Research Report Secondary Organic Aerosol Formation from Photochemical Reaction of Aromatic Hydrocarbons Hideto Takekawa

Abstract

A temperature-controlled smog chamber was used to investigate the temperature dependence of secondary organic aerosol (SOA) formation from photochemical reaction of three aromatic hydrocarbons (toluene, *m*-xylene and 1,2,4trimethylbenzene). The experiments were performed at 283 K and 303 K for each hydrocarbon. A higher SOA yield was obtained at lower temperature and at a higher concentration of SOA generated. The relationship of SOA yield to temperature and SOA concentration is expressed by a gas/particle partitioning absorption model considering temperature dependence. Under the condition of the same SOA concentration, the SOA yield at 283 K was approximately twice that at 303 K. It has been clarified experimentally that temperature is one of the most important factors in SOA formation. The SOA yields of the aromatic hydrocarbons were higher in the order of toluene, m-xylene and 1,2,4-trimethylbenzene. The order of the SOA yield was the reverse of the reaction rate constant with OH radicals, which indicated the probability of SOA being generated by the secondary reaction.

Keywords

Gas/particle partitioning, Secondary organic aerosol, Aerosol yield, Aromatic hydrocarbons, Photochemical reaction

1. Introduction

Particulate matter (PM) is one of the main pollutants in urban and suburban air. Reduction of emissions from factories, vehicles and other sources effects a decrease in PM concentration. Modeling of all processes for PM is needed for an air quality model to evaluate such a decrease. PM is divided into two classes, primary generation and secondary formation. The former is the case in which pollutant sources emit PM directly and the latter is the case in which the PM is produced in the atmosphere by the reaction of gaseous species exhausted from the sources. Secondary formation requires a more complex model than primary generation because not only quantification of precursor gas emissions, but also estimation of the amount of PM production by the subsequent reaction of the gas is required for a secondary formation model. PM formed secondarily is composed of inorganic and organic species. Inorganic PM in the atmosphere is composed of a small number of compounds such as sulfates and nitrates, and is quantified by a thermodynamic equilibrium model. On the other hand, organic PM is composed of a large number of compounds, most of which have not been identified. Therefore, quantifying secondary organic aerosol (SOA), that means organic PM formed secondarily is more difficult than quantifying inorganic PM formed secondarily.

In the atmosphere, SOA is formed from organic gases by two processes, production of condensable organic compounds (COC) through reaction and subsequent condensation of the COC. Organic gases are mainly consumed by photo-dissociation or reaction with OH, O_3 or NO₃. Absorption crosssections, quantum yields and reaction rate constants for these active species have already been obtained for many organic compounds.^{1, 2)} On the other hand, little information for COC has been obtained on the components, yields and ratios existing in the aerosol phase. Therefore, simplified models have been used to quantify SOA.

In the SOA formation model constructed by Pandis et al.³⁾, when the concentration $\triangle ROG$ of the reactive organic gas has reacted, the concentration of SOA formed is obtained by

$$\Delta M = Y \Delta ROG \,. \tag{1}$$

Y : aerosol yield

In the Pandis model, *Y* is considered a constant value for each ROG.

Odum et al.⁴⁾ indicated from experimental results that Y depends on the total mass concentration of the organic aerosol M_0 and expressed the relationship between Y and M_0 by the gas/particle partition of COC_i as

$$Y = \sum_{i} M_{\rm o} \frac{\alpha_i K_{\rm om, i}}{1 + K_{\rm om, i} M_{\rm o}} . \qquad (2)$$

 α : COC yield of *ROG*

 $K_{\rm om}$: gas/particle partition constant

 $K_{\rm om}$ is defined as

 $K_{\text{om, }i} = G_i / (A_i M_o)$. (3)

G : concentration of COC in the gas phase

A : concentration of COC in the aerosol phase The influence of other factors on Y has not been clarified based on the experimental results. K_{om} depends on temperature theoretically; ^{5, 6)} therefore, Y is also expected to depend on temperature.

In the present study, the influence of temperature on SOA formation from photo-oxidation of aromatic hydrocarbons was investigated experimentally.

