Fundamental Chamber Experiment on Indoor Secondary Aerosol Derived from Ozone/VOC Reactions

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Abstract
Recently, theoretical analysis and investigations have begun to evaluate that secondary organic aerosols (SOA) are generated by chemical reactions in indoor air. The overarching goal of this work was to better understand ozone and VOCs (volatile organic compounds) distribution within rooms. Towards this end, this paper reports the development of a cylindrical test chamber that can be used to obtain the second order rate constant \( k_b \) for the bi-molecular chemical reaction of ozone and VOC in the air phase and the fractional aerosol yield \( Y \) for partitioning from the air phase to aerosol phase.

Keywords: ozone; VOCs; secondary organic aerosol; bi-molecular chemical reaction

1. Introduction
Many studies have reported associations with ozone-initiated chemistry in indoor environments. Weschler made it appear that ozone chemistry produces relatively short-lived products. Examples include primary and secondary ozonides, peroxyhemiacetals, \( \alpha \)-hydroxy ketones, and peroxyacyl nitrates. Secondary organic aerosols are also important stable products resulting from chemical reaction with ozone. They are formed from low vapor-pressure oxidation products that partition between the gas phase and the surface of pre-existing aerosols or nucleate to form new aerosols. The reaction of ozone with various terpenoids in indoor settings has been shown to contribute tens of \( \mu \)g/m\(^3\) to the indoor concentration of sub-micron particles under appropriate conditions (Weschler, 2006). The final purpose of this study was to develop a numerical method based on Computational Fluid Dynamics to predict ozone and VOCs distributions and their chemical reactions in indoor environments. Towards this end, this study developed a reliable method, using a cylindrical test chamber, to examine ozone and VOC reactions in the air phase and estimate the corresponding second order rate constant \( k_b \) and fractional aerosol yield \( Y \) which represents the bi-molecular chemical reactions of ozone and VOC. In this study, d-limonene (terpene), toluene (aromatic hydrocarbon) and nonanal (aldehyde) are targeted as representative of VOC in an indoor environment.

2. Theory
2.1 Equations for ozone and VOC transport in indoor air
Assuming the concentration of ozone at a point in space to be \( C_1 \) [ppm] and the concentration of VOC at a point to be \( C_2 \) [ppm], the transports are expressed by equations (1) respectively:

\[
\begin{align*}
\frac{\partial \bar{C}_1}{\partial t} + \frac{\partial U \bar{C}_1}{\partial x} &= \frac{\partial}{\partial x} \left( D_1 \frac{\partial \bar{C}_1}{\partial x} \right) + S_1 \\
\frac{\partial \bar{C}_2}{\partial t} + \frac{\partial U \bar{C}_2}{\partial x} &= \frac{\partial}{\partial x} \left( D_2 \frac{\partial \bar{C}_2}{\partial x} \right) + S_2
\end{align*}
\]

Here, overbar (\( \bar{\cdot} \)) denotes the ensemble-mean value. \( D_j \) [m\(^2\)/sec] is the molecular diffusion coefficient of ozone in the gas phase, \( [m/sec] \) is the ensemble-mean velocity, \( [m^2/sec] \) is the turbulent eddy viscosity, and \( S \) is the source term.

2.2 Modeling the bi-molecular chemical reaction
The bi-molecular chemical reaction of ozone and VOC is expressed by equation (2):

\[ S_1 = S_2 = -k_b \bar{C}_1 \bar{C}_2 \]  \hspace{1cm} (2)

Here, \( k_b \) is the second order rate constant [1/ppm/sec]. Equation (2) is incorporated within equation (1) as the source term. From equation (2), changes over time in the concentration of ozone \( "C_1" \) and VOC \( "C_2" \) due to the bi-molecular reaction are computed.

