

Article

Four- and Five-Carbon Dicarboxylic Acids Present in Secondary Organic Aerosol Produced from Anthropogenic and Biogenic Volatile Organic Compounds

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Abstract: To better understand precursors of dicarboxylic acids in ambient secondary organic aerosol (SOA), we studied C4–C9 dicarboxylic acids present in SOA formed from the oxidation of toluene, naphthalene, α -pinene, and isoprene. C4–C9 dicarboxylic acids present in SOA were analyzed by offline derivatization gas chromatography–mass spectrometry. We revealed that C4 dicarboxylic acids including succinic acid, maleic acid, fumaric acid, malic acid, DL-tartaric acid, and *meso*-tartaric acid are produced by the photooxidation of toluene. Since *meso*-tartaric acid barely occurs in nature, it is a potential aerosol tracer of photochemical reaction products. In SOA particles from toluene, we also detected a compound and its isomer with similar mass spectra to methyltartaric acid standard; the compound and the isomer are tentatively identified as 2,3-dihydropentanedioic acid isomers. The ratio of detected C4–C5 dicarboxylic acids to total toluene SOA mass had no significant dependence on the initial VOC/NO_x condition. Trace levels of maleic acid and fumaric acid were detected during the photooxidation of naphthalene. Malic acid was produced from the oxidation of α -pinene and isoprene. A trace amount of succinic acid was detected in the SOA produced from the oxidation of isoprene.

Keywords: volatile organic compound; secondary organic aerosol; aerosol tracer; environmental chamber; chemical mechanism; aerosol source apportionment



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1. Introduction

Secondary organic aerosol (SOA) is a major component of atmospheric PM_{2.5} that affects climate [1] and human health [2–4]. An SOA tracer is defined as a compound that maintains its identity in the atmosphere with the SOA produced from a particular precursor. SOA tracers present in the aerosol are used to estimate the source and amount of SOA constituting the atmospheric aerosol [5]. Dicarboxylic acids detected in atmospheric aerosol have traditionally been believed to be SOA tracers. Azelaic acid (C9), adipic acid (C6), and oxalic acid (C2) are reported to be tracers of SOA derived from oleic acid [6], cyclohexene [7,8], and isoprene [9], respectively. In particular, photochemical aging and aqueous-phase reactions are thought to play an important role in the formation of oxalic acid [10,11]. However, the sources of dicarboxylic acids in atmospheric organic aerosols have not been fully characterized.

Four-carbon dicarboxylic acid tracers, including fumaric acid, maleic acid, succinic acid, malic acid, and tartaric acid, are observed in urban [12–14], rural [12], and forest aerosols [15]. Recently, C4–C5 dicarboxylic acid tracers derived from toluene and isoprene,

major atmospheric precursors of SOA, have been reported. Methyl tartaric acid has been suggested as a tracer for highly oxidized SOA produced from isoprene [16]. Methyl tartaric acid is present in both SOA produced in a chamber and in PM_{2.5} collected in the United States and Poland [16]. C4–C5 multifunctional organic acids, such as 2,3-dihydroxypentanedioic acid (DHPDA) [17,18], malic acid [18], and tartaric acid [18] are known to be present in SOA from toluene. These small dicarboxylic acids may also be produced by different SOA precursors.

In this study, oxidation experiments of toluene, naphthalene, α -pinene, and isoprene, which are typical precursors of SOA in the atmosphere, were carried out in a photochemical chamber to quantify classical SOA tracers in addition to C4–C9 dicarboxylic acids in the produced SOA. From the quantification results, the percentage of each dicarboxylic acid in the total SOA mass was determined. For anthropogenic volatile organic compounds (VOCs), the measurements were performed as a function of the VOC/NO_x ratio. The purpose of this study is to provide basic information for interpreting the source of dicarboxylic acids in atmospheric SOA and to discuss possible reaction mechanisms for dicarboxylic acid formation.

2. Method

2.1. Chemicals

An aqueous solution of hydrogen peroxide (50wt%, Sigma-Aldrich, St. Louis, MO, USA) was used without purification as the OH radical source for the chamber experiments. Methyl nitrite was used as the OH radical source for the chamber experiments under high NO_x conditions. Methyl nitrite (CH₃ONO) was prepared by the reaction of sodium nitrite with methanol under acidic conditions. Prepared CH₃ONO was then purified by vacuum distillation. The synthesized CH₃ONO (purity = 99%) was stored at 77 K until it was used.

Ketopinic acid, malonic acid-¹³C₂, succinic acid-d₄, glutaric acid-d₆, 3-hydroxyglutaric acid-d₅, phthalic acid-d₄, levoglucosan-¹³C₆, mannitol-d₈, and palmitic acid-d₃₁ were used as analytical and internal recovery standards. These standards were purchased from CDN Isotopes (Pionte-Claire, QC, Canada), Santa Cruz Biotechnology (Dallas, TX, USA), Tokyo Kasei Kogyo (Saitama, Japan), Toronto Research Chemicals (North York, ON, Canada), and Fujifilm Wako Pure Chemical Corporation (Osaka, Japan). The purity of all of these analytical and internal recovery standards was more than 95%. Methyl tartaric acid was synthesized by Kanto Chemical Industry Co. (Tokyo, Japan).