2. Experimental

A schematic of the experimental system⁷⁾ is shown in Fig. 1. Experiments were performed using a smog chamber that was constructed of 50 μ m thick Teflon film and had a volume of 2 m^3 . The chamber was surrounded by forty blacklights (NEC, FL40SBL) as a light source. The chamber and the blacklights were assembled in a temperaturecontrolled room (Tabai Espec, TBUU-3HW0G2C). Prior to each experiment, the chamber was flushed for forty hours with purified air. The flushing was conducted with exposure of UV light from the blacklights, followed by an additional period of at least 6 hours without exposure. After the chamber was flushed, humid air was established through the chamber. A specific hydrocarbon was then injected by syringe into a heated glass tube connected to the chamber by a Teflon line, and the evaporated hydrocarbon was introduced into the chamber by allowing purified air to flow through the Teflon line.

As seed particles, Na₂SO₄ was introduced into the chamber through a Teflon line. The initial concentrations of the seed particles were typically 3000-15000 particles cm⁻³ with a diameter of approximately 50 nm. NO and NO₂, approximately 500 ppm in nitrogen, was injected into the chamber through a Teflon line. Propene was also injected to accelerate the photochemical reaction. Approximately 500 ppm of propene in nitrogen was used for the injection. The initial concentration of propene was approximately 1 ppm. The reactants were then mixed by flushing purified air into the chamber, the initial conditions were measured, and the experiment was started by turning on the blacklights. The irradiation was continued for several hours.

A scanning mobility particle sizer (SMPS, TSI, Model 3934) was used to measure the size distribution of the aerosol with diameters between 17 and 1000 nm. The concentrations of hydrocarbons were measured using a gas chromatograph (Shimadzu, GC-14B) equipped with a flame ionization detector. The concentrations of NO and NO_x were monitored with a chemi-luminescence analyzer (Thermo Environmental Instruments, Model 42). The concentrations of ozone and CO were measured by UV and IR absorption analyzers (Thermo Environmental Instruments, Model 48C and 49C), respectively.

The total amount of aerosol deposited on the walls of the chamber was estimated for each experiment.



Fig. 1 Schematic of experiment.

To determine the deposition rate of the aerosol, the decay of the aerosol was observed under the dark condition. The deposition rate constant (k_{dep} , h^{-1}) of the aerosol depended on its diameter (d_p , nm) and can be expressed as⁷

$$k_{\rm dep}(d_{\rm p}) = 1.47 \times 10^{-8} d_{\rm p}^{2.57} + 1.02 \times 10^2 d_{\rm p}^{-1.28}.$$

Both suspended and deposited aerosol

concentrations were corrected considering the drying effect of using air from the temperature-controlled room as the sheath air in the SMPS⁷).

Hydrocarbons were consumed by deposition on the walls as well as by photo-oxidation. The deposition rate of all hydrocarbons was considered to be 0.6% h^{-1} based on the measurements obtained by observing the decay of the hydrocarbons under the dark condition. Concentrations of the hydrocarbons that had reacted were calculated from the consumed and deposited concentrations.

3. Results and discussions

3.1 Aerosol formation

For each hydrocarbon, four or five experiments were performed at a temperature of 283 or 303 K and a relative humidity of approximately 60%. The initial reactant concentrations are shown in **Table 1**. NO comprised approximately 50% of the initial NO_x. **Figure 2** shows typical results obtained by irradiating a mixture of 4.33 ppm toluene and 0.413 ppm NO_x in air at a temperature of 303 K (TOL-301). As seen in Fig. 2, aerosol formation in the

> chamber was observed after approximately 1.0 hour of irradiation. The experiment was terminated after 4.0 hours of irradiation. The measured aerosol concentration became the highest value of 90 $\mu m^3 cm^{-3}$ after 3.6 hours of irradiation, at which time 0.33 ppm of the toluene had been consumed. Suspended and deposited SOA concentrations were estimated to be 92 and 24 μ m³cm⁻³, respectively. Assuming that the density of SOA is unity, the suspended and deposited SOA masses were 92 and 24 μ g m⁻³, respectively, and a total of 116 μ g m⁻³