In addition, assuming the concentration of the hypothetical reaction products in air (vapor) phase...
to be \( C_p \) [ppm], the amount of change over time is expressed by equations (3) and (4). Here, \( k_p \) is the first order rate constant [1/sec] of the hypothetical reaction product \( C_p \).

\[
\frac{\partial C_p}{\partial t} + \frac{\partial U \cdot C_p}{\partial x_j} = \frac{\partial}{\partial x_j} \left( D_p + \frac{v_j}{\sigma_j} \right) \frac{\partial C_p}{\partial x_j} + S_p \quad (3)
\]

\[
S_p = k_p \cdot C_p = k_p \cdot C_1 \cdot C_2 \quad (4)
\]

2.3 Numerical modeling of SOA formation

In this research, assuming the concentration of the hypothetical reaction products in air (vapor) phase to be \( C_p \) [ppm], the amount of change over time is expressed by equation (5) (same as equation (4) when convection and diffusion terms are disregarded). Indoor ozone chemistry produces relatively short-lived products, such as primary and secondary ozonides, peroxynitrites, \( \alpha \)-hydroxy ketones, peroxyacyl nitrates, and secondary organic aerosol (SOA) in the aerosol phase.

\[
\frac{\partial C_p}{\partial t} = k_p \cdot C_1 \cdot C_2 \quad (5)
\]

In this paper, it is assumed that the seeding or nucleating particles such as low vapor pressure compounds and water vapor become the nuclei to form coagulation and aggregation, and that a size change in the SOA then begins.

\[
C_p \rightarrow \text{nucleation, cond, coag} \rightarrow C_{SOA} \quad (6)
\]

Although SOA concentration is usually expressed as the total aerosol mass \([g/m^3]\), in this paper, the volume fraction [ppm(vf)] is used to reflect the output of the Wide-Range Particle Spectrometer (WPS) based on differential mobility analyzer and application to CFD models.

Here, the fractional aerosol yield \( (Y) \) [ppm(vf)/ppm] between hypothetical reaction products \( C_p \) and SOA is expressed by equation (7):

\[
Y = \frac{\Delta C_{SOA}}{\Delta C_p} \quad (7)
\]

The change in SOA over time is expressed by using the fractional aerosol yield \( (Y) \) as follows:

\[
\frac{\partial C_{SOA}}{\partial t} = Y \cdot \frac{\partial C_p}{\partial t} = Y \cdot \left( k_p \cdot C_1 \cdot C_2 \right) \quad (8)
\]

This paper reports the fundamental data for the second order rate constant \( (k_p) \) expressed in equation (4) and the fractional aerosol yield \( (Y) \) expressed in equation (7) in the chemical reaction between ozone and VOC.

3. Methods

3.1 Overview of the cylindrical test chamber experiment

Fig. 1 shows a perspective layout of the cylindrical test chamber. The cylindrical test chamber is a duct cavity and consists of three sections (55 mm (diameter) \( \times \) 2,500 mm (length)) and these are connected using a U-bend (R=80[mm]). The inner boundaries for air passing through the chamber are made of electro-polished SUS 304 stainless steel. The air inlet velocity \((U_{in})\) was set at 1.0 m/s and 0.25 m/s. The inlet air and all the walls were maintained at isothermal conditions (293 ± 0.5 K). The supply air was passed through activated carbon and ULPA filters to keep the concentration of background contaminants (including VOCs and aerosols) low. The relative humidity of supplied air was controlled at 10% and below. In order to prevent photochemical reactions involving ozone, the experiments were carried out in a dark room. The points of measurement in the chamber are shown in Fig. 1. (Positions (1)-(7)).

Ozone was analyzed using a UV Photometric Analyzer at a wavelength of 254 nm; its concentration range was 0 - 9.999 ppm, and its precision was 0.001 ppm. The sampling flow rate of the UV Photometric Analyzer was 1.5 L/min and the ozone concentration was calculated as a time-averaged concentration over ten minutes. The adsorption sampling using Cartrapt 349 (Gestel) and thermal desorption (Gestel TDS) and GC/MS system (Agilent Tech., HP6890/ HP5973 MSD) were used to measure the VOCs. A Wide-range
Particle Spectrometer (MSP, Model 1000XP) was used to measure background ultra-fine particles (10 nm -10 µm diameter) and generated SOA. The accuracy of the WPS system is ± 3% for particle diameter and ± 10% for number concentrations.

These experiments focused on the heterogeneous reactions between ozone (or VOCs) and the inner surface of the chamber (Case x-1 and Case x-2) and homogeneous reactions between ozone and VOCs in the air phase (Cases x-3).

4. Results

4.1 Measurement results of concentration distribution of Ozone and VOC in the cylindrical test chamber

The background concentration of the sum of the airborne organic compounds was confirmed to be below 30 µg/m³, while the particulate matter in the supply air was below the detection limit of the WPS. Hence, gas phase reactions of ozone (except for reactions with targeted VOCs), as well as reactions on particle or aerosol surfaces, were negligible in the cylindrical test chamber experiment.

