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Analytical characterization of O_3 samples prepared for investigation of tropospheric heterogeneous reactions

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Abstract: In this study, ozone (O_3) samples were prepared for investigating the heterogeneous reactions between O_3 and tropospheric aerosols and were characterized by spectroscopic methods. O_3 generated from an ozone generator was purified by selective adsorption on refrigerated silica gel, followed by transfer to a sample bulb. The amount of UV light ($\lambda = 256$ nm) absorbed by O_3 was measured as a function of time at two different temperatures (room temperature and 50 °C) and under different irradiation conditions. A correlation plot of $1/[O_3]$ versus time showed that O_3 decomposition follows the 2nd order reaction rate under a steady-state approximation. The initial concentration of O_3, observed rate constants (k_{obs}), and the half-life of O_3 in the sample stored at room temperature were determined to be 2.74 [±0.14] × 10^{16} molecules·cm^{-3}, 4.47 [±0.64] × 10^{-23} $molecules^{-1}\cdot cm^3\cdot s^{-1}$, and 9.5 [±1.4] days, respectively. The evaluation of O_3 stability under various conditions indicated that special care should be taken to prevent the exposure of the O_3 samples to high-temperature environment and/or UV radiation. This study established a protocol for the preparation of highly purified O_3 samples and confirmed that the O_3 samples can be stored for a day after preparation for further experiments.

Key words: Ozone, Stability of O_3, Troposphere, Heterogeneous reaction

1. Introduction

Ozone (O_3) is one of the most powerful oxidants in the troposphere.[1] O_3 plays an important role in homogeneous reactions as well as in heterogeneous reactions by oxidizing the surfaces of various tropospheric aerosols.[2-5] As an example, organic aerosols are chemically activated by O_3 to shorten the length of the carbon chain or to bind oxygen atoms to molecules. This results in modified functional properties of aerosols[5] and eventually affects the chemical properties and concentrations of various tropospheric species of interest. The heterogeneous reactivity of O_3 is lower than that of hydroxyl radicals (OH radicals). However, the higher concentration of O_3 (by a factor of 10^3–10^5) contributes to the oxidation reactions in the troposphere in a manner comparable to that of OH radicals.[6-8] Subsequently, information about kinetics and mechanism of the heterogeneous reactions of O_3 is important to update atmospheric models and

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gain better understanding of the atmosphere, especially the troposphere.

The prerequisite for the experimental investigation of the heterogeneous reactions of O_3 is the use of high-purity O_3 samples. Because O_3 is produced by an ozone generator that initiates production by the discharge of oxygen (O_2), the resulting O_3 is mixed with a large amount of O_2, which then needs to be removed from the samples for O_3 purification. One of the ways to selectively increase the O_3 content of samples is to utilize the difference in the boiling points between O_3 and O_2 (-112 and -183 ºC, respectively). Therefore, O_3 can be separated from O_2 by adsorption on silica gel at a low temperature (approximately -100 ºC).[9] Due to its high reactivity and, thus, relative instability, the concentration of O_3 in the samples immediately decreases upon preparation. This implies that long-term storage of O_3 samples may not be possible and the evaluation of the O_3 samples is necessary to meet the experimental requirements.

In this technical note, the procedure for preparing purified O_3 samples using the fractional distillation technique is described in detail. Absorption spectroscopy using ultraviolet (UV) light was applied for the accurate measurement of the O_3 concentration and to derive the correlation between the concentration by estimation and measurement. The stability of the sample was estimated by a kinetic study, which provides preliminary information to design an experiment for studying the heterogeneous reaction of O_3 on tropospheric aerosols, such as primary organic aerosols (POA) and secondary organic aerosol (SOA).

2. Experimental

2.1. Preparation and purification of O_3 samples

A vacuum line system, as shown in *Fig.* 1, was used for the preparation and purification of the O_3 samples. The vacuum line system consisted of a mixing chamber (AF-0061-03, Chemglass, USA), a pumping system equipped with a cold trap and mechanical pump (DUO 5M, Pfeiffer Vacuum Technology, USA), and four connection ports. An O_3 sample bulb (3 L, Home-made) was connected to the vacuum line system through a connection port (*Fig.* 1). A pressure gauge (275 Mini-Convenctron, MKS, USA) was used to monitor the pressure of the vacuum line system and estimate the O_3 concentration in the sample bulb.

