated in the negative mode with an ionization voltage of 4 kV at 400 °C. The selected *m/z* range was 120 to 300 Da. The data processing was performed with the software package Analyst (version QS1.1, Applied Biosystems MDS SCIEX, Toronto, Canada). The room and column temperature were kept at 296 K, and the injection volume was 100 µL. The chromatographic separation of all investigated compounds was performed with a ReproSil-Pur C_{18}-AQ column (250 mm × 2.1 mm I.D., 5 µm particle size) in a stainless steel cartridge (Dr. Maisch GmbH, Ammerbuch, Germany) at a flow rate of 400 µ L min^{-1}. For the first 0.5 min of each chromatographic run, the composition of the mobile phase was kept at 100% water with formic acid (HCOOH volume fraction 0.1%, Chromasolv, Sigma, Seelze, Germany). Then the acetonitrile (ACN, Chromasolv, Sigma, Seelze, Germany) content was increased to 15% within 3.5 min, and further to 95% within 16 min. Finally, the mobile phase was reset to initial conditions within 3 min, and the column was equilibrated for 6 min before the next run (Winterhalter et al., 2009). Chromatograms were recorded using the deprotonated molecule signals of the analytes ($[M\text{-}H]^-$ detected at $m/z = M\text{-}1$). The molar masses and retention times of the investigated compounds are listed in Table 1.

The analytes were identified by comparison of retention time and mass spectra with reference standards (Sigma/Fluka, purity ≥ 98%; 3-MBTCA from M. Claeys, University of Antwerp) (Winterhalter et al., 2009). As pure *cis*-pinic acid was not available, we used the mixture of *cis*- and *trans*-pinic acid as reference standard and assumed a response factor of unity between the two isomers for the quantification of *cis*-pinic acid in aerosol filter samples. Due to limited availability and purity of the 3-MBTCA reference standard, we used a calibration curve obtained with 1,3,5-pentatricarboxylic acid and assumed a response factor of unity for the quantification of 3-MBTCA. Small aliphatic dicarboxylic acids consisting of less than five carbon atoms were eluted in the dead volume of the chromatographic column and were thus not investigated in this study.

For every analyte, a linear calibration function of peak area vs. concentration was established and applied for quantification (correlation coefficient $R^2 > 0.98$, number of data points $n = 12$). As detailed in Table 1, the analytical limits of detection (LOD, 3 s method, 0.59–20.10 nmol L^{-1},) and quantification (LOQ, 10 s method, 1.98–67.00 nmol L^{-1}) correspond to effective limits of 0.002–0.05 ng m^{-3} (ELOD) and 0.01–0.17 ng m^{-3} (ELOQ) for the detection and quantification of the investigated compounds in the coarse and fine aerosol samples, respectively. Measurement results for blank filter samples were generally below the LOD, except for adipic acid (C_6) and azelaic acid (C_9). For these two acids blank values larger than the LOQ, were observed and subtracted from the aerosol sample measurement results. The relative standard deviation of repeated measurements was generally less than 5%. Therefore, the precision of the measurement accounting for imprecision of sample flow control and recovery (Winterhalter et al., 2009) is estimated to be less than 20%.

Mass concentrations of the analytes in the investigated air samples were determined by scaling with the extract volume, filter aliquot fraction, and sampled air volume. Due to the operating principle of the dichotomous sampler, the coarse particle filter samples contained a contribution of fine particles corresponding to the ratio of air flow through the coarse filter to total air flow (∼1/10). To correct for this interference, 1/10 of the concentration determined for fine particles was subtracted from the concentration determined for coarse particles. All measurement results are listed in the online supplement (Tables S1 and S2). Correlation analyses were performed for all investigated compounds, and the correlation coefficients obtained for coarse and fine particle samples are also listed in the online supplement (Tables S3 and S4). Exponential fits were also performed between concentrations of investigated compounds and inverse temperature, and Arrhenius-type temperature dependencies were found for 3-MBTCA and pinic acid, which is discussed below.

2.3 Supporting data and model calculations

Ambient temperature and precipitation data were recorded on top of the 7-story building of the Institute of Atmospheric Physics of the University of Mainz, which is located less than 500 m away from the sampling site. For correlation analysis, the available temperature data (daily minimum and maximum values) were averaged over the filter sampling period (arithmetic mean values as listed in Tables S1 and S2).

Hydroxyl radical (OH) concentration data were obtained from a simulation (1998–2008) with the ECHAM/MESSy Atmospheric Chemistry model (EMAC, time resolution: 15 min, output frequency: 5 h, averaged over filter sampling period) (Jöckel et al., 2006). The OH concentration data were used for model calculations investigating the observed Arrhenius-type temperature dependence of 3-MBTCA as detailed in the online supplement and discussed below.

3 Result and discussion

3.1 Concentration levels and seasonal variations

For a series of linear dicarboxylic acids with 5 to 16 carbon atoms as well as phthalic acid, nitrophenols and pinene oxidation products investigated in this study, the observed concentration ranges, mean values and standard deviations are summarized in Table 2. For comparison we have also performed a comprehensive literature search and compiled data from other atmospheric aerosol studies and locations where these WSOCs have been analyzed.

The mean concentrations of individual dicarboxylic acids in fine particulate matter (PM_3, 0.09–3.76 ng m^{-3}) were generally lower than the values reported from polluted urban areas and megacity regions (Houston, USA; Hong Kong, and 14 economically developed or developing cities in China; 0.29–35.6 ng m^{-3}). With regard to total suspended particles (TSP = fine plus coarse particulate matter), the mean concentrations observed in Mainz (0.14–5.71 ng m^{-3}) were higher than values reported from Arctic regions (0.06–0.9 ng m^{-3}), similar to values reported from Philadelphia, USA (PM_{10}, 0.5–3.5 ng m^{-3}), and generally lower than the values reported from Tokyo, Japan, and Melpitz, Germany (PM_{10}, n.d. –25.8 ng m^{-3}). The highest mean concentrations in Mainz were observed for phthalic acid (PM_3: 3.76 ng m^{-3}; TSP: 5.71 ng m^{-3}) and for the pinene oxidation products pinic acid (PM_3: 1.51 ng m^{-3}; TSP: 2.32 ng m^{-3}) and 3-MBTCA (PM_3: 5.89 ng m^{-3}; TSP: 6.88 ng m^{-3}).