2.2. Chamber Experiments

Experiments were conducted using a 6-m³ Teflon-coated stainless-steel chamber [19,20]. Before each experiment, the reactants listed in Table 1 were mixed in purified air in the chamber. The temperature of the gas mixture was maintained at 298 ± 1 K and the relative humidity of the air was less than 1%. When toluene, α -pinene, and isoprene were introduced, a required amount of pure precursor vapor was collected in a calibrated gas reservoir at room temperature. The collected vapor was introduced into the chamber using nitrogen as a carrier gas. Naphthalene was introduced into the chamber using nitrogen as a carrier gas while a required amount of solid naphthalene was evaporated in a glass vessel at 343 K. No seed particles were added. When necessary, the gaseous mixture was irradiated with light from 19 Xe arc lamps (1 kW each) through Pyrex. The concentrations of the gaseous compounds were measured by a Fourier transform-infrared spectrometer (model 6800, Jasco, Tokyo, Japan) with an optical length of 221.5 m. The size distribution of the particles produced during the reaction was measured using a scanning mobility particle sizer (SMPS, model 3934, TSI, Shoreview, MN, USA), and the volume concentration was calculated. Particles produced during the experiment were collected on a Teflon filter (Fluoropore, 47 mm diameter, 1 μ m pore size, Sumitomo Electric Industries, Osaka, Japan) to serve as an off-line SOA analysis sample. The collection flow rate and time were 16.7 L min⁻¹ and 1 to 2 h, respectively. According to Sato et al. [20], the reproducibility of SOA concentration by the chamber apparatus used in this study is less than ±12%.

Table 1. Initial concentrations and light conditions, where SOA is secondary organic aerosol.

Run	Reactants (conc. in Units of ppm)	Light	SOA ($\mu\text{g}\cdot\text{m}^{-3}$)
1	toluene (0.97), H ₂ O ₂ (20)	On	29
2	toluene (3.76), H ₂ O ₂ (20)	On	80
3	toluene (0.94), NO (0.20), CH ₃ ONO (0.01)	On	35
4	toluene (1.85), NO (0.19), CH ₃ ONO (0.01)	On	54
5	toluene (3.76), NO (0.19), CH ₃ ONO (0.01)	On	77
6	toluene (0.95), NO (0.10), CH ₃ ONO (0.01)	On	20
7	toluene (0.95), NO (0.46), CH ₃ ONO (0.01)	On	25
8	toluene (0.96), NO (0.46), CH ₃ ONO (0.5)	On	106
9	toluene (0.96), NO (0.47), CH ₃ ONO (1) ^a	On	233
10	toluene (0.96), NO (0.47), CH ₃ ONO (1) ^a	On	123
11	naphthalene (0.49), H ₂ O ₂ (20)	On	142
12	naphthalene (0.21), H ₂ O ₂ (20)	On	46
13	naphthalene (0.52), NO (0.09), CH ₃ ONO (0.01)	On	19
14	naphthalene (0.98), NO (0.09), CH ₃ ONO (0.01)	On	44
15	naphthalene (1.80), NO (0.10), CH ₃ ONO (0.01)	On	48
16	naphthalene (0.99), NO (0.05), CH ₃ ONO (0.01)	On	55
17	naphthalene (1.00), NO (0.19), CH ₃ ONO (0.01)	On	51
18	naphthalene (0.51), NO (0.10), CH ₃ ONO (0.5)	On	735
19	naphthalene (0.50), NO (0.10), CH ₃ ONO (1)	On	935
20	α -pinene (0.09), H ₂ O ₂ (20)	On	29
21	α -pinene (0.20), NO (0.10), CH ₃ ONO (0.01)	On	62
22	isoprene (1.91), O ₃ (3)	Off	104
23	isoprene (1.85), NO (0.46), CH ₃ ONO (0.01)	On	29

^a Experiments were conducted under similar initial conditions for runs 9 and 10. However, in run 9, filter collection was performed for 25 min from 108 min after the start of irradiation, and in run 10, filter collection was performed for 120 min from 186 min after the start of irradiation.

As shown in Table 1, VOC/H₂O₂/air + light experiments (OH oxidation under low NO_x conditions; runs 1, 2, 11, and 12) and VOC/NO/CH₃ONO/air + light experiments (OH oxidation under high NO_x conditions; runs 3–10 and runs 13–19) were performed on precursors of toluene and naphthalene. The initial concentrations of CH₃ONO were set higher in runs 8, 9, 10, 18, and 19 than in the other runs to investigate higher exposure to hydroxyl radicals. In the experiments with α -pinene and isoprene, the VOC/H₂O₂/air + light experiments (run 20), VOC/NO/CH₃ONO/air + light experiments (runs 21 and 23), and VOC/O₃/air experiment (ozonolysis and oxidation by secondary OH radicals; run 22).

We focused on experiments using anthropogenic VOCs because, as described later, target C4 and C5 dicarboxylic acid tracers were barely detected in SOA formed from biogenic VOCs. Preliminary H₂O₂ photooxidation experiments were also conducted for isoprene, although it is not shown in Table 1. These preliminary experiments did not produce a sufficient concentration of SOA particles. Therefore, for isoprene, an ozone reaction experiment (run 22) was conducted as an alternative oxidation experiment.

