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Chemical Compositions of Secondary Organic Aerosol from the Ozonolysis of Cyclohexene in the Absence of Seed Particles

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The composition of the aerosol from the ozonolysis of cyclohexene in the absence of seed particles has been investigated by laboratory chamber experiments. The aerosol collected on filters was analyzed by a liquid chromatography/atmospheric pressure chemical ionization-mass spectrometry. Low-molecular weight products, i.e., dicarboxylic acids, oxocarboxylic acids, and hydroxydicarboxylic acids, as well as oligomers with molecular weights more than 200 were found in the aerosol.

The ozonolysis of cyclohexene is one of typical gas-phase reactions leading to formation of condensable products, and its reaction mechanism may be analogous to the monoterpene ozonolysis contributing potentially to formation of atmospheric secondary organic aerosol.[1] As the molecules contained in aerosol from the title reaction, multifunctional species such as dicarboxylic acids, oxocarboxylic acids, and hydroxydicarboxylic acids have been known from previous studies using gas chromatography–mass spectrometry.[2,3]

Very recently, Tolocka et al. applied liquid chromatography (LC) combined with matrix-assisted laser desorption ionization (MALDI), electrospray ionization (ESI), and desorption ammonia chemical ionization (CI)-mass spectrometry (MS) for aerosol from the monoterpene ozonolysis and found oligomers in aerosol with the soft ionization techniques, i.e., MALDI and ESI.[4] Gao et al. used an LC/ESI-MS to analyze aerosol from the ozonolysis of six cyclic alkenes and found that oligomers were contained in late eluent of reverse phase chromatography for all aerosol.[5]

In this work, an atmospheric pressure chemical ionization (APCI) method was employed for the LC/MS analysis of aerosol from the ozonolysis of cyclohexene. APCI is generally a powerful soft ionization technique for molecules with moderate polarities[6] and may provide high sensitivities for analytes included in late eluent for reverse phase chromatography. A purpose of this work is to test APCI-MS to probe oligomers in aerosol.

The experiments were conducted with a 6-m^3 laboratory chamber[7,8] without using seed particles at 298 ± 1 K. Prior to each experiment, the chamber was filled with 760-Torr dry purified air. 1.0–2.5-ppmv ozone was introduced into the chamber from an ozone generator (Nippon Ozone, Type-012). Equimolecular gaseous cyclohexene was collected in a calibrated bulb and was then injected into the chamber with a nitrogen carrier gas. Ozone and cyclohexene were monitored by an FTIR spectrometer (Nicolet, Nexus 670) with an optical length of 221.5 m. The reaction was almost concluded in 40 min. After the conclusion of the reaction, the aerosol was collected on a Teflon membrane filter with 47-mm diameter and 0.45-µm pore size (Sumitomo Electric, FP-045) at a flow rate of 10 L min^{-1} for 40 min. The filter was weighed with an electric balance (Mettler Toledo, AG285) before and after the sampling in order to measure the mass of the collected aerosol. The average of aerosol yield with the error of the standard deviation was 24 ± 8 wt % for eight experiments, showing agreement with the literature values (19.1–21.1 wt %).[9]

The pretreatment and the analysis were performed just after the sampling. The filter was sonicated in 3-mL dichloromethane for 10 min. The extract was evaporated to nearly dryness under a gentle stream of nitrogen. The concentrated sample was dissolved in 1.0-mL acidic methanol water (0.043% formic acid, 15% methanol). 50 µL of the solution was loop-injected into an LC/APCI-MS instrument (Shimadzu, LC8000α) equipped with an Inertsil ODS-3 C_{18} column with 3-µm particle size (GL science, 150×3.0 mm) kept at 35 °C. Methanol and 0.05% aqueous solution of formic acid was used as the mobile phases. The concentration of methanol was programmed to be 15, 15, 90, and 90% at retention times of 0, 5, 25, and 30 min, respectively. The total flow rate of the mobile phase was set to 0.4 mL min^{-1}. The separated analytes were detected by the APCI mass spectrometer run in negative ion mode. As standard mass spectra, the spectra of dodecanedioic acid, octanedioic acid, heptanedioic acid, hexanedioic acid, pentanedioic acid, butanedioic acid, 4-oxobutanoic acid, and 2-hydroxy-2-methylbutanedioic acid were measured. The quasi-molecular ions were detected without serious fragmentations for all the molecules examined.

Figure 1 shows mass spectra of a flow-injected aerosol sample at the methanol concentration of 15%. The highest peak at mass to charge ratio (m/z) of 145 is attributed to adipic acid with molecular weight (MW) of 146. Mass peaks appeared also in a region from $m/z = 146$ to ca. $m/z = 500$. Especially, the group of peaks in the m/z range between 200 and 300 showed regular mass differences of $m/z = 14$, 16, and 18. Such a regular structure is typical for oligomers.[10]

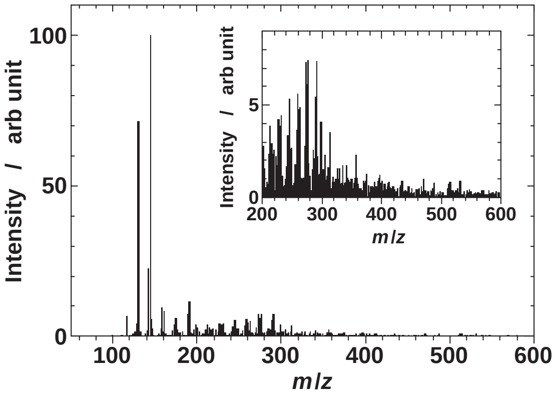

Figure 1. Mass spectra of aerosol from ozonolysis of cyclohexene (Intensity at $m/z = 145$ is set to 100).