Seasonal variations of investigated compounds were studied (Figs. 1, 2 and S1), and, to our knowledge, this is the first study reporting a full annual cycle and characteristic differences in the seasonal variation of nitrophenols and 3-MBTCA. For most aliphatic dicarboxylic acids the seasonal mean concentration was highest in summer and spring, indicating biogenic or photochemical sources as discussed below (Fig. S1, online supplement). Some of the lower seasonal values found in summer could be attributed to wet deposition of water-soluble compounds due to large amount of precipitation in summer. The total precipitation recorded during the measuring period (2006–2007) amounted to 186.5 mm in summer, 107.6 mm in autumn, 136.0 mm in winter, and 121.6 mm in spring. 4-Nitrocatechol and 2-nitrophenol also exhibited maximum concentrations in summer, whereas 4-nitrophenol exhibited maximum concentrations in winter

Table 2. Mass concentrations of the investigated compounds in comparison to other studies (range, arithmetic mean and standard deviation).

Compound	Concentration ($ng\,m^{-3}$)		Particle	Location, time	Reference
	Range	Mean ± SD[a]	size		
Glutaric Acid (C_5)	0.16–6.15	1.28 ± 0.99	PM_3^b	Mainz, Germany, May 2006–June 2007	this study
		30	$PM_{2.5}^c$	14 cities, China, summer 2003	Ho et al., 2007
		22.1	$PM_{2.5}$	14 cities, China, winter 2003	Ho et al., 2007
		35.56	$PM_{2.5}$	Hong Kong (urban), summer 2006	Hu et al., 2008
		7.73	$PM_{2.5}$	USA Houston area (suburban), 2000	Yue and Fraser, 2004
		2.3	PM_{10}^d	Philadelphia, USA, July–August 1999	Ray and McDow, 2005
		6.8	PM_{10}	Melpitz, Germany (rural), 2005	van Pinxteren and Herrmann, 2007
	1.24–18.41	2.56 ± 1.27	TSP^e	Mainz, Germany, May 2006–June 2007	this study
		0.9	TSP	Alert, Arctic, July 1987–June 1988	Kawamura et al., 1996a
		11	TSP	Tokyo, Japan (urban), July 1989	Kawamura and Yasui, 2005
		23.1	TSP	Tokyo, Japan (urban), June 1989	Kawamura and Yasui, 2005
		18.2	TSP	Tokyo, Japan (urban), November 1989	Kawamura and Yasui, 2005
Adipic Acid (C_6)	0.17–2.71	0.78 ± 0.57	PM_3	Mainz, Germany, May 2006–June 2007	this study
		23.5	$PM_{2.5}$	14 cities, China, summer 2003	Ho et al., 2007
		15	$PM_{2.5}$	14 cities, China, winter 2003	Ho et al., 2007
		11.376	$PM_{2.5}$	Hong Kong (urban), summer 2006	Hu et al., 2008
		7.52	$PM_{2.5}$	USA Houston area (suburban), 2000	Yue and Fraser, 2004
		2	PM_{10}	Philadelphia, USA, July–August 1999	Ray and McDow, 2005
		13.8	PM_{10}	Melpitz, Germany (rural), 2005	van Pinxteren and Herrmann, 2007
	0.59–4.69	1.51 ± 0.84	TSP	Mainz, Germany, May 2006–June 2007	this study
		0.82	TSP	Alert, Arctic, July 1987–June 1988	Kawamura et al., 1996a
		13	TSP	Tokyo, Japan (urban), July 1989	Kawamura and Yasui, 2005
		25.8	TSP	Tokyo, Japan (urban), June 1989	Kawamura and Yasui, 2005
		14.2	TSP	Tokyo, Japan (urban), November 1989	Kawamura and Yasui, 2005
Pimelic Acid (C_7)	BDL^f-1.77	0.32 ± 0.31	PM_3	Mainz, Germany, May 2006–June 2007	this study
		6.34	$PM_{2.5}$	14 cities, China, summer 2003	Ho et al., 2007
		6.7	$PM_{2.5}$	14 cities, China, winter 2003	Ho et al., 2007
		4.564	$PM_{2.5}$	Hong Kong (urban), summer 2006	Hu et al., 2008
		2.58	$PM_{2.5}$	USA Houston area (suburban), 2000	Yue and Fraser, 2004
		1.6	PM_{10}	Melpitz, Germany (rural), 2005	van Pinxteren and Herrmann, 2007
	BDL-2.05	0.58 ± 0.39	TSP	Mainz, Germany, May 2006–June 2007	this study
		0.13	TSP	Alert, Arctic, July 1987–June 1988	Kawamura et al., 1996a
		4.6	TSP	Tokyo, Japan (urban), July 1989	Kawamura and Yasui, 2005
		9.9	TSP	Tokyo, Japan (urban), June 1989	Kawamura and Yasui, 2005
		8.2	TSP	Tokyo, Japan (urban), November 1989	Kawamura and Yasui, 2005
Suberic Acid (C_8)	0.11–1.87	0.44 ± 0.35	PM_3	Mainz, Germany, May 2006–June 2007	this study
		9.06	$PM_{2.5}$	14 cities, China, summer 2003	Ho et al., 2007
		5.98	$PM_{2.5}$	14 cities, China, winter 2003	Ho et al., 2007
		5.43	$PM_{2.5}$	USA Houston area (suburban), 2000	Yue and Fraser, 2004
		0.5	PM_{10}	Philadelphia, USA, July–August 1999	Ray and McDow, 2005
		2.1	PM_{10}	Melpitz, Germany (rural), 2005	van Pinxteren and Herrmann, 2007
	0.32–2.44	0.78 ± 0.45	TSP	Mainz, Germany, May 2006–June 2007	this study
		0.15	TSP	Alert, Arctic, July 1987–June 1988	Kawamura et al., 1996a
		2.4	TSP	Tokyo, Japan (urban), July 1989	Kawamura and Yasui, 2005
		11	TSP	Tokyo, Japan (urban), June 1989	Kawamura and Yasui, 2005
		9.1	TSP	Tokyo, Japan (urban), November 1989	Kawamura and Yasui, 2005

Table 2. Continued.