2.3. Chemical Analysis

In this study, dicarboxylic acids, i.e., succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, fumaric acid, maleic acid, malic acid, DL-tartaric acid, and meso-tartaric acid, as well as conventional SOA tracers, i.e., 2,3-dihydroxy-4-oxopentanoic acid (DHOPA), phthalic acid, pinic acid, 3-hydroxyglutaric acid, 2-methylthreitol, and 2-methylerythritol were analyzed. Details of the chemical analysis procedure are described elsewhere [21]. SOA tracers were analyzed by a gas chromatograph-mass spectrometer (GC-MS; GC: Agilent 7890, MS: Agilent 5975, Agilent Technologies, Inc., Santa Clara, CA, USA). A portion of the SOA sample filter was spiked with an internal recovery standard, and the SOA tracer was extracted by sonication with dichloromethane/methanol (2:1, v/v, 10 mL, Fujifilm Wako Pure Chemical Industries) for 20 min. The filtered extract was concentrated with pure nitrogen gas. The dried extracts were silylated with 40 μL of *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA; GL Science, Tokyo, Japan) containing

1% trimethylsilyl chloride and 10 μL of pyridine by mixing at 343 K for 1.5 h. The resulting derivative was diluted with 100 μL of isooctane containing the recovery standard (*n*-pentacosane- d_{52} ; CDN Isotopes) and analyzed by GC–MS. The gas chromatograph system was equipped with a splitless injector and an InertCap 5MS fused silica capillary column (30 + 5 m \times 0.25 mm i.d., 0.25 mm film thickness, GL Science). The mass spectrometer was operated in both selective ion monitoring (SIM) and scan mode in 70-eV electron ionization mode. The scanning mass range in scan mode was 50–650 Da. The SIM signal intensity for each compound was normalized with the corresponding internal standard and quantified with a linear calibration curve ($r^2 > 0.995$).

In this study, oxalic acid and malonic acid were not analyzed. Trimethylsilyl derivatization analysis of oxalic acid may underestimate the concentration due to volatilization of the derivative [22,23]. Therefore, oxalic acid was not selected as an analytical target. A preliminary analysis was performed for malonic acid. However, since the calibration curve for malonic acid was not linear, malonic acid was not included in the analytical target of this study.

Several new filters were used as blank filters. Each blank filter was set once in the filter holder used in the chamber experiment and then removed from the holder. Each blank filter was stored separately and analyzed in the same way as the chamber samples; the background signal of the SOA tracer was close to or below the detection limit. The average background signal intensity for each SOA tracer was subtracted from the signal intensity of the SOA sample before calculating the concentration of the OA tracer on each filter.

2.4. Calculation Method of $f_{\text{SOA}0}$

The f_{SOA} value was calculated by dividing the mass concentration of tracer (C_{tr}) obtained from chemical analysis by the mass concentration of SOA (C_{SOA}):

$$f_{\text{SOA}} = C_{\text{tr}}/C_{\text{SOA}} \quad (1)$$

The C_{SOA} value was calculated by multiplying the volume concentration observed using the SMPS and the aerosol density. For aerosol density, we used the existing data of SOA produced from toluene [24], naphthalene [25], α -pinene [26], and isoprene [27] in this study. Error propagation analysis was performed considering the following major uncertainties: f_{SOA} error was estimated to be less than 17% of the f_{SOA} value; SOA density uncertainty was reported to be about 8% of the density [24,26]; SMPS volume concentration repeatability error was measured to be \sim 5% of the volume concentration during chamber experiments; uncertainty in SOA tracer recovery during pretreatment was reported to be \sim 10% of recovery [21]; GC–MS instrumental repeatability error was measured to be \sim 10% of the intensity of the signal above the limit of quantification.

2.5. Saturation Concentration

The saturation concentration of the SOA tracer was calculated using the SPARC (SPARC Performs Automated Reasoning in Chemistry) chemical property estimator [28]. When experimental vapor pressures at 298 K are compared with the vapor pressures calculated by SPARC for more than 7000 organic compounds, the mean squared deviation error was evaluated to be 0.096 [28]. Vapor pressure at 298 K was calculated assuming vaporization from the liquid phase.

3. Results and Discussion

3.1. Saturation Concentration

The saturation concentrations at 25°C calculated by SPARC were 94 $\mu\text{g}\cdot\text{m}^{-3}$ for maleic acid, 720 $\mu\text{g}\cdot\text{m}^{-3}$ for succinic acid, 8.8 $\mu\text{g}\cdot\text{m}^{-3}$ for malic acid, 0.13 $\mu\text{g}\cdot\text{m}^{-3}$ for tartaric acid, 3.3 $\mu\text{g}\cdot\text{m}^{-3}$ for DHOPA, 0.17 $\mu\text{g}\cdot\text{m}^{-3}$ for methyl tartaric acid, 0.012 $\mu\text{g}\cdot\text{m}^{-3}$ for DHPDA, 0.044 $\mu\text{g}\cdot\text{m}^{-3}$ for 2,4-dihydroxyglutaric acid, 8.3 $\mu\text{g}\cdot\text{m}^{-3}$ for phthalic acid, 0.18 $\mu\text{g}\cdot\text{m}^{-3}$ for pinic acid, 0.33 $\mu\text{g}\cdot\text{m}^{-3}$ for 3-hydroxyglutaric acid, and 26 $\mu\text{g}\cdot\text{m}^{-3}$ for 2-methylerythritol. Since SPARC is based on structure–activity relationships, the calculated

results for geometric isomers, such as maleic acid and fumaric acid, and diastereomers, such as 2-methylerythritol and 2-methylthreitol, are identical.

The calculated saturation concentration was used to determine the gas-particle partitioning. Based on the gas-particle partitioning model [29], the distribution ratio of the gas phase to the particle phase was determined to be equal to the ratio of the calculated saturation concentration to a typical ambient organic aerosol concentration. Since the saturation concentrations of maleic acid and succinic acid are equal to or higher than the $PM_{2.5}$ concentration in the atmosphere ($1\text{--}100\ \mu\text{g}\cdot\text{m}^{-3}$), it is expected that under 25°C conditions, maleic and succinic acids will be mainly distributed in the gas phase. However, succinic acid is also known to exist in atmospheric aerosols and may be present as ammonium and metal salts [30].