Tables 6., 7. and 8. show the average concentration of ozone and VOCs (d-limonene, toluene and nonanal) at each sampling point (see Fig.1.).

In Case x-1, in which only ozone was introduced to the cylindrical test chamber, the measured concentration decays were caused by wall surface deposition on the inner SUS304 surfaces. Correspondingly, in Case x-2, in which only target chemical compound (d-limonene, toluene or nonanal) was introduced to the cylindrical test chamber, the measured concentration decays were also caused by wall surface deposition. The concentration decreased, while air passing from the inlet (sampling position (1) in Fig.1.) to the outlet (sampling position (7) in Fig.1.) became about 10% for Case 1-1, and 10-15% for Case 1-2. In Case 1-3, in which ozone and limonene were supplied at the same time from the supply inlet, the decrease in the concentrations of ozone and limonene grew rapidly, and the concentration decrease from inlet (1) to outlet (7) became about 60% for ozone and 40% for limonene. In Case 1-3, SOA formation that originated in the chemical reactions of ozone and limonene was observed.

In Cases 3-3 and 4-3, in which ozone and toluene were supplied at the same time from the supply inlet, the decrease in the concentrations of ozone and toluene were not obviously compared with Case 1-3, and the concentration decrease from inlet (1) to outlet (7) became about 10% for ozone including the concentration decay of wall surface deposition. In Cases 3-3 and 4-3, SOA formation that originated in the chemical reactions of ozone and toluene was not observed. When nonanal was targeted, the tendencies of concentration decay were almost consistent with the results of the toluene and ozone.

4.2 Estimation of second order rate constant ($k_b$)

Using the data for the averaged concentration of ozone and target chemical compound at each sampling point in the cylindrical test chamber, the second order rate constant ($k_b$) for the bi-molecular chemical reaction of ozone and target chemical compound in the air phase was estimated according to Equation (2). The concentration difference in each sampling point

### Table 1. Cases Analyzed in the Cylindrical Test Chamber Experiment

| Case | Supply Inlet Vel. | Ozone | d-Limonene |
|------|-------------------|-------|------------|
| Case 1-1 | $U_{in}=1.00$ [m/s] | 1.00 [ppm] | - |
| Case 1-2 | - | - | 19.5 [µg/s] |
| Case 1-3 | - | 1.00 [ppm] | 19.5 [µg/s] |
| Case 2-1 | - | 5.00 [ppm] | - |
| Case 2-2 | - | - | 8.1 [µg/s] |
| Case 2-3 | - | 5.00 [ppm] | 8.1 [µg/s] |

| Case | Supply Inlet Vel. | Ozone | Toluene |
|------|-------------------|-------|---------|
| Case 3-1 | $U_{in}=1.00$ [m/s] | 1.00 [ppm] | - |
| Case 3-2 | - | - | 6.1 [µg/s] |
| Case 3-3 | - | 1.00 [ppm] | 6.1 [µg/s] |
| Case 4-1 | - | 5.00 [ppm] | - |
| Case 4-2 | - | - | 6.0 [µg/s] |
| Case 4-3 | - | 5.00 [ppm] | 6.0 [µg/s] |

| Case | Supply Inlet Vel. | Ozone | Nonanal |
|------|-------------------|-------|---------|
| Case 5-1 | $U_{in}=1.00$ [m/s] | 1.00 [ppm] | - |
| Case 5-2 | - | - | 19.3 [µg/s] |
| Case 5-3 | - | 1.00 [ppm] | 19.3 [µg/s] |
| Case 6-1 | - | 5.00 [ppm] | - |
| Case 6-2 | - | - | 2.3 [µg/s] |
| Case 6-3 | - | 5.00 [ppm] | 2.3 [µg/s] |

(Isothermal conditions; 293 ± 0.5 K, Low relative humidity; <10%)
was calculated based on estimated concentration at the inlet position. The concentration changes over time were calculated by using the pre-estimated data on the age of the air in Table 6. The age of air distributions in the cylindrical test chamber were analyzed by CFD (Computational Fluid Dynamics) and SVE concepts [Kato, 1988] beforehand.