Compound	Concentration ($ng\,m^{-3}$) Range	Mean±SD[a]	Particle size	Location, time	Reference
Azelaic Acid (C_9)	0.12–4.64	1.60 ± 1.04	PM_3	Mainz, Germany, May 2006–June 2007	this study
		31.6	$PM_{2.5}$	14 cities, China, summer 2003	Ho et al., 2007
		28.9	$PM_{2.5}$	14 cities, China, winter 2003	Ho et al., 2007
		10.07	$PM_{2.5}$	USA Houston area (suburban), 2000	Yue and Fraser, 2004
		1	PM_{10}	Philadelphia, USA, July–August 1999	Ray and McDow, 2005
		2.1	PM_{10}	Melpitz, Germany (rural), 2005	van Pinxteren and Herrmann, 2007
	0.13–1.45	2.91 ± 1.25	TSP	Mainz, Germany, May 2006–June 2007	this study
		0.26	TSP	Alert, Arctic, July 1987-June 1988	Kawamura et al., 1996a
		11	TSP	Tokyo, Japan (urban), July 1989	Kawamura and Yasui, 2005
		15.1	TSP	Tokyo, Japan (urban), June 1989	Kawamura and Yasui, 2005
		20.6	TSP	Tokyo, Japan (urban), November 1989	Kawamura and Yasui, 2005
Sebacic Acid (C_{10})	0.06–1.31	0.24 ± 0.20	PM_3	Mainz, Germany, May 2006–June 2007	this study
		2.49	$PM_{2.5}$	14 cities, China, summer 2003	Ho et al., 2007
		4.4	$PM_{2.5}$	14 cities, China, winter 2003	Ho et al., 2007
		2.58	$PM_{2.5}$	USA Houston area (suburban), 2000	Yue and Fraser, 2004
		n.d.[g]	PM_{10}	Melpitz, Germany (rural), 2005	van Pinxteren and Herrmann, 2007
	0.13–1.45	0.39 ± 0.24	TSP	Mainz, Germany, May 2006–June 2007	this study
		1.1	TSP	Tokyo, Japan (urban), July 1989	Kawamura and Yasui, 2005
		4.9	TSP	Tokyo, Japan (urban), June 1989	Kawamura and Yasui, 2005
		7.3	TSP	Tokyo, Japan (urban), November 1989	Kawamura and Yasui, 2005
Dodecanedioic Acid (C_{12})	BDL-1.24	0.09 ± 0.17	PM_3	Mainz, Germany, May 2006–June 2007	this study
		0.91	$PM_{2.5}$	14 cities, China, summer 2003	Ho et al., 2007
		0.29	$PM_{2.5}$	14 cities, China, winter 2003	Ho et al., 2007
	BDL-1.34	0.15 ± 0.18	TSP	Mainz, Germany, May 2006–June 2007	this study
Tridecanedioic Acid (C_{13})	BDL-2.04	0.09±0.27	PM_3	Mainz, Germany, May 2006–June 2007	this study
	BDL-2.11	0.14 ± 0.29	TSP	Mainz, Germany, May 2006–June 2007	this study
Tetradecanedioic Acid (C_{14})	BDL-2.05	0.11 ± 0.28	PM_3	Mainz, Germany, May 2006–June 2007	this study
	BDL-2.21	0.18 ± 0.31	TSP	Mainz, Germany, May 2006-June 2007	this study
Hexadecanedioic Acid (C_{16})	BDL-2.05	0.13 ± 0.29	PM_3	Mainz, Germany, May 2006–June 2007	this study
	BDL-2.18	0.20 ± 0.31	TSP	Mainz, Germany, May 2006–June 2007	this study
Phthalic Acid (Ph)	0.69–13.38	3.76 ± 2.87	PM_3	Mainz, Germany, May 2006–June 2007	this study
		3.36	$PM_{2.5}$	Hong Kong (urban), summer 2006	Hu et al., 2008
		12.4	PM_{10}	Melpitz, Germany (rural) 2005	van Pinxteren and Herrmann, 2007
		3.5	PM_{10}	Philadelphia, USA, July–August 1999	Ray and McDow, 2005
	1.24–18.41	5.71 ± 3.73	TSP	Mainz, Germany, May 2006–June 2007	this study
3-Methyl-1,2,3-butanetricarboxylic acid (3-MBTCA)	1.6–99.3	13[h]	PM_1[i]	Hyytiälä, Finland, July–August 2005	Kourtchev et al., 2008a
	1.9–74	15.8	$PM_{2.5}$	K-puszta, Hungary, summer 2003	Kourtchev et al., 2009
		5.2	$PM_{2.5}$	Jülich, Germany, July 2003	Kourtchev et al., 2008b
	n.d.–1.6		$PM_{2.5}$	Balbina, Brazil, March–April 1998	Kubatova et al., 2000[j]
	15.8–130	41.95	$PM_{2.5}$	Research Triangle Park, NC, USA, summer 2003	Lewandowski et al., 2007[k]
	12.0–62.9		$PM_{2.5}$	SEARCH network, June 2004	Gao et al., 2006[l]
	0.13–26.00	5.89 ± 6.15	PM_3	Mainz, Germany, May 2006–June 2007	this study
	0.13–29.72	6.88 ± 7.04	TSP	Mainz, Germany, May 2006–June 2007	this study
	3.47–25.9		TSP	Mt. Tai, China, May–June 2006	Fu et al., 2009b
	0.005–2.613	0.647 ± 0.786	TSP	Canadian high Arctic, February–June 1991	Fu et al., 2009a

Table 2. Continued.