3.2. Results of f_{SOA} Measurements

In this study, we attempted to detect C4–C9 dicarboxylic acids, but only C4 and C5 dicarboxylic acids were detected in SOA. The results of f_{SOA} measurements obtained in this study are shown in Figure 1. Figure 1a shows a stacked bar graph of the f_{SOA} ratio measured for dicarboxylic acids. The experimental values of the ratios of these dicarboxylic acid tracers are listed in Table S1 of the supplementary material. No normal-chain dicarboxylic acids above C5 were produced above the detection limit. Succinic acid, maleic acid, fumaric acid, malic acid, DL-tartaric acid, meso-tartaric acid, and two isomers of dihydroxypentanedioic acid (DHPDA1 and DHPDA2) were produced from toluene. DHPDA1 and DHPDA2 were tentatively identified based on the mass spectrum in a similar manner to the previous study [17]; this is discussed at the end of this section. DHPDA1 and DHPDA2 were quantified using DL-tartaric acid as the surrogate standard. Trace amounts of maleic acid and fumaric acid were detected in the SOA from naphthalene. Malic acid was detected in the SOA produced from pinene and isoprene. A trace amount of succinic acid was detected in the SOA produced from the oxidation of isoprene.

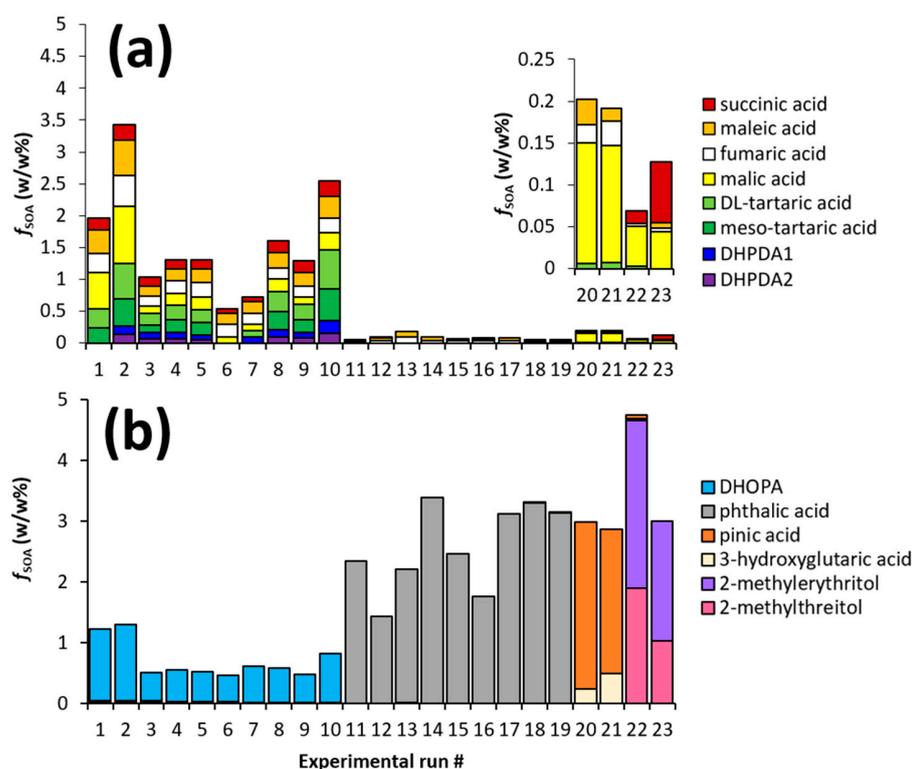


Figure 1. Ratio of tracers to total SOA mass (f_{SOA}) determined for (a) C4 and C5 dicarboxylic acids present in SOA and (b) conventional tracers present in SOA. The insert shows extended figure for results of biogenic SOAs (runs 20–24). DHPDA represents 2,3-dihydroxypentanedioic acid.

Figure 1b shows results of the f_{SOA} ratios of representative SOA tracers to SOA mass. The experimental values of the ratios of these conventional SOA tracers were reported in another paper of this group [31]. DHOPA is an SOA tracer from toluene. DHOPA was produced only from toluene, phthalic acid only from naphthalene, pinic acid and 3-hydroxyglutaric acid only from α -pinene, and 2-methylerythritol and 2-methylthreitol only from isoprene.

In the toluene-derived SOA sample, *meso*-tartaric acid was detected with a signal intensity comparable to that of DL-tartaric acid (Figure 2). Lau et al. [18] detected tartaric acid in toluene SOA, but they did not distinguish diastereomers. To the best of our knowledge, this is the first report of the identification of *meso*-tartaric acid in toluene-derived SOA. L-Tartaric acid occurs naturally, but *meso*-tartaric acid barely occurs in nature [32]. *meso*-Tartaric acid may be used as an aerosol tracer for photochemical reaction products.