In Case 1, second order rate constant ($k_b$) estimated from the decrease in concentration of ozone ranged from $7.8 \times 10^{-2}$ to $2.4 \times 10^{-3} \text{ [1/ppm/sec]}$, and was $1.3 \times 10^{-1} \text{ [1/ppm/sec]}$ on average. The second order rate constant ($k_b$) estimated from the decrease in concentration of d-limonene ranged from $3.6 \times 10^{-1}$ to $3.6 \times 10^{-1} \text{ [1/ppm/sec]}$, and was $1.3 \times 10^{-1} \text{ [1/ppm/sec]}$ on average. This was reasonably consistent with the $k_b$ estimated from the ozone data. In Case 2, $k_b$ estimated from experimental data for ozone was $3.0 \times 10^{-2} \text{ [1/ppm/sec]}$ and was $1.3 \times 10^{-1} \text{ [1/ppm/sec]}$ on average. It was found that the $k_b$ estimated from the ozone data was consistent with the $k_b$ estimated from the experimental data for ozone.

### Table 2. For each of the Experimental Cases, Ozone, Limonene and SOA Concentrations at each Sampling Point

| Sampling Point | Inlet (1) | Outlet (7) |
|----------------|----------|------------|
| Case 1-1 (Ozone) [ppm] | 1.00 | 0.97 |
| Case 1-2 (limonene) [ppm] | 1.75 | 1.57 |
| Case 1-3 (Ozone) [ppm] | 1.00 | 0.97 |
| Case 1-3 (limonene) [ppm] | 1.75 | 1.57 |
| Case 1-3 (SOA) [ppm (vf)] | 3.57 | 0.95 |

### Table 3. For each of the Experimental Cases, Ozone, Toluene and SOA Concentrations at each Sampling Point

| Sampling Point | Inlet (1) | Outlet (7) |
|----------------|----------|------------|
| Case 2-1 (Ozone) [ppm] | 5.00 | 4.91 |
| Case 2-2 (limonene) [ppm] | 2.08 | 2.03 |
| Case 2-3 (Ozone) [ppm] | 5.00 | 2.91 |
| Case 2-3 (limonene) [ppm] | 1.74 | 1.80 |
| Case 2-3 (SOA) [ppm (vf)] | 7.03×10^{-2} | 7.55×10^{-2} |

### Table 4. For each of the Experimental Cases, Ozone, Nonanal and SOA Concentrations at each Sampling Point

| Sampling Point | Inlet (1) | Outlet (7) |
|----------------|----------|------------|
| Case 3-1 (Ozone) [ppm] | 1.00 | 0.96 |
| Case 3-2 (toluene) [ppm] | 0.67 | 0.34 |
| Case 3-3 (Ozone) [ppm] | 1.00 | 0.90 |
| Case 3-3 (toluene) [ppm] | 0.67 | 0.31 |
| Case 3-3 (SOA) [ppm (vf)] | 2.13×10^{-6} | 2.17×10^{-6} |

### Table 5. For each of the Experimental Cases, Ozone, Nonanal and SOA Concentrations at each Sampling Point

| Sampling Point | Inlet (1) | Outlet (7) |
|----------------|----------|------------|
| Case 4-1 (Ozone) [ppm] | 5.00 | 4.91 |
| Case 4-2 (toluene) [ppm] | 2.62 | 0.52 |
| Case 4-3 (Ozone) [ppm] | 5.00 | 0.53 |
| Case 4-3 (toluene) [ppm] | 2.62 | 0.55 |
| Case 4-3 (SOA) [ppm (vf)] | 2.55×10^{-6} | 2.52×10^{-6} |

### Table 6. For each of the Experimental Cases, Ozone, Toluene and SOA Concentrations at each Sampling Point

| Sampling Point | Inlet (1) | Outlet (7) |
|----------------|----------|------------|
| Case 5-1 (Ozone) [ppm] | 1.00 | 0.96 |
| Case 5-2 (nonanal) [ppm] | 1.37 | 0.36 |
| Case 5-3 (Ozone) [ppm] | 1.00 | 0.95 |
| Case 5-3 (nonanal) [ppm] | 1.37 | 0.44 |
| Case 5-3 (SOA) [ppm (vf)] | 3.27×10^{-6} | 7.08×10^{-3} |
| Case 6-1 (Ozone) [ppm] | 5.00 | 4.91 |
| Case 6-2 (nonanal) [ppm] | 0.66 | 0.50 |
| Case 6-3 (Ozone) [ppm] | 5.00 | 0.45 |
| Case 6-3 (nonanal) [ppm] | 0.66 | 0.43 |
| Case 6-3 (SOA) [ppm (vf)] | - | - |
estimation, \(k_b\) seems to be time dependent.