Compound	Concentration (ng m^{-3})		Particle	Location, time	Reference
	Range	Mean±SD[a]	size		
Pinic Acid	2–29.6	7.7[h]	PM_1	Hyytiälä, Finland, July–August 2005	Kourtchev et al., 2008a
	0.6–135	12.2	PM_2	K-puszta, Hungary, summer 2003	Kourtchev et al., 2009
	1.1–21		$PM_{2.5}$	Tábua, Portugal, August 1996	Kavouras et al., 1999b
		3.0	$PM_{2.5}$	Jülich, Germany, July 2003	Kourtchev et al., 2008b
	4.5–15.5	9.98	$PM_{2.5}$	Research Triangle Park, NC, USA, summer 2003	Lewandowski et al., 2007
	0.38–4.7		$PM_{2.5}$	Hyytiälä, Finland, 2001	Warnke et al., 2006
	1.1–21		$PM_{2.5}$	Hyytiälä, Finland, 2003	Warnke et al., 2006
	0.43–3.8		$PM_{2.5}$	Jülich, Germany, 2002	Warnke et al., 2006
	0.94–12		$PM_{2.5}$	Jülich, Germany, 2003	Warnke et al., 2006
	BDL-9.05	1.51 ± 2.24	PM_3	Mainz, Germany, May 2006–June 2007	this study
	0.06–12.17	2.32 ± 2.72	TSP	Mainz, Germany, May 2006–June 2007	this study
	0.36–6.27		TSP	Mt. Tai, China, May–June 2006	Fu et al., 2009b
	0.03–1.357	0.514 ± 0.401	TSP	Canadian high Arctic, February–June 1991	Fu et al., 2009a
		2.4 ± 1.5	TSP	Pertouli, Greece, August 1998	Kavouras and Stephanou, 2002
	0.4–82.7		TSP	Pertouli, Greece, August 1998	Kavouras et al., 1999a
	0.48–0.59	0.54	TSP	Nova Scotia, Canada, July 1996	Yu et al., 1999b
		0.5	TSP	San Bernadino, Canada, September 1998	Yu et al., 1999b
Pinonic Acid (PA)	7.1–98		$PM_{2.5}$	Tábua, Portugal, August 1996	Kavouras et al., 1998, 1999b
	0.91–8.2		$PM_{2.5}$	Hyytiälä, Finland, 2001	Warnke et al., 2006
	0.99–74		$PM_{2.5}$	Hyytiälä, Finland, 2003	Warnke et al., 2006
	1.1–5.9		$PM_{2.5}$	Jülich, Germany, 2002	Warnke et al., 2006
	1.4–78		$PM_{2.5}$	Jülich, Germany, 2003	Warnke et al., 2006
	BDL-5.60	0.60 ± 1.01	PM_3	Mainz, Germany, May 2006–June 2007	this study
	BDL-5.60	1.22 ± 1.33	TSP	Mainz, Germany, May 2006–June 2007	this study
	0.21–21.8		TSP	Mt. Tai, China, May–June 2006	Fu et al., 2009b
	0.038–0.108	0.069 ± 0.023	TSP	Canadian high Arctic, February–June 1991	Fu et al., 2009b
		9.7 ± 11	TSP	Pertouli, Greece, August 1998	Kavouras and Stephanou, 2002
	1–25.7		TSP	Pertouli, Greece, August 1998	Kavouras et al., 1999a
	0.13–0.39	0.26	TSP	Nova Scotia, Canada, July 1996	Yu et al., 1999b
		0.8	TSP	San Bernadino, Canada, September 1998	Yu et al., 1999b
4-Nitrocatechol	BDL-26.30	6.40 ± 17.55	PM_3	Mainz, Germany, May 2006–June 2007	this study
	BDL-28.72	4.49 ± 5.32	TSP	Mainz, Germany, May 2006–June 2007	this study
2-Nitrophenol	BDL-8.51	1.57 ± 1.45	PM_3	Mainz, Germany, May 2006–June 2007	this study
		3.5 ± 1.5	PM_5	Rome, Italy, Spring, 2003	Cecinato et al., 2005
	BDL-8.51	1.81 ± 1.70	TSP	Mainz, Germany, May 2006–June 2007	this study
4-Nitrophenol	BDL-10.22	2.48 ± 2.12	PM_3	Mainz, Germany, May 2006–June 2007	this study
		17.8 ± 5.6	PM_5	Rome, Italy, Spring 2003	Cecinato et al., 2005
	BDL-12.52	3.78 ± 2.89	TSP	Mainz, Germany, May 2006–June 2007	this study

[a] standard deviation;
[b] aerodynamic diameters < 3 µm (cut-off of the dichotomous sampler in this study);
[c] aerodynamic diameters < 2.5 µm;
[d] aerodynamic diameters < 10 µm;
[e] total suspended particles (in this study: sum of fine and coarse PM);
[f] below detection limit (ELOQ, Table 1);
[g] not detected;
[h] median value;
[i] aerodynamic diameter < 1 µm;
[j] reported as "MW 204";
[k] reported as "2-hydroxy-4-isopropyladipic acid";
[l] reported as "norpinic diperoxy acid".

(Fig. 1). The different seasonalities can be attributed to the different sources and formation pathways as discussed below.