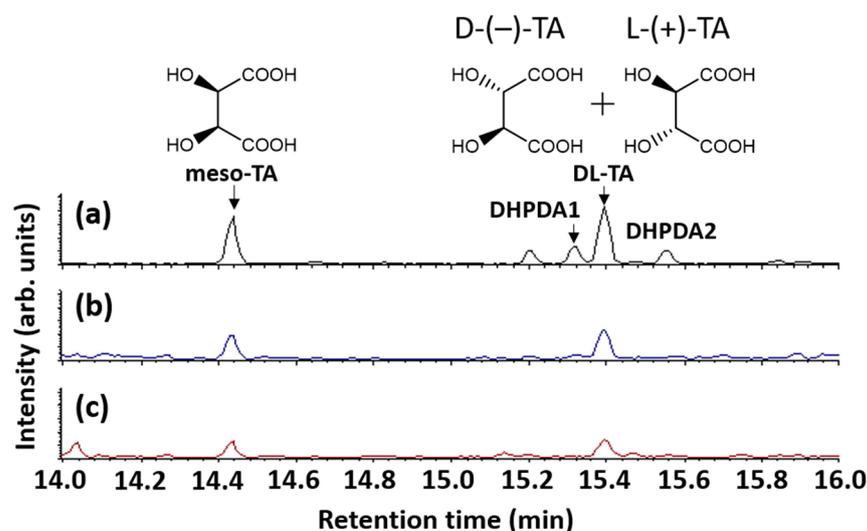


Figure 2. Mass-selected chromatograms of (a) m/z 292, (b) m/z 219, and (c) m/z 189 observed for SOA formed from toluene (run 10). The chemical structure of *meso*-, D-(-)-, and L-(+)-tartaric acid (TA) are shown together with the chromatograms. The peak of *meso*-TA, DL-TA, DHPDA1, and DHPDA2 appear in chromatogram of m/z 292.

Methyl tartaric acid was recently reported to be present in SOA from isoprene [16]. In this study, we also attempted to detect methyl tartaric acid in SOA from isoprene, but we were unable to detect methyl tartaric acid under the analytical conditions of this study, where $f_{\text{SOA}} = 0.04\%$ was the lower limit of detection. The value of f_{SOA} of methyl tartaric acid from isoprene in the previous experiment of Jaoui et al. [17] was estimated to be 0.001%. Here, the value of f_{SOA} of methyl tartaric acid from isoprene was calculated from the concentration of methyl tartaric acid produced from isoprene [17]; and the concentration of SOA produced was estimated using the initial isoprene concentration in that experiment and the previously reported SOA yield curve [27].

Jaoui et al. [17] reported that a compound similar to methyl tartaric acid is also found in SOA produced from toluene. They tentatively identified the methyl tartaric acid-like compound as DHPDA based on its mass spectrum. They reported that the mass spectrum of methyl tartaric acid-like compound was similar to that of DHPDA rather than that of methyl tartaric acid. We also found two chromatographic peaks that have very similar mass spectra to methyl tartaric acid. Figure 3a the mass spectrum of the methyl tartaric acid standard, Figure 3b the mass spectrum of DHPDA1 detected in the toluene SOA of this study, and Figure 3c the mass spectrum of DHPDA2. The retention time of a single chromatographic peak of methyl tartaric acid that we purchased was very close to that of DHPDA1 present in SOA from toluene. However, the mass spectrum of methyl tartaric acid was slightly different from that of DHPDA1 in terms of the signal ratio of m/z 133 to

m/z 147 (Figure 3a,b). Because no experimental evidence to reject tentative identification by Jaoui et al. [17] was found, the detected compound was tentatively identified as an isomer of DHPDA also in this study. However, as shown in Figure 3a,c, the mass spectrum of DHPDA2 was very similar to that of methyl tartaric acid. In the present study, we tentatively identified the methyl tartaric acid-like compound as DHPDA, but diastereomers of methyl tartaric acid cannot be excluded as candidates for these compounds.

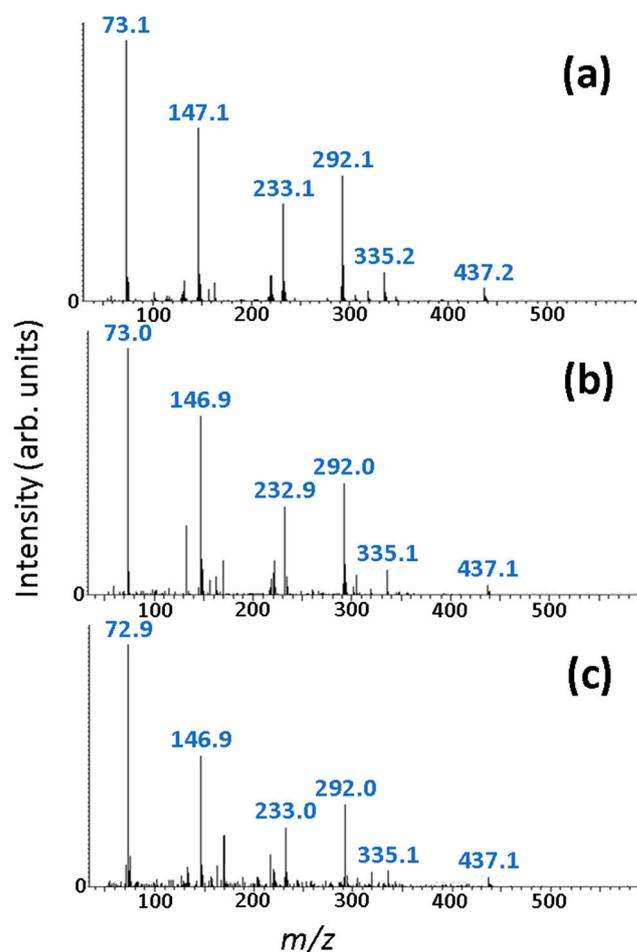


Figure 3. Mass spectrum of (a) standard sample of methyl tartaric acid, (b) DHPDA1 isomer present in toluene SOA (run 10), and (c) DHPDA2 isomer present in toluene SOA (run 10).

