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Kinetics of the Reactions of Ozone with 2,5-Dimethylfuran and Its Atmospheric Implications

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To determine the reaction rate coefficient of volatile organic compounds with ozone, the reduction of ozone through a flow-tube reactor was measured by a chemiluminescent detector. The validity of the method was confirmed by examination on isoprene. Consequently, the reaction rate coefficient of 2,5-dimethylfuran, DMF, with ozone was determined as $(4.2 \pm 0.9) \times 10^{-16}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$ for the first time. It was suggested that ozonolysis can be important for the fate of DMF in the atmosphere.

Volatile organic compounds (VOCs) have been a focus as critical precursors of photochemical oxidants and secondary organic aerosols (SOAs).[1,2] VOCs are emitted into the atmosphere from various sources. Initial reactions of VOCs with atmospheric radicals are important to capture both the atmospheric degradation of VOCs and production of oxidants and SOAs. In general, the atmospheric lifetimes of VOCs are dominated by daytime OH radical due to high reaction coefficients. However, for some VOCs like alkenes, reactions with ozone (O_3) are also significant. It is known that the first step of ozonolysis of alkenes is the addition of O_3 to the C=C double bonds.[1] To discuss the fate of VOCs and the secondary products in the atmosphere, reactions of VOCs with both OH and O_3 should be explored. However, there are many kinds of VOCs whose reaction coefficients with radicals are still not reported at present. Especially, studies of kinetics of oxygenated VOCs (OVOCs) are insufficient.

2,5-Dimethylfuran (DMF) has been focused on as a new biofuel.[3,4] Thus, it is possible for DMF emission into the atmosphere to increase in the future. DMF is also recognized as an effective marker of environmental tobacco smoke (ETS).[5,6] Thus, it is important to study the fate of DMF in the atmosphere and/or indoor air. Kinetics of the reaction of OH radical with DMF has been studied.[7,8] However, that of O_3 with DMF has not been reported yet to the best of our knowledge. In this study, measurement of rate coefficients of O_3 with DMF is conducted utilizing a combination of a flow-tube reactor and a fast-response O_3 monitor based on a chemiluminescent detector (CLD-O_3). This is the first trial to determine the reaction rate coefficient, k, of O_3 with DMF. Atmospheric lifetime of DMF is also investigated.

When O_3 is added to the standard gas of VOC, O_3 is reduced due to the reaction as:

$$\mathrm{VOC} + O_3 \rightarrow \text{products} \tag{R1}$$

If VOC is in much excess to O_3 and the variation of VOC is negligible, the reduction of O_3 through the reactor can be described as follows (pseudo-first-order reaction):

$$[O_3(\tau_R,\mathrm{VOC})]/[O_3(0)] = \exp\{-(k_{O_3+\mathrm{VOC}}[\mathrm{VOC}] + k_w)\tau_R\} \tag{1}$$

where τ_R is the reaction time in the reactor, k_w is the rate of wall loss of O_3, and k is the reaction rate coefficient. Meanwhile, when O_3 is mixed with clean air without VOCs (zero gas, ZG), the reduction of O_3 through the reactor can be described as follows:

$$[O_3(\tau_R,\mathrm{ZG})]/[O_3(0)] = \exp\{-k_w\tau_R\} \tag{2}$$

From the division (1)/(2), the contribution of k_w can be cancelled out as follows:

$$[O_3(\tau_R,\mathrm{VOC})]/[O_3(\tau_R,\mathrm{ZG})] = \exp\{-k_{O_3+\mathrm{VOC}}[\mathrm{VOC}]\tau_R\} \tag{3}$$

From the natural logarithm of (3), the relationship as follow can be acquired:

$$Y = -k_{O_3+\mathrm{VOC}}X \tag{4}$$

where $Y \equiv \ln\{[O_3(\tau_R,\mathrm{VOC})]/[O_3(\tau_R,\mathrm{ZG})]\}$, $X \equiv [\mathrm{VOC}]\tau_R$

k can be determined as the slope of the regression line between X and Y. In this study, the measurements of O_3 reduction due to VOC were conducted for several settings of VOC level and reaction time. From the experiment, dependence of Y on X was acquired and k was determined.