Atkinson et al. (1990) report the measurement results of \(k_b\) for ozone and limonene to be \(2.1 \times 10^{-16}\) \([\text{cm}^3 \text{molecules}^{-1} \text{sec}^{-1}]\) and the order of this value is close to the estimated result in Case 2.

In Cases 3 and 4, in which ozone and toluene were supplied at the same time from the supply inlet, obvious concentration decay that originated in the chemical reaction was not observed, therefore, the presumption of \(k_b\) was difficult. As well as Cases 3 and 4, in Cases 5 and 6, in which ozone and nonanal were supplied at the same time from the supply inlet, obvious concentration decay that originated in the chemical reaction was not observed.

As for three kinds of chemicals (d-limonene, toluene and nonanal) that had been targeted in this experiment, it was confirmed that there was a chemical dependency concerning the reaction with ozone.

4.3 Measurement results for SOA in a cylindrical test chamber

The concentration distributions of SOA formed by the bi-molecular chemical reaction of ozone and d-limonene at each of the sampling points are shown in Fig.2. (Case 1-3) and Fig.3. (Case 2-3).

In Case 1-3, in which ozone and d-limonene were introduced from the supply inlet at the same time with the inlet velocity set to 1.00 \([\text{m/s}]\), rapid generation of SOA was confirmed at sampling point (2) and the peak concentration in the distribution of particle size was about 20 \([\text{nm}]\). The age of air at sampling point (2) is 2.06 \([\text{sec}]\). In accordance with the flow in the cylindrical test chamber from supply inlet to exhaust outlet, the peak concentration of the SOA decreased gradually and the overall particle size became larger.

In Case 2-3, in which the inlet air velocity was set to 0.25\([\text{m/s}]\) and the nominal time constant (time scale defined by chamber volume and ventilation rate) in the cylindrical test chamber was four times as long as for Case 1, the rapid generation of an SOA with a peak concentration in the distribution of particle size of about 40 \([\text{nm}]\) was confirmed at sampling point (2). The peak concentration in the distribution of particle size was about 50% lower than in Case 1-3, and plenty of SOA of about 100 \([\text{nm}]\) in size or more was generated. Although the tendency is not obvious, two peaks (about 40 \([\text{nm}]\) and 100 \([\text{nm}]\)) can be observed in the generated SOA particles. As in Case 1-3, the peak concentration in the distribution of particle size in the SOA decreased gradually and the overall particle size became larger in accordance with the flow in the cylindrical test chamber from supply inlet to exhaust outlet.

A wide range particle spectrometer (WPS) system was used to analyze the particle size and concentration distribution in the cylindrical test chamber. The WPS system consists of a differential mobility analyzer (DMA) and a laser particle counter (LPC), and is based on the classification of electrical mobility. Thus the measurement results depend on the shape and size of the particles, rather than on their mass density. Although the SOA concentration is usually expressed as the total aerosol mass \([\text{g/m}^3]\), in this paper, the volume fraction \([\text{ppm(vf)}]\) is used to reflect the output of the WPS system.

The overall tendency in Case 1-3 and Case 2-3 was for the SOA concentration to rise in the leeward direction of the cylindrical type chamber. The SOA
concentration and change in the size distribution along the chamber from the supply inlet to the exhaust outlet position expresses the progress with time of coagulation or aggregation with surrounding compounds in the air.

In Cases 3-3 and 4-3 in which ozone and toluene were targeted and in Cases 5-3 and 6-3 in which ozone and nonanal were targeted, the generation of SOA that was able to be obviously measured with the WPS system was not confirmed.

### 4.4 Estimation of the fractional aerosol yield (Y)

Using the data for the average concentration of the SOA at each sampling point, the fractional aerosol yield (Y) was estimated from Equation (9). The estimated results are shown in Table 2.

In Case 1, the fractional aerosol yield (Y) estimated from the ozone concentration change over time ranged from 1.1 × 10^{-2} to 3.6 × 10^{-3} [-] and changed greatly at each measurement point. The fractional aerosol yield (Y) was estimated at 7.8 × 10^{-3} [-] on average. The value of Y estimated from the change in the d-limonene concentration over time ranged from 2.5 × 10^{-2} to 2.3 × 10^{-3} [-], and was 1.1 × 10^{-2} [-] on average. The value of Y estimated from the change in the limonene concentration is reasonably consistent with the Y value estimated from the change in the ozone concentration.