3.3. Effect of NO_x /Toluene Ratio on f_{SOA} of Toluene-Derived Tracer

The ratio of the tracer determined in the toluene experiment to the SOA mass was examined against the initial NO_x /toluene concentration ratio of the experiment (Figure 4). In order to display data with a wide dynamic range, a semi-logarithmic plot was employed. $\log_{10}(f_{SOA})$ and NO_x/VOC ratio do not necessarily have a linear relationship, but for convenience, a linear fit of $\log_{10}(f_{SOA})$ as a function of NO_x/VOC ratio was performed. Experimental data obtained by the toluene/ $NO/CH_3ONO/air + light$ system (runs 3–10) were used for the fitting. The slope values of the fitted lines were 4.8 ± 11.3 for succinic acid, -4.0 ± 6.0 for maleic acid, -1.2 ± 3.4 for fumaric acid, 0.4 ± 11.1 for malic acid, 4.7 ± 16.5 for DL-tartaric acid, 2.5 ± 3.6 for *meso*-tartaric acid, 6.1 ± 8.7 for DHPDA1, and 9.7 ± 8.0 for DHPDA2, where the error is 2σ . The ratios of all examined dicarboxylic acid tracers showed little dependence on the NO_x /toluene ratio.

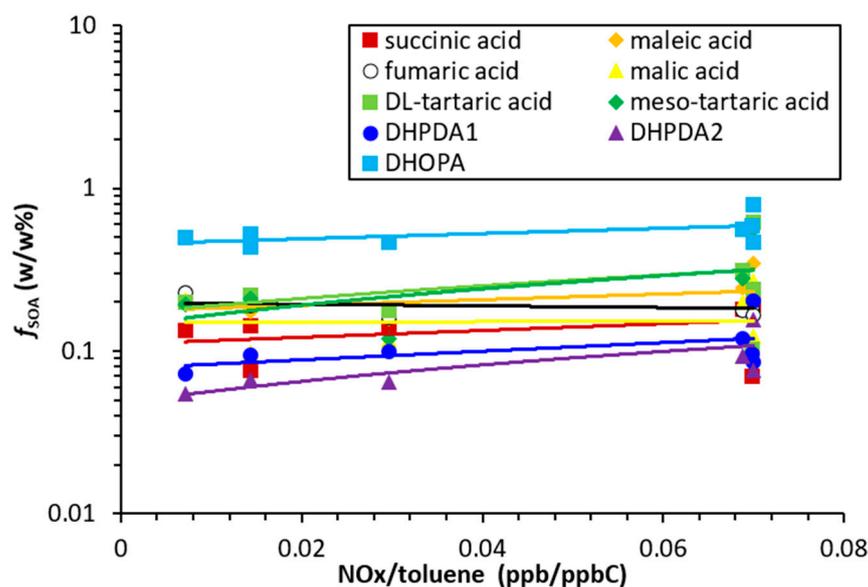


Figure 4. Ratio of tracers to total SOA mass (f_{SOA}) observed in experiments with toluene as a function of $\text{NO}_x/\text{toluene}$ ratio.

According to Table 1, the concentration of SOA produced increased with the increase in initial CH_3ONO concentration. This indicates that the increase in CH_3ONO concentration increases the concentration of OH radicals generated during the reaction and hence increases the SOA produced. In contrast, as shown in Figure 4, there was no clear effect of increasing CH_3ONO on the f_{SOA} values of C4–C5 dicarboxylic acids under examined OH exposure conditions.

3.4. Formation Mechanism of Multifunctional Organic Acids from Toluene

The suggested formation mechanism of multifunctional organic acids from toluene is shown in Figure 5. Because the f_{SOA} of dicarboxylic acid tracers from toluene was approximately independent of experimental conditions examined in this study, these dicarboxylic acid tracers may be formed by instantaneous reaction during the photooxidation of toluene. To explain a similar result of DHOPA, Sato et al. [31] recently suggested that DHOPA is formed by the OH radical-initiated autoxidation of 4-oxo-2-pentenal, a gas-phase oxidation product of toluene. The reaction of 4-oxo-2-pentenal with OH radical may lead to rapid multi-functionalization due to intramolecular hydrogen abstraction of alkoxy radicals. Similarly, tartaric acid is likely formed by subsequent OH oxidation of 2-butenedial, a gas-phase oxidation product of toluene. The intramolecular hydrogen abstraction of alkoxy radicals may play a major role also in the formation process of tartaric acid. As for maleic acid and succinic acid, it has been suggested that they are produced by hydrolysis of maleic anhydride and succinic anhydride, respectively, by aerosol-containing water [20,33]. Maleic anhydride is known as a gas-phase oxidation product from toluene. Succinic anhydride is thought to be produced by absorption of gaseous maleic anhydride into existing particles and subsequent photochemical processes, in which maleic anhydride absorbs UV light to form an excited state maleic anhydride [34]. Similarly, malic acid is likely formed by the hydrolysis of malic anhydride, which is produced by OH oxidation process of maleic anhydride in the particle phase.