Figure 1 shows the schematic diagram of the experimental apparatus and gas flow. The clean zero gas (ZG) without VOCs was continuously supplied by a zero air generator (TECO, Model 111). Flow rates were controlled by mass flow controllers (MFC). Standard samples of VOCs were prepared by gas diffusion tube (Gastec Corp, PD-1B). The concentration of VOC was determined from the reduction rate of mass of reagent in PD-1B and the flow rate of sample in the reactor. One of the ZG flows was irradiated by UV of a low-pressure mercury lamp (Jelight Inc.) and O_3 was generated. The O_3/ZG flow was mixed with the standard VOC sample in the reactor. Initial mixing ratio of O_3 was 20–200 ppbv (10^{-9} mol/mol by volume), which corresponded to $(5–50) \times 10^{11}\,\mathrm{molecule\,cm^{-3}}$ in number density. In this study, a glass double-tube flow reactor was constructed. The inner tube was for the O_3/ZG flow, and the outer was for the VOC sample. The reaction time τ_R in the reactor was controlled by the position of the inner tube of the reactor and/or the sample flow rate. The air temperature of the

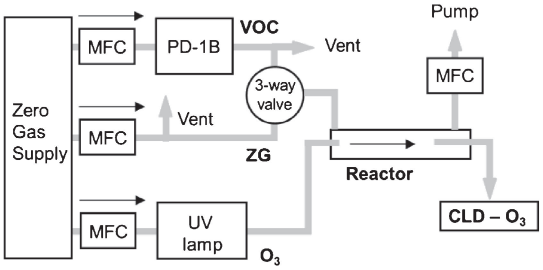

Figure 1. Schematic diagram of experimental setup.

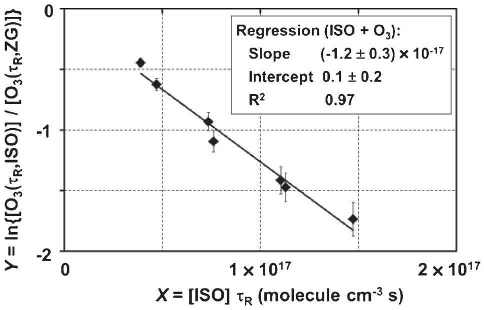

Figure 2. Correlation plot for isoprene.

laboratory was well controlled to 295 K. To measure the reduction of O_3 due to VOC in eq 4, the flows of VOC and ZG were automatically switched every 8 or 12 min by a solenoid three-way valve and a timer. O_3 concentration after the sample passed through the reactor was continuously monitored with the temporal resolution of 1 s by the CLD-O_3.[9] In this study, the detection limit of CLD-O_3 analyzer was 0.3 ppbv for 100-s average ($S/N = 3$).

To validate the method, O_3 reduction was monitored at first for standard samples of isoprene (ISO) whose reaction rate coefficient k was published.[10,11] In this study, the adopted ranges of number density of ISO and the reaction time τ_R were (3.7–4.0) × 10^{15} molecule cm^{-3} and 10–37 s, respectively.

Figure 2 shows a correlation plot between X and Y for isoprene. Y showed a strong correlation with X ($R^2 = 0.97$). No significant differences were shown between the intercept and zero. The slope of the regression was $(1.2 \pm 0.3) \times 10^{-17}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$. The uncertainty was estimated to be ± 28% (3σ) from the propagation of errors ([ISO], τ_R, and the regression). The value excellently agreed with $k_{\mathrm{O_3+ISO}}$ at 295 K which was calculated as $1.2 \times 10^{-17}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$ from the Arrhenius equation.[10] Consequently, the observed relationship between X and Y for ISO could be explained reasonably by eq 4. Note that other VOCs and/or radicals can be produced secondarily after the reaction.[10,11] However, in this study, VOC was much in excess to O_3 and such secondary products were considered negligible because of the following reasons: (a) secondary VOCs were much lower than the target VOC. O_3 reduction was dominated by the target VOC; (b) secondary OH radical was scavenged by the target VOC rather than O_3. O_3 reduction by OH was negligible. VOC reduction by secondary OH was also small. (c) It is known that isoprene can significantly produce secondary OH through ozonolysis.[10,11] In this study, the measured correlation between X and Y completely agreed with eq 4 which did not include the contribution of OH. This also supported that secondary VOCs and radicals were negligible. It was confirmed that the method for determination of k be valid.