HC NO NO_x HC/NO_x Т ΔROG Y No. C_3H_6 $\Delta M_{\rm o}$ $R_{\rm s}$ $(\mu g m^{-3})$ (ppm/ppm) (ppm) (ppm) (ppm) (ppm) (K) (ppm) (%) Toluene TOL-101 0.234 0.79 22 2.64 0.118 11.3 1.0 283 0.12 84 TOL-102 3.25 0.142 0.284 11.4 1.1 283 0.16 99 0.77 20 TOL-103 2.20 0.094 0.186 10.5 1.1 283 0.13 0.73 16 61 TOL-301 10.5 0.9 4.33 0.211 0.413 303 0.24 92 0.79 13 TOL-302 3.35 0.169 0.337 9.9 1.0 303 0.19 57 0.85 9.5 *m*-Xylene 0.185 11.8 1.1 283 0.23 130 0.79 17 XYL-101 2.19 0.098 XYL-102 1.57 0.073 0.147 10.7 1.2 283 0.16 69 0.76 13 XYL-301 3.13 0.153 0.292 10.7 1.0303 0.48 123 0.85 7.0 XYL-302 1.98 0.100 0.196 10.1 1.0 303 0.26 43 0.80 4.9 XYL-303 2.83 0.144 0.275 10.3 1.0 303 0.44 98 0.81 6.5 1,2,4-Trimethylbenzene 0.9 101 11 TMB-101 1.66 0.069 0.141 11.8 283 0.22 0.77 TMB-102 1.11 0.067 0.128 8.7 1.2 283 0.21 58 0.77 6.9 10.0 TMB-301 3.00 0.154 0.301 1.0 303 0.49 115 0.86 5.8 TMB-302 1.91 0.106 0.217 8.8 1.0 303 0.38 42 0.79 3.4

Table 1 Summary of experiment.



Fig. 2 Typical time variation in the gas and the aerosol concentrations during UV irradiation of a $HC/NO_x/air$ mixture.

of SOA had been generated. It was estimated that 0.09 ppm of toluene had been deposited. Consequently, the concentration of toluene reacted was calculated to be 0.24 ppm (890 μ g m⁻³ at 303 K). The SOA yield was estimated to be 0.13. All results are shown in Table 1. **Figure 3** shows plots of the aerosol yield of toluene as a function of suspended SOA concentration at 283 and 303 K. The higher SOA yield was obtained at a lower temperature and in a higher concentration of SOA.

3. 2 Temperature dependence of gas/particle partition absorption

The temperature dependence of SOA yield is expressed by developing the gas/particle partition model described by Odum et al.⁴⁾.

The influence of particle deposition on the wall is also considered. When the deposited aerosol concentration is not negligible and the deposited aerosol compounds are assumed not to influence the gas/particle partition absorption, the SOA yield *Y* is expressed as a function of SOA concentration M_0 by⁷⁾

$$Y = M_{\rm o} \sum_{i} \frac{\alpha_i K_{\rm om, i}}{R_{\rm s, i} + K_{\rm om, i} M_{\rm o}} \quad \dots \qquad (5)$$

 α : COC yield

 $R_{\rm s}$: ratio of suspended to total concentration of SOA

In the case where deposited concentration of SOA is considered to be negligible, R_s is equal to unity and Eq. (5) is equivalent to Eq. (2).

 $K_{\rm om}$ is defined by Odum et al.⁴⁾ as

$$K_{\text{om},i} = \frac{760RT}{MW_{\text{om}} \, 10^6 \zeta_i p_{\text{L},i}^0} \qquad (6)$$

R : ideal gas constant $(8.206 \times 10^{-5} \text{ m}^3 \text{ atm mol}^{-1} \text{ K}^{-1})$ *MW*_{om} : molecular weight of the organic matter phase (g mol⁻¹)

 ζ : activity coefficient in the organic matter phase

$$p_{\rm L}^{0}$$
: liquid vapor pressure (torr, sub-cooled if necessary)

As shown in Eq. (6), K_{om} has temperature dependence. The relationship between p_L^{0} and *T* is expressed by the Clapeyron-Clausius equation as



Fig. 3 Aerosol yield (*Y*) as a function of the organic aerosol mass (M_o) for toluene. Open and closed plots indicate experimental data at 303 K and 283 K, respectively. Lines indicated at these temperatures were obtained using an optimized value for the three parameters and $R_s = 0.79$, average value of all experiments for toluene.

$$p_{\mathrm{L},i}^{0} = A \exp\left(-\frac{\Delta H_{\mathrm{vap},i}}{RT}\right). \qquad (7)$$