The most pronounced seasonal cycles and summertime maxima were observed for the pinene oxidation products 3-MBTCA, pinic acid and pinonic acid (Fig. 2), which exhibited also pronounced Arrhenius-type temperature dependencies that can be attributed to photochemistry and biogenic emissions as discussed below. The average particulate concentration level decreased with increasing volatility from 3-MBTCA (non-volatile) via pinic acid (low/semi-volatile) to pinonic acid (high/semi-volatile, see online supplement).

The concentration of 3-MBTCA was generally higher in the fine particle fraction than in the coarse fraction. During summer and autumn the pinic acid concentration was also higher in the fine fraction than in the coarse fraction, but during winter and spring the concentration was similar in the fine and coarse fractions. The pinonic acid concentration was similar in the fine and coarse fractions during summer and autumns, but during winter and spring the concentration was higher in the coarse fraction. These differences may be related to the different volatilities and concentration levels of the three compounds, to seasonal differences in ambient temperature, and possibly also to seasonal differences in the overall aerosol particle size distribution and composition. Information about the latter parameters is unfortunately not available and further investigations would go beyond the scope of the present study. Nevertheless, we suggest and intend to investigate these effects and interactions in future studies, because they may be relevant for comprehensive characterisation, understanding and modelling of the sources and properties of organic aerosols.

3.2 Source attribution of dicarboxylic acids and nitrophenols

Atmospheric photooxidation of volatile and semi-volatile organic compounds is considered to be the main source of dicarboxylic acids in air particulate matter. Mochida et al. (2003a) proposed that small dicarboxylic acids containing up to 7 carbon atoms originate mostly from anthropogenic precursors. Glutaric acid (C_5) is formed upon oxidation of cyclopentene, cyclohexene and glutardialdehyde (Winterhalter et al., 2009). Adipic acid (C_6) originates mainly from the oxidation of cyclohexene in the atmosphere (Hatakeyama et al., 1987; Koch et al., 2000), and from the ozonolysis of methylene-cyclohexane and 1-methyl-cyclohexene (Koch et al., 2000). As an aromatic compound, phthalic acid is also considered to originate mostly from anthropogenic sources, including direct emission from automobile, industrial and other anthropogenic sources (manufacturing of plastics, hydrolysis of phthalate esters in the aging of plastics), and the oxidation of polycyclic aromatic hydrocarbons (PAH, Kawamura and Ikushima, 1993; Shiraiwa et al., 2009). The correlation coefficients between phthalic acid and the sum of C_5-C_7 dicarboxylic acids ($R^2 = 0.65$ for coarse particles PM and 0.47 for fine particles) suggest that these compounds originate indeed from related sources.

According to Mochida et al. (2003a), the oxidation of biogenic precursors like unsaturated fatty acids is the main source of C_8-C_{10} dicarboxylic acids (Kawamura and Gagosian, 1987; Stephanou and Stratigakis, 1993). The most abundant of these compounds was azelaic acid (C_9, 2.9 ng m^{-3} in TSP). It originates from the oxidation of unsaturated fatty acids containing a double bond at position 9 (Kawamura and Gagosian, 1987), including oleic acid, which is relatively abundant in air particulate matter and has been studied extensively (Shiraiwa et al., 2010; Zahardis and Petrucci, 2007). The concentrations of suberic acid (C_8, 0.8 ng m^{-3} in TSP) and sebacic acid (C_{10}, 0.4 ng m^{-3} in TSP) were substantially lower than that of azelaic acid. The correlation coefficients suggest that the sources of C_8 and C_{10} are similar ($R^2 = 0.71$ and 0.81 for coarse and fine PM), and related but not identical to the sources of C_9 ($R^2 = 0.36 - 0.52$, Tables S3 and S4).

Long-chain dicarboxylic acids (C_{12}-C_{16}) are generally attributed to the oxidation of ω-hydroxy fatty acids from vascular plants or other biogenic sources (Stephanou and Stratigakis, 1993). The correlation coefficients suggest that the sources of C_{12}-C_{16} are more closely related to each other ($R^2 = 0.33 - 0.97$) than to C_8-C_{10} ($R^2 = 0.07 - 0.75$) or C_9 ($R^2 = 0.00 - 0.19$, Tables S3 and S4).

According to Ho et al. (2006), the ratios of adipic acid (C_6) and phthalic acid (Ph) to azelaic acid (C_9) can be used to estimate the relative influence of anthropogenic and biogenic sources of organic aerosol. The lower values of the two ratios represent typically biogenic emission; whereas the higher values indicate influence of anthropogenic origin. Comparisons of the two ratios in this study and other location around the world were performed (Table 3).

The mean C_6/C_9 ratio in PM_3 (0.65, ranged from 0.21 to 4.35) were generally comparable with the values reported from Houston, USA and 14 economically developed or developing cities in China (0.52–0.75). With regard to TSP, the mean ratio observed in Mainz (0.58, ranged from 0.23 to 1.81) was generally lower than the other region around the world (TSP: Tokyo, Japan and Arctic, 0.69–3.15; PM_{10}: Melpitz, Germany and Philadelphia, USA, 2.00–6.57). 84% of samples in PM_3 and 91% in TSP had the ratio lower than 1.

The mean Ph/C_9value in PM_3 was 3.13 (ranged from 0.76 to 11.78). In TSP, the mean ratio (2.16, ranged from 0.60 to 11.78) was lower than the values in other region (PM_{10}, Melpitz, Germany and Philadelphia, USA, 3.50–5.90). The low values of the two ratios indicate that aerosols in Mainz were mainly influenced by biogenic sources.