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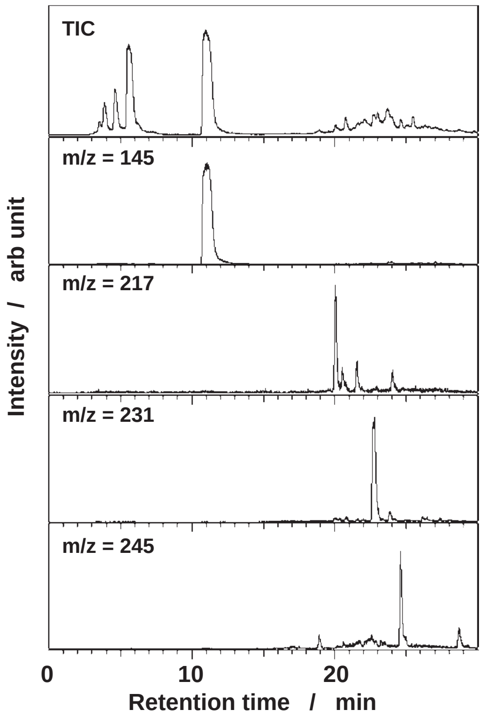

Figure 2. Total ion chromatogram and extracted ion chromatograms of ions with $m/z = 145$, 217, 231, and 245.

Figure 2 illustrates total ion chromatogram (TIC) and extracted ion chromatograms (EIC) of ions with $m/z = 145$, 217, 231, and 245 of the aerosol sample. Though overlaps of peaks were observed in TIC, all peaks were successfully separated in EIC of each m/z ion. The chromatographic peaks of ions with $m/z < 200$ appeared in a retention time region earlier than 15 min. These low-MW components were identified from the mass spectra and the retention times as dicarboxylic acids (hexanedioic acid, pentanedioic acid, and butanedioic acid), oxocarboxylic acids (oxohexanoic acid, oxopentanoic acid, 4-oxobutanoic acid, dioxohexanoic acid, and dioxopentanoic acid), and hydroxydicarboxylic acids (hydroxyhexanedioic acid, hydroxypentanedioic acid, and hydroxybutanedioic acid). Dioxohexanoic acid is a newly identified molecule. C_n ($n > 6$) dicarboxylic acids and dicarboxylic acid esters reported as minor components by Gao et al.[5] were not found.

The chromatographic peaks of ions with $m/z \geq 200$ appeared in a region latter than 15 min. Strong peaks were observed at $m/z = 215$, 217, 229, 231, 243, 245, 257, 259, 273, and 289. This component was tentatively identified as oligomers. In order to confirm that no oligomer was produced during the sampling, the pretreatment, and the analysis, the following two checks were performed: First, oligomer formation during the ionization were checked by analyzing equal-mass methanol solution of hexanedioic acid, 4-oxobutanoic acid, 2-hydroxy-2-methylbutanedioic acid, and pentanedial. No oligomer was found in the mixture solution. Next, oligomer formation during the sampling and the pretreatment was studied. The mixture solution was dried on a Teflon filter, and 0.1-ppmv ozone/air gaseous mixture was then flowed through the filter at 10 L min^{-1} for 40 min. In the extract of the filter, no oligomer was detected. These results indicate that the oligomers are produced by reactions occurring in the chamber. Gao et al. suggested that the oligomers found in the absence of seed particles might be produced by heterogeneous reactions catalyzed by organic acids,[4] while Ziemann proposed gas-phase radical–radical reactions leading to dimeric products.[11] The formation mechanism of oligomers is still unclear.

The quantifications of dicarboxylic acids were carried out using the corresponding standards, whereas those of oxocarboxylic acids, hydroxydicarboxylic acids, and oligomers were, respectively, performed by employing 4-oxobutanoic acid, 2-hydroxy-2-methylbutanedioic acid, and dodecanedioic acid as surrogate standards. The mass fractions of dicarboxylic acids, oxocarboxylic acids, hydroxydicarboxylic acids, and oligomers in the total aerosol were obtained to be 30 ± 8, 4.8 ± 1.4, 1.1 ± 0.6, and 5.3 ± 3.8 wt %, respectively. Gao et al. reported these values for dicarboxylic acids, oxocarboxylic acids, hydroxydicarboxylic acids, and oligomers to be 24, 4, 3, and 3 wt %, respectively.[5] Although their value of hydroxydicarboxylic acids is slightly higher than the present result, the other results show agreement with the corresponding present results, respectively.

In conclusion, an LC/APCI-MS method was firstly examined for the analysis of aerosol from the ozonolysis of cyclohexene, and low-MW and oligomeric components in aerosol were successfully analyzed. APCI-MS was shown to be one of powerful detection techniques for oligomers. The formation mechanism of oligomers in the absence of seed particles is still unclear. One of possible approaches to study the formation mechanism is measurements of the concentrations of aerosol constituents as a function of reaction time.[2] Such measurements are now in progress.

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