In Case 2, in which the inlet velocity was set relatively low, Y estimated from experimental data for ozone was 3.1 × 10^{-2} [-] and Y estimated from the experimental data on d-limonene ranged from 8.3 × 10^{-2} to 5.1 × 10^{-1} [-], and was 2.2 × 10^{-1} [-] on average.

In the experimental cases intended for the toluene or nonanal, Y reached a very small value because of the small amount of SOA generation.

### 5. Discussion

The result of estimating the second order rate constant (k_b) between ozone and limonene as a function of the age of the air is shown in Fig.4. The k_b value was estimated to be large in the initial stage of the bimolecular chemical reaction and became relatively small as time progressed. Under these experimental conditions, k_b was assumed to have a time-varying characteristic and its dependency on the initial concentration was relatively small.

As shown in the various previous reports, it was confirmed that an SOA of nanometer [nm] order was rapidly generated from the coexistence of ozone and d-limonene in the air. Though the tendency is not clear, two peaks (about 40 [nm] and 100 [nm] in particle size) could be observed in the size and concentration distribution of the SOA in Case 2-3. As already mentioned, the ozone-limonene reaction products include both organic acids and aldehydes. These species have different vapor pressures and different affinities for water. It is conceivable that the nucleation of new seed particles occurs as an external mixture, i.e. that the seed particles have a different chemical composition. If so, then subsequent condensational growth may occur at different rates on different particles because of the different chemical affinity for the condensing species on particular seed particles. In this manner, one could envision rapid growth of a subset of the particles, followed by slower growth of the others.

The result of estimating the fractional aerosol yield (Y) as a function of the age of the air is shown in Fig.5. The fractional aerosol yield (Y) was estimated to be small in the initial stage of partitioning from the vapor phase to the aerosol phase and became relatively large with the progress of time. Under these experimental conditions, the value of Y was assumed to have a time-varying characteristic and the dependency on the initial concentration was relatively small.

The development of an SOA partitioning model that can reproduce the size distribution of particles remains the subject of future work.

### 6. Conclusions

The findings obtained from the cylindrical test chamber study can be summarized as follows:
(1) This work has produced a reliable method which permits estimations of the second order rate constant ($k_b$) for bi-molecular chemical reactions in the gas phase based on the concentrations measured along the stream line in the chamber.

(2) The $k_b$ values for ozone and limonene reactions were estimated to be between $1.1 \times 10^{-4}$ and $1.1 \times 10^{-3}$ [1/ppm/sec] on the average and was confirmed to be almost identical to the values of $k_b$ reported by Atkinson.

(3) As for toluene or nonanal, obvious concentration decay that originated in the chemical reaction with ozone was not observed. It was confirmed that there was a chemical dependency concerning the air phase reaction and SOA generation derived from oxidation.

(4) The $Y$ value for partitioning of the vapor phase (ozone, limonene and hypothetical products) to the aerosol phase (SOA) were estimated to be between $7.8 \times 10^{-6}$ and $1.1 \times 10^{-7}$ [-] in Case 1 and to be between $3.1 \times 10^{-5}$ and $2.2 \times 10^{-5}$ in Case 2.

(5) In this experimental case intended for the toluene or nonnal, $Y$ reached a very small value because of the small amount of SOA generation.

Notes

1) This paper is the re-composition of new experimental results and considerations in the content on which it has previously reported by Ito [2007].

2) Ozone (Chemical formula; O$_3$, molecular weight; M=48, Molecular diffusion coefficient in air; D=1.81 $\times 10^{-5}$ [m$^2$/s] at 293 K), d-limonene (Chemical formula; C$_{10}$H$_{16}$, molecular weight; M=136.23, Molecular diffusion coefficient in air; D=6.2 $\times 10^{-9}$ [m$^2$/s] at 293 K)

3) The generation devises and mixture of ozone has confirmed the dependence of atmospheric pressure for the generation rate. In this experiment, generation rate of ozone was affected by the air velocity. The generation rate of VOC was controlled in accordance with the change of ozone concentration.

4) The estimation of rate constant which rules ozone/VOC reactions is assumed based on the fact that there is no dependency of concentration level.

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