2-Nitrophenol and 4-nitrophenol can be directly emitted as primary pollutants in combustion exhaust (Tremp et al., 1993), and they can also be formed as secondary pollutants by nitration of phenols in the atmosphere (Atkinson et al., 1992; Dumdei and Obrien, 1984; Grosjean, 1985; Nojima

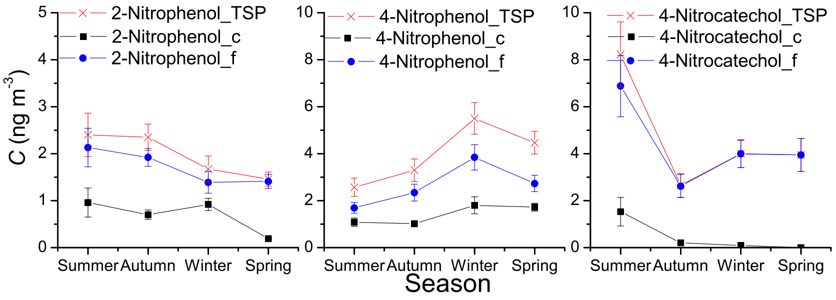

Fig. 1. Seasonal variation of 2-nitrophenol, 4-nitrophenol and 4-nitrocatechol mass concentrations in fine (f), coarse (c), and total particulate matter (TSP). The data points are mean values for different seasons (summer: JJA, autumn: SON, winter: DJF, spring: MAM). The error bars are standard errors of the mean, and the lines are to guide the eye.

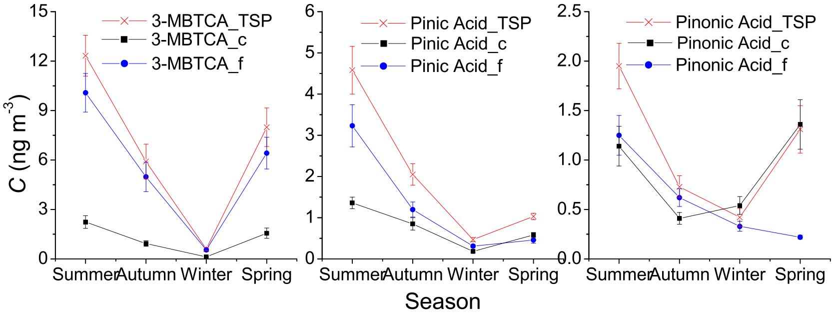

Fig. 2. Seasonal variation of pinene oxidation products: mass concentrations of 3-MBTCA, pinic acid and pinonic acid in fine (f), coarse (c), and total particulate matter (TSP). The data points are mean values for different seasons (summer: JJA, autumn: SON, winter: DJF, spring: MAM). The error bars are standard errors of the mean, and the lines are to guide the eye.

et al., 1975; Olariu et al., 2002). 2-Nitrophenol and 4-nitrophenol can originate from the irradiation of benzene-NO_x-air mixture (Nojima et al., 1975), whereas only 2-nitrophenol can form from various reaction including OH-initiated reaction in the presence of NO_x, NO_3-initiated reaction and OH-initiated reactions in the presence of NO_3 (Atkinson et al., 1992; Olariu et al., 2002). The distinctly different seasonal variations and low correlation coefficients of the two isomers of nitrophenol ($R^2 = 0.27$ and 0.33 for coarse and fine PM) indicate that their main sources are different.

The observed summer maximum and correlations with phthalic acid and various aliphatic dicarboxylic acids (R^2 up to 0.59, Table S4) suggest that atmospheric photochemistry is a major source of 2-nitrophenol. In contrast, the winter maximum of 4-nitrophenol and low correlation coefficients of with dicarboxylic acids ($R^2 < 0.32$, Table S4) suggest that primary emissions are more important for this compound than secondary formation. Interestingly, 4-nitrocatechol exhibits a summer maximum like 2-nitrophenol but no correlation with dicarboxylic acids ($R^2 < 0.11$, Table S4). These observations indicate primary sources that are enhanced during summer, which could be evaporation from soil as proposed by Gelencser et al. (2002) for humic-like substances (HULIS, Graber and Rudich, 2006). We suggest that further analyses of nitrophenols, nitrocatechol and other nitrated and oxygenated aromatic compounds by HPLC/MS may help to unravel combustion- and soil-related sources of organic particulate matter (Letzel et al., 2001; Schauer et al., 2004).

3.3 Temperature dependence of pinene oxidation products

In Fig. 3 the concentrations of 3-MBTCA, pinic acid and pinonic acid observed in the coarse and fine particle fractions and in total plotted against the inverse of average ambient temperature (275–300 K).

Each of the data sets was fitted with an Arrhenius-type expression of the form $X = A \cdot \exp{\cdot}[-E_a/(R \cdot T)]$, and the fit parameters are summarized in Table 4. The results obtained for coarse, fine particulate matter and TSP (fine plus coarse particles) were in overall agreement (Fig. 3), and for simplicity the following discussion is focused on the TSP results.

3-MBTCA exhibited a strong Arrhenius-type temperature dependence with high activation energy and correlation coefficient ($E_a = 126 \pm 10\,\mathrm{kJ\,mol^{-1}}$, $R^2 = 0.74$, Table 4). Pinic acid also exhibited a pronounced temperature dependence albeit with lower activation energy and correlation coefficient ($E_a = 84 \pm 9\,\mathrm{kJ\,mol^{-1}}$, $R^2 = 0.60$, Table 4), whereas the temperature dependence of pinonic acid was very weak

Table 3. Ratios between the mass concentrations of adipic acid, phthalic acid and azelaic acid (C_6/C_9 and Ph/C_9) in comparison to other studies.