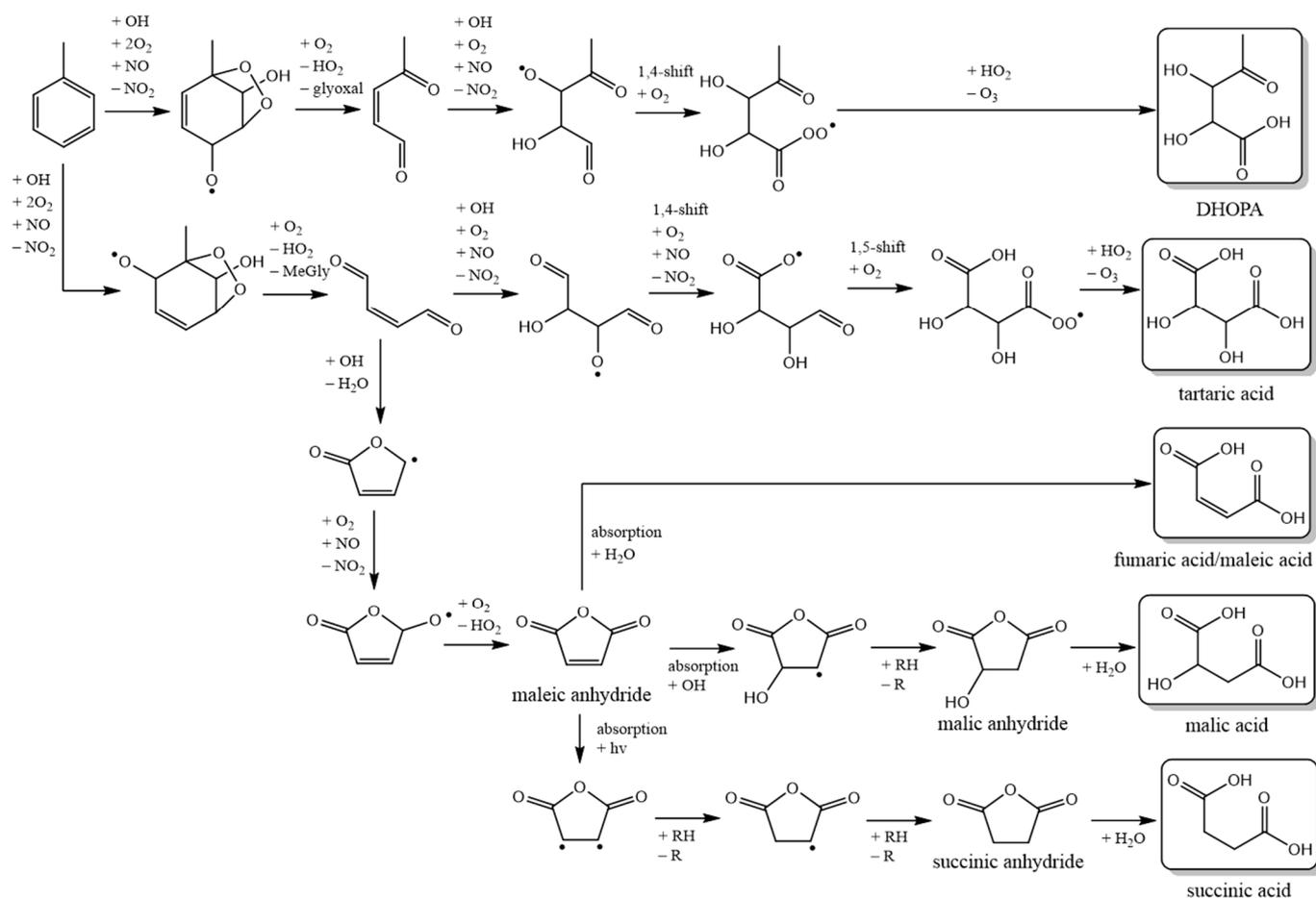


Figure 5. Formation mechanisms suggested for four- to five-carbon multifunctional carboxylic acids from the toluene photooxidation. Here, DHOPA is 2,3-dihydroxy-4-oxopentanoic acid; MeGly is methyl glyoxal; absorption is the absorption from the gas phase to the particle phase, R is organic group; and $h\nu$ is photoexcitation.

3.5. Atmospheric Implication

The C4 dicarboxylic acids measured in this study have been observed in atmospheric aerosols [12–15]. For example, C4 dicarboxylic acids of succinic acid, malic acid, tartaric acid, fumaric acid, and maleic acid have been observed in atmospheric aerosols in urban and rural areas of Germany [12]. The concentrations of all C4 dicarboxylic acids are higher in summer than in winter and are thought to be derived from secondary production. The concentrations of C4 dicarboxylic acids in urban areas are higher than in rural areas, suggesting that succinic acid, malic acid, tartaric acid, fumaric acid, and maleic acid have an anthropogenic origin. The results of this previous field observation in Germany provide a good example of the results of this study, which show that C4 dicarboxylic acids are formed primarily from the oxidation of toluene, which is abundant in urban rather than rural areas. The C2–C4 dicarboxylic acids observed in Tokyo were reported to have significant correlations with oxidant concentrations, and the results from Tokyo suggest that secondary production contributes highly to C4 dicarboxylic acids [13].