A : preexponential constant

 $\Delta H_{\rm vap}$: enthalpy of vaporization

Substituting Eq. (6) with Eq. (7) and using 303 K for the reference temperature, $K_{\rm om}$ is finally defined as^{7, 8)}

$$K_{\text{om, }i} = K_{303, i} \frac{T}{303} \exp\left[B_i \left(\frac{1}{T} - \frac{1}{303}\right)\right]$$
. (8)

 $K_{303}: K_{\rm om}$ at 303 K

B : equal to $\Delta H_{\rm vap}/R$

The temperature dependence of the SOA yield is represented by substituting Eq. (8) for Eq. (5). Since the temperature dependence of α has not been clarified fully, α is assumed to have a constant value. Three parameters, α , K_{303} and B, are required for each *i*.

In this study, all COCs were considered to be classified in the same category (*i*=1 in Eqs. (5) and (8)), and three parameters, α , K_{303} and B, were obtained for each hydrocarbon with optimization of the experimental results (**Table 2**). In Fig. 3, the optimized lines at 283 and 303 K obtained using $R_s = 0.79$, the average value of all experiments for toluene, are also indicated. It is clear that temperature is one of the most important factors in SOA formation. Under the condition of 100 μ g m⁻³, the SOA yield at 283 K was from 1.6 to 2.4 times higher than that at 303 K (Table 2).

3.3 Comparison of the SOA yields between hydrocarbons

Figure 4 shows the Y versus M_0 lines for all hydrocarbons with R_s equal to unity at two temperatures. The SOA yields of the aromatic

 Table 2 Estimated parameters for SOA formation.

НС	α	K_{303} ($\mu g^{-1} m^3$)	В	$\frac{Y(283K)^{*}}{Y(303K)}$
Toluene	0.33	0.0058	3900	1.56
<i>m</i> -Xylene	0.25	0.0030	6300	2.38
124-TMB**	0.31	0.0019	3800	1.90

*at $M_0 = 100 \ \mu \text{g m}^{-3}$ and $R_s = 1.00$.

**1,2,4-trimethylbenzene.

hydrocarbons were higher in the order of toluene, *m*-xylene and 1,2,4-trimethylbenzene. The reaction rate constants of these hydrocarbons with OH radicals at 298 K are 5.96×10^{-12} , 23.6×10^{-12} and 32.5×10^{-12} cm³ molecule⁻¹ s⁻¹, respectively²). The order of the SOA yield of the aromatic hydrocarbons was the reverse of the reaction rate constant with OH radicals, and a possible explanation is as follows: in the case of toluene, as Hurley et al.⁹ suggested, SOA was produced by the secondary reaction. Assuming that SOA is generated by the secondary



Fig. 4 Aerosol yield (*Y*) as a function of the organic aerosol mass (M_0) for each hydrocarbon at 303 K (top) and 283 K (bottom). Every line was obtained using R_s equal to unity. 124-TMB stands for 1,2,4-trimethylbenzene.

reaction and the rate constants of the secondary reactions are similar between all of the aromatic hydrocarbons, the hydrocarbon with a lower rate constant for the primary reaction has a higher reaction ratio of secondary to primary. The SOA yield is defined as the concentration ratio of generated SOA to reacted hydrocarbon, which is proportional to the reaction ratio of secondary to primary. Therefore, it is possible that an aromatic hydrocarbon with a lower rate constant for reaction with OH radicals has a higher SOA yield.

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References

- Jeffries, H. E., et al. : Final Report, EPA-600/3-89-010d (1989)
- Atkinson, R. : J. Phys. Chem. Ref. Data, Monogr., 2(1994), 1-216
- Pandis, S. N., et al. : Atmos. Environ., 13(1992), 2269-2282
- Odum, J. R., et al. : Environ. Sci. Technol., 30(1996), 2580-2585
- 5) Pankow, J. F. : Atmos. Environ., 28(1994), 185-188
- 6) Pankow, J. F. : Atmos. Environ., 28(1994), 189-193
- 7) Takekawa, H., et al. : Atmos. Environ., (in press)
- Sheehan, P. E. and Bowman, F. M. : Environ. Sci. Technol., 35(2001), 2129-2135
- Hurley, M. D., et al. : Environ. Sci. Technol., 35 (2001), 1358-1366

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