Location	Time	C_6/C_9	Ph/C_9	Particle size	Reference
Mainz, Germany	June 2006–May 2007	0.65	3.13	PM_3	this study
14 cities, China	2003	0.52–0.74		$PM_{2.5}$	Ho et al., 2007
Houston area, USA	2000	0.75		$PM_{2.5}$	Yue and Fraser, 2004
Melpitz, Germany	2005	6.57	5.90	PM_{10}	van Pinxteren and Herrmann, 2007
Philadelphia, USA	July–August 1999	2.00	3.50	PM_{10}	Ray and McDow, 2005
Mainz, Germany	June 2006–May 2007	0.58	2.16	TSP	this study
Alert, Arctic	July 1987–June 1988	3.15		TSP	Kawamura et al., 1996a
Tokyo, Japan	1989	0.69–1.71		TSP	Kawamura and Yasui, 2005

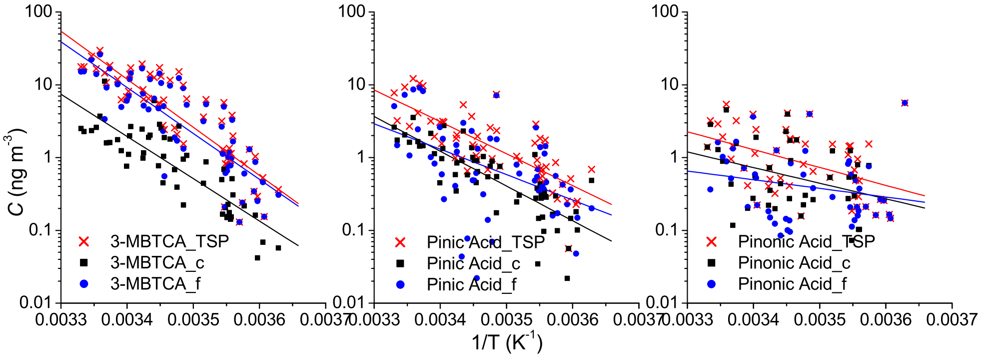

Fig. 3. Arrhenius-type temperature dependencies observed for pinene oxidation products (275–300 K): mass concentrations of 3-MBTCA, pinic acid and pinonic acid in fine (f), coarse (c) and total particulate matter (TSP) plotted against inverse temperature. The data points represent individual samples, the lines are exponential fits, and the corresponding Arrhenius parameters are listed in Table 4.

($E_a = 47 \pm 13$ kJ mol^{-1}, $R^2 = 0.21$, Table 4). In order to explain the observed temperature dependencies and differences, we considered the following steps involved in the atmospheric oxidation of pinene and formation of pinic acid, pinonic acid and 3-MBTCA: (1) emission of pinene; (2) oxidation of pinene and formation of pinic and pinonic acid; (3) oxidation of pinonic acid and formation of 3-MBTCA.

As detailed in the online supplement and illustrated in Table 4, the temperature dependence of the pinene emission rate can be described by an Arrhenius activation energy of ∼ 76 kJ mol^{-1} (Komenda et al., 2003).

The oxidation rate of pinene depends primarily on the concentration of oxidants (ozone, OH, etc.) and on rate coefficients of the involved gas phase reactions. For typical atmospheric conditions and oxidant concentration levels, however, the lifetime of pinene is relatively short (∼ 5 h for α-pinene and ∼ 3.5 h for β-pinene, $k\,(\mathrm{OH}) = 5.3 \times 10^{-11}$ cm^3 s^{-1} for α-pinene and $k\,(\mathrm{OH}) = 7.9 \times 10^{-11}$ cm^3 s^{-1} for β-pinene (Atkinson et al., 2006) and typical average $C_{\mathrm{OH}} = 1 \times 10^6$ cm^{-3}) compared to the transport, mixing and averaging times involved in the collection of air samples in this study (of the order of one week). Thus, we assume that the oxidation of pinene is not rate-limiting and that the temperature dependence of the formation of pinic and pinonic acid can be approximated by the temperature dependence of pinene emission. The plausibility of this assumption is confirmed by the agreement between the observed temperature dependence of pinic acid concentration and the calculated temperature dependence of pinene emission (Table 4).

The oxidation rate of pinonic acid depends primarily on gas-particle partitioning, on the concentration of OH radicals, and on the OH reaction rate coefficient (Jimenez et al., 2009; Hallquist et al., 2009). As detailed in the online supplement and illustrated in Fig. 4, the temperature dependence of gas-particle partitioning of pinonic acid is very weak and can be approximated by an Arrhenius activation energy of ∼ 0.21 kJ mol^{-1} (Table 4). Moreover, pinonic acid

Table 4. Arrhenius parameters for observed and modeled temperature dependencies (275–300 K): pinene oxidation product mass concentrations (3-MBTCA, pinic acid, pinonic acid) in fine, coarse and total particulate matter (TSP) as shown in Fig. 3; emission of pinene, gas-particle partitioning of pinonic acid, and concentration of OH radicals as described in the online supplement and shown in Fig. 4.

	A[a]	E_a (kJ mol^{-1})[b]	R^2[c]	n[d]
3-MBTCA (TSP)	3.29×10^{23} ng m^{-3}	126 ± 10	0.74	52
(fine)	2.41×10^{22} ng m^{-3}	121 ± 11	0.69	58
(coarse)	1.05×10^{20} ng m^{-3}	111 ± 10	0.72	52
Pinonic acid (TSP)	2.82×10^{8} ng m^{-3}	46.9 ± 12.7	0.21	35
(fine)	5.49×10^{3} ng m^{-3}	22.8 ± 15.0	0.05	36
(coarse)	1.45×10^{7} ng m^{-3}	41.1 ± 18.3	0.12	35
Pinic acid (TSP)	2.54×10^{15} ng m^{-3}	83.9 ± 9.1	0.60	56
(fine)	9.78×1^{11} ng m^{-3}	66.8 ± 16.3	0.24	56
(coarse)	2.05×10^{16} ng m^{-3}	91.3 ± 8.9	0.66	57
Pinene emission	6.31×10^{14} ng m^{-3}	75.6 ± 3.3		
Pinonic acid gas-particle-partitioning	1.09	0.213 ± 0.011	0.95	27
OH concentration	4.52×10^{24} cm^{-3}	110 ± 8	0.79	59

[a] pre-exponential factor (Fig. 3 and online supplement);
[b] activation energy (Fig. 3 and online supplement);
[c] correlation coefficient;
[d] number of data points.

is expected to reside almost exclusively in the gas phase ($>$ 99%, online supplement) under the conditions relevant for this study (Müller et al., 2010), and thus gas-particle partitioning should have little influence on the observed temperature dependencies.