In this study, the f_{SOA} of malic acid formed from toluene, α -pinene, and isoprene was shown to be 0.163%, 0.140%, and 0.044% in the presence of NO_x . The values for toluene are the average values of the experiments in the presence of NO_x . Based on the results of this study, we evaluated diurnal production amounts of malic acid from the photooxidation of these three VOCs under summer urban conditions. The concentration

of malic acid produced from a particular VOC ($[\text{malic acid}]_{\text{VOC}}$) was calculated by the following equation:

$$[\text{malic acid}]_{\text{VOC}} = f_{\text{SOA}} \cdot Y_{\text{SOA}} \cdot k_{\text{VOC}+\text{OH}} \cdot [\text{VOC}]_{\text{av}} \cdot [\text{OH}]_{\text{av}} \cdot \Delta t \quad (2)$$

Here Y_{SOA} is the SOA yield; $k_{\text{VOC}+\text{OH}}$ is the rate constant for the reaction of OH radicals with the target VOC; $[\text{VOC}]_{\text{av}}$ is the average VOC concentration; $[\text{OH}]_{\text{av}}$ is the average OH radical concentration, and Δt is the reaction time. The average concentrations of toluene, α -pinene, and isoprene at nine urban sites in the greater Tokyo area, Japan in summer 2013 were reported to be 6.8, 0.77, and 0.95 $\mu\text{g}\cdot\text{m}^{-3}$, respectively [35]. We assumed $2 \times 10^6 \text{ molecule}\cdot\text{cm}^{-3}$ as $[\text{OH}]_{\text{av}}$ and 3 h as Δt . We used 13%, 21%, and 2% as Y_{SOA} for toluene [24], α -pinene [26], and isoprene [27]. As a result of the calculations, the concentrations of malic acid produced in the reaction of toluene, α -pinene, and isoprene were calculated to be 0.20, 0.32, and 0.017 $\text{ng}\cdot\text{m}^{-3}$, respectively. These results indicate that malic acid present in an atmospheric aerosol may have both anthropogenic and biogenic origins under urban summer conditions.

The average concentration of malic acid present in atmospheric aerosols is reported to be 23 $\text{ng}\cdot\text{m}^{-3}$ in Tokyo, Japan [13], 19 $\text{ng}\cdot\text{m}^{-3}$ in Nagoya, Japan [14], and 42 $\text{ng}\cdot\text{m}^{-3}$ at inland sites in Germany [12]. The concentration reported for malic acid in Tokyo, Japan was higher than the concentrations of malic acid generated from toluene, α -pinene, and isoprene in Tokyo predicted using the results of this study (0.017–0.32 $\text{ng}\cdot\text{m}^{-3}$). This result indicates that the photooxidation of toluene, α -pinene, and isoprene are not the dominant source of malic acid in the urban areas; according to Kawamura et al. [13] the malic acid/succinic acid ratio is positively correlated with oxidant concentration, suggesting that malic acid is formed from the atmospheric photochemical aging process of less-oxygenated C4 dicarboxylic acids, e.g., succinic acid. Aqueous-phase reactions of dialdehydes also significantly contribute to the formation of C2–C4 dicarboxylic acids in atmospheric aerosols [10,11], although they were not considered in the formation mechanism of dicarboxylic acids in the dry experimental conditions of this study (Figure 5). In addition, malic acid, which is thought to be derived from isoprene, has been found in organic aerosols from forests [15]. The malic acid in forest aerosols may also be produced by aging or aqueous-phase reactions. The lower concentration of malic acid predicted to be produced from the photooxidation of toluene, α -pinene, and isoprene compared with that in atmospheric aerosols is probably a result of the effects of photochemical aging and/or aqueous-phase reactions of both anthropogenic and biogenic organic compounds.

Using the f_{SOA} values measured by chamber experiments in this study, the amounts of succinic, maleic, and fumaric acids produced by the photooxidation of toluene for 3 h in summer in Tokyo were determined to be 0.18 $\text{ng}\cdot\text{m}^{-3}$, 0.26 $\text{ng}\cdot\text{m}^{-3}$, and 0.23 $\text{ng}\cdot\text{m}^{-3}$, respectively. Similar calculations were performed for the photooxidation of naphthalene, α -pinene and isoprene. Results of these calculations show that the photooxidation of toluene is the major source of succinic acid, maleic acid, and fumaric acid. On the other hand, the average concentrations of succinic acid, maleic acid, and fumaric acid in organic aerosols observed in Tokyo were reported to be 37 $\text{ng}\cdot\text{m}^{-3}$, 5.6 $\text{ng}\cdot\text{m}^{-3}$, and 3.7 $\text{ng}\cdot\text{m}^{-3}$, respectively [13]. The amounts of succinic acid, maleic acid, and fumaric acid observed in the ambient atmosphere in Tokyo were higher than those generated by photooxidation of toluene. These results suggest the importance of photochemical aging and/or aqueous-phase reactions during the formation of these C4 dicarboxylic acids.

4. Conclusions

Four- and five-carbon dicarboxylic acids including DL-tartaric acid, *meso*-tartaric acid, DHPDA, malic acid, succinic acid, maleic acid, and fumaric acid were detected in toluene SOA. The ratio of C4–C5 dicarboxylic acids formed in the reaction of toluene to SOA was independent of the initial NO_x /toluene ratio. Trace amounts of maleic acid and fumaric acid were detected in the photooxidation of naphthalene. Malic acid was produced in the oxidation of α -pinene and isoprene. A trace amount of succinic acid was detected in the

SOA produced from the oxidation of isoprene. The saturation concentrations of tartaric acid, DHPDA, and malic acid were low enough to be partitioned into the particle phase at typical atmospheric aerosol concentrations. A signal of *meso*-tartaric acid comparable to that of DL-tartaric acid was detected in SOA from toluene. Since *meso*-tartaric acid barely occurs in nature, it is a potential aerosol tracer of photochemical reaction products. Further investigation will be necessary for the identification of the molecules tentatively identified as DHPDAs in SOA from toluene. The emission sources related to the precursors of tartaric acid and malic acid in atmospheric aerosols should also be evaluated by observation of atmospheric fine aerosol particles in the future.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/atmos12121703/s1>, Table S1: Numerical data of the ratio of dicarboxylic acid tracer to total SOA mass.

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