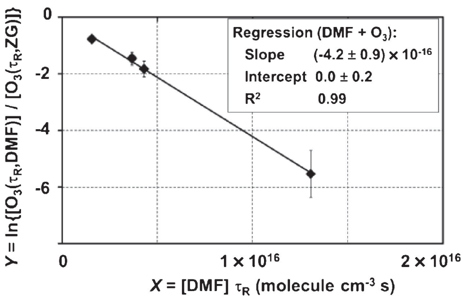

Figure 3. Correlation plot for DMF.

As a next step, O_3 reduction was monitored for standard samples of 2,5-dimethylfuran (DMF) whose reaction rate coefficient k was not published. In this study, the adopted ranges of number density of DMF and the reaction time τ_R were (5.7–47) × 10^{13} molecule cm^{-3} and 27–50 s, respectively. Figure 3 shows a correlation plot between X and Y for DMF. Y showed a strong correlation with X ($R^2 = 0.99$). The intercept of the regression line was zero. The relationship of eq 4 was observed also in the case of DMF. As a result, k was acquired as the slope of the regression as follows:

$$k_{\mathrm{DMF+O_3}}(295\,\mathrm{K}) = (4.2 \pm 0.9) \times 10^{-16}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}} \quad (5)$$

The reaction of DMF with O_3 is 180 and 20 times faster than those of furan and 3-methylfuran (3-MF), respectively.[7] High reactivity of DMF with O_3 was confirmed. It can be implied that alkyl-substitution at C=C double bonds in furans can accelerate ozonolysis.

Finally, the atmospheric lifetime of DMF by O_3 was estimated, and the fate of DMF in the atmosphere was discussed. When O_3 was assumed to be 7.5×10^{11} molecules cm^{-3} (30 ppbv) as a usual level,[7] the lifetime of DMF by O_3 was estimated as follows:

$$\tau_{\mathrm{DMF,O_3}}(295\,\mathrm{K}) = \{k_{\mathrm{DMF+O_3}}(295\,\mathrm{K})[\mathrm{O_3}]\}^{-1} = 0.9\,\mathrm{h} \quad (6)$$

Meanwhile, the lifetime of DMF by OH radical was reported as 2.1 h.[7] Additionally, O_3 is significant all day but OH reaction is only effective during daylight. Consequently, it was confirmed that ozonolysis is more critical than OH reaction to determine the lifetime of DMF in the atmosphere.

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References

1 R. Atkinson, *Atmos. Environ.* **2000**, *34*, 2063.
2 N. M. Donahue, A. L. Robinson, S. N. Pandis, *Atmos. Environ.* **2009**, *43*, 94.
3 Y. Román-Leshkov, C. J. Barrett, Z. Y. Liu, J. A. Dumesic, *Nature* **2007**, *447*, 982.
4 G. Tian, R. Daniel, H. Li, H. Xu, S. Shuai, P. Richards, *Energy Fuels* **2010**, *24*, 3898.
5 M. Alonso, A. Godayol, E. Antico, J. M. Sanchez, *Environ. Sci. Technol.* **2010**, *44*, 8289.
6 S. M. Charles, S. A. Batterman, C. Jia, *Atmos. Environ.* **2007**, *41*, 5371.
7 B. Cabañas, F. Villanueva, P. Martin, M. T. Baeza, S. Salgado, E. Jiménez, *Atmos. Environ.* **2005**, *39*, 1935.
8 S. M. Aschmann, N. Nishino, J. Arey, R. Atkinson, *Environ. Sci. Technol.* **2011**, *45*, 1859.
9 J. Matsumoto, N. Kosugi, A. Nishiyama, R. Isozaki, Y. Sadanaga, S. Kato, H. Bandow, Y. Kajii, *Atmos. Environ.* **2006**, *40*, 3230.
10 R. Atkinson, J. Arey, *Chem. Rev.* **2003**, *103*, 4605.
11 J. G. Calvert, R. Atkinson, J. A. Kerr, S. Madronich, G. K. Moortgat, T. J. Wallington, G. Yarwood, *The Mechanisms of Atmospheric Oxidation of the Alkenes*, Oxford University Press, New York, **2000**.