As detailed in the online supplement, the E_a of OH reaction rate coefficient cause insignificant temperature dependence of overall OH oxidation of pinonic acid.

The atmospheric concentration of OH radicals depends on a wide range of processes, including the photolysis of ozone by solar UV radiation (Crutzen et al., 1999; Rohrer and Berresheim, 2006). Due to radiative heating, the intensity of solar radiation at a given location usually varies in conjunction with diurnal and seasonal variations of temperature. To explore the effective dependence of OH radical concentration on ambient temperature at our sampling location, we used model data from the ECHAM/MESSy Atmospheric Chemistry Model (EMAC, Jöckel et al., 2006). As detailed in the online supplement, these data could be fitted with an Arrhenius-type expression ($R^2 = 0.79$) and with an apparent Arrhenius activation energy of 110 ± 8 kJ mol^{-1}.

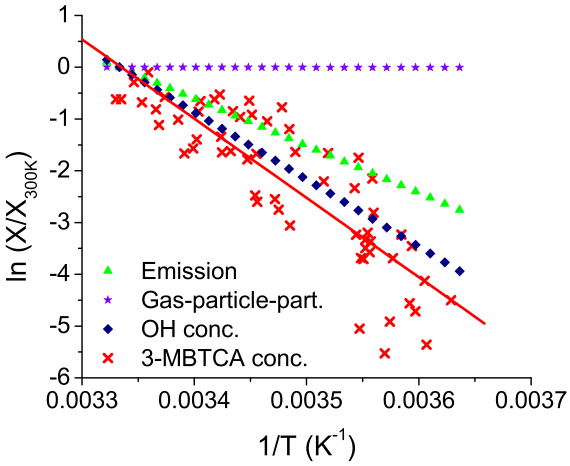

Fig. 4. Normalized Arrhenius-type plot of the temperature dependencies (275–300 K) observed for the concentration of 3-MBTCA ($C_{\mathrm{3-MBTCA,TSP}}$, data points and solid line) and modeled for the emission of pinene (C_{PE}), the gas-particle partitioning of pinonic acid (FGP$_{\mathrm{PA}}$), and the concentration of OH radicals (C_{OH}, dotted lines). For each parameter, $X_{300\mathrm{K}}$ is the fit value at 300 K. The model assumptions and calculations are described in the online supplement.

As illustrated in Fig. 4, the model-derived effective temperature dependence of OH radical concentration is similar to the observed temperature dependence of 3-MBTCA concentration and shows only 16 kJ mol^{-1} difference, which is within the error range. The agreement suggests that the OH-initiated oxidation of pinonic acid is indeed the rate-limiting step in the formation of 3-MBTCA, because the temperature dependence of a process consisting of multiple steps is generally dominated by the temperature dependence of the rate-limiting step. None of the other temperature dependencies considered above and illustrated in Fig. 4 appears strong enough to explain the observed temperature dependence of 3-MBTCA, and it appears plausible that the formation and concentration of 3-MBTCA is limited by the OH-initiated oxidation of pinonic acid. The result is also consistent with regard to the very weak temperature dependence observed for the pinonic acid concentration, which may result from an effective cancelation of the temperature dependencies of the formation from pinene emission and oxidation (in analogy to pinic acid) and the loss by OH oxidation. Reaction rate coefficient k (OH) is larger for pinonic acid (1.04×10^{-11} cm^3 s^{-1}) than for pinic acid (8.7×10^{-12} cm^3 s^{-1}) at 298 K (Vereecken and Peeters, 2002), resulting in an OH lifetime of $\sim$27 h for pinonic acid and $\sim$32 h for pinic acid, using a typical average OH concentration of 1×10^6 radical cm^{-3}. It appears not very likely that potential temperature dependencies of other relevant processes, like dry and wet deposition of the investigated compounds, would be more important and better suited to explain the observations.

Nevertheless, the above considerations have to be regarded as a first approximation and simple conceptual model approach to explain the observations. A full mechanistic understanding and quantification will require detailed numerical model studies including potential effects of atmospheric transport and deposition. This would go beyond the scope of the present study, but we suggest and intend to pursue such investigations in follow-up studies. Similarity of E_a for observed Arrhenius concentration and model OH concentration suggests that the OH-initiated oxidation is the rate–limiting step of 3-MBTCA formation. The difference of 16 kJ mol^{-1} is within the range of uncertainties and might also be related to sink processes (chemical loss, dry/wet deposition).

4 Conclusions

Based on the results of this study we suggest that further analyses of nitrated and oxygenated aromatic compounds by HPLC/MS may help to unravel combustion- and soil-related sources of organic particulate matter in comparison to primary biological aerosols containing fatty acids and SOA formed from gaseous biogenic precursors like pinene.

To our knowledge, this is the first study to explain field observations of pinene oxidation products (pinic acid, pinonic acid, 3-MBTCA) with a model analysis of the temperature dependencies of emissions, gas-particle partitioning and chemical reactions. The model calculations suggest that the OH radical concentration and the OH-initiated oxidation of pinonic acid limit the formation and explain the observed Arrhenius-type temperature dependence of 3-MBTCA, whereas the influence of gas-particle partitioning appears negligible. Thus, 3-MBTCA appears to be a suitable molecular tracer for the chemical aging of biogenic SOA by OH radicals.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys.net/10/7859/2010/acp-10-7859-2010-supplement.pdf.

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