O_3 was generated from the sequential reactions occurring in an ozone generator (LAB-1, Ozone Tech, Daejeon, Korea) connected to the O_3 trap. The reaction was initiated by the electrical discharge of oxygen flow (O_2, 99.999 %, 0.03 MPa, 1.5 L/min) to produce atomic oxygen [Reaction (1)], which combines with molecular oxygen to generate O_3 [Reaction (2)]. A small amount of O_2 participated in the generation of O_3; hence, the output was a mixture of O_3 and O_2 gases.

$$O_2(g) \rightarrow 2O(g) \quad \text{(by electrical discharge)} \qquad (1)$$

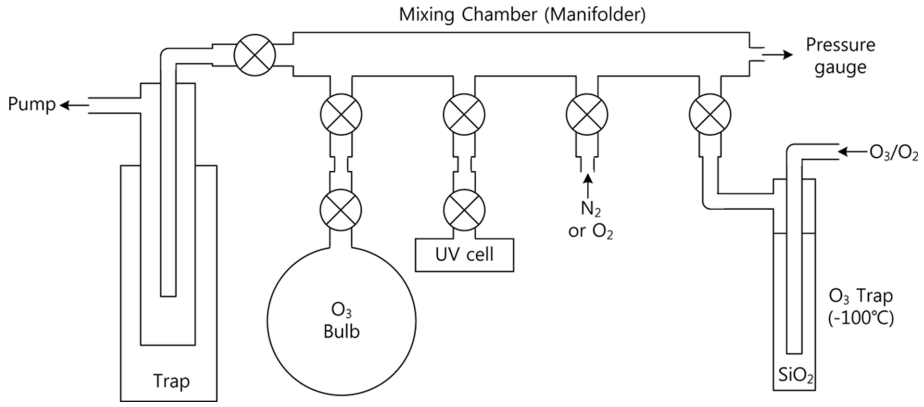

Fig. 1. Diagram of the vacuum line system.

$$O(g)+O_2(g)\rightarrow O_3(g) \quad (2)$$

An O_3 trap filled with silica gel (mesh size 15-25) was placed in a cold bath (8640, POPE Scientific Inc., USA), whose temperature was maintained at around -100 ºC by using a mixture of ethyl alcohol (99.5 %, Samchun Inc, Korea) and liquid nitrogen. O_3 was introduced into the trap, followed by selective adsorption on the refrigerated silica gel surface, whereas most of the O_2 passed the O_3 trap without being adsorbed and was discarded. Upon the adsorption of O_3, the silica gel turned purple. After O_3 was collected for 10 min, the ozone generator was turned off and disconnected from the O_3 trap. The O_3 trap was then connected to the vacuum line system, which removed the other gaseous species (e.g., O_2) from the trap. The vacuum pump was closed once all the impurities were removed, and the cold bath was removed from the O_3 trap to desorb O_3 from silica gel by increasing the temperature. When the pressure of the vacuum line system reached ~1.5 Torr, the valve to the O_3 bulb was opened to fill O_3, followed by dilution with nitrogen (up to 700 Torr).

2.2. Characterization of O_3 samples

O_3 was transferred from the sample bulb to a homemade quartz UV cell (5 cm) by using a vacuum line system. The pressure drop in the sample bulb during the transfer was considered to estimate the partial pressure of O_3 in the UV cell. For the kinetic study, initial time (t = 0) was set as the moment O_3 transfer was completed. The initial concentration of O_3 in the UV cell ($[O_3]_0'$), which was equivalent to concentration of O_3 in sample bulb after the transfer, was calculated from the absorbance measured using a UV/Vis spectrophotometer (Cary 100, Agilent Technologies, USA). The cross section of O_3 by 256 nm light is 1.17×10^{-17} molecules^{-1}·cm^2.

The UV cell was then stored under the one of the following conditions:

a) Condition 1 : Room temperature (~25 ºC) with blocking external light using aluminum foil
b) Condition 2 : High temperature (~50 ºC) with blocking external light using aluminum foil
c) Condition 3 : Room temperature (~25 ºC) with UV light irradiation using a UV lamp (254 nm, < 0.1 mW, TN-4LC, Korea Ace Sci., Korea)
d) Condition 4 : Room temperature (~25 ºC) under a usual LED light condition (400 nm < λ < 800 nm)

The O_3 concentrations in the UV cell at various times were calculated using the method described above. The same method was used for kinetic studies of the O_3 samples stored under conditions 1-4 and in that order.

3. Results and Discussion

3.1. Initial concentration of O_3 in the sample

The initial concentration of O_3 (molecules·cm^3) in the sample ($[O_3]_0$) was determined by measuring the absorbance of O_3 in the UV cell. However, measuring the absorbance of each O_3 samples is not technically practical. On the other hand, estimating $[O_3]_0$ using the values of pressure measured during sample preparation is relatively feasible whereas the estimated values of $[O_3]_0$ may differ from the actual concentrations because of the existence of impurities, including O_2. The following equation was used for calculating $[O_3]_0$:

$$[O_3]_0 \text{ (molecules·cm}^{-3}) = P_{O_3} \cdot c \cdot f \quad (3)$$

where P_{O_3} is the measured pressure (Torr) of O_3 in the sample bulb during preparation, c is the conversion factor (3.54×10^{16} molecules·cm^{-3}·Torr^{-1}), and f is the correction factor. The correction factor, f, excludes the contribution of impurities as following:

$$f = \frac{P'_{O_3,Abs}}{P'_{O_3}} \quad (4)$$

P'_{O_3} and $P'_{O_3,Abs}$ are the partial pressures of O_3 in the UV cell measured by pressure and absorbance, respectively, as shown below:

$$P'_{O_3} = P_{O_3} \cdot \frac{P_{Trans}}{P_{Prep}} \quad (5)$$

$$P'_{O_3,Abs} = \frac{[O_3]'_0}{c} \quad (6)$$

where P_{Prep} and P_{Trans} are the total pressures (Torr) of the sample bulb measured during preparation and

transfer, respectively, and $[O_3]_0'$ is the initial concentration of O_3 in the UV cell, determined by absorbance.

The mean values of $[O_3]_0'$, P'_{O_3}, and $P'_{O_3,Abs}$ for four individual O_3 samples were 2.74 [±0.14] × 10^{16} molecules·cm^{-3}, 1.60 [±0.34] Torr, and 0.773 [±0.004] Torr, respectively. Therefore, the correction factor was calculated to be 0.48 [±0.11], which indicates that the O_3 concentration calculated from the pressure values was overestimated by a factor of 2.1 [±0.5].

3.2. Half-life of O_3 in the samples

O_3 typically decomposes by the following mechanism:

$$O_3 + M \xrightarrow{k_1} O_2 + O + M \quad (7)$$

$$O_2 + O + M \xrightarrow{k_2} O_3 + M \quad (8)$$

$$O_3 + O \xrightarrow{k_3} 2O_2 \quad (9)$$

where M is gaseous matter (N_2, O_2, or O_3, in this case); k_1, k_2, and k_3 are the rate constants for Reactions (7), (8), and (9), respectively. Reaction (9) was the rate-determining step.

The reaction rates involving O and O_3 are as follows:

$$\frac{d[O]}{dt} = k_1[O_3][M] - k_2[O_2][O][M] - k_3[O_3][O] \quad (10)$$

$$\frac{d[O_3]}{dt} = -k_1[O_3][M] + k_2[O_2][O][M] - k_3[O_3][O] \quad (11)$$

As atomic oxygen (O) is the intermediate of the mechanism (the steady-state approximation) and Reaction (9) is the rate-determining step (i.e., $k_3[O_3] \ll k_2[O_2][M]$), Eq. (11) can be rewritten as follows:

$$\frac{d[O_3]}{dt} = \frac{-2k_1k_3[M][O_3]^2}{k_2[O_2][M] + k_3[O_3]} = -k_{obs}[O_3]^2 \quad (12)$$

$$k_{obs} = \frac{2k_1k_3}{k_2[O_2]} \quad (13)$$

where k_{obs} is the observed rate constant of O_3 decomposition.

Eq. (12) shows that the decomposition of O_3 follows the 2nd order reaction rate, and the half-life ($t_{1/2}$) is equal to $1/(k_{obs}[O_3]_0')$. *Fig.* 2 shows the correlation between $1/[O_3]$ and time (s) for the O_3 sample stored under Condition 1. The slope of the linear regression (the solid line in *Fig.* 2, which is 4.47 × 10^{-23} molecules^{-1}·cm^3·s^{-1}) is equal to the value of k_{obs}. Moreover, the average value of $[O_3]_3'$ was calculated as 2.74 × 10^{16} molecules·cm^{-3}, and the half-life of O_3 in the sample stored under Condition 1 was estimated to be 9.5 [±1.4] days. Assuming that ~10 % change in the O_3 concentration is acceptable for heterogeneous reaction experiments, the O_3 sample can be stably used for one day after preparation.

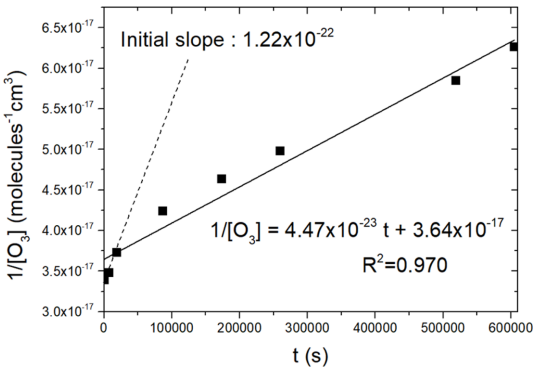

Fig. 2. Plot of $1/[O_3]$ versus time(s). The solid line and the dashed line represent the linear regression and the initial slope, respectively.

3.3. Initial concentration of O_2 in the sample

Although linear regression showed a reasonably good fit (R^2 = 0.970), the plot for the early decomposition (i.e., t < 10000 s) deviated significantly from linearity, as shown in *Fig.* 2. The accumulation of O_2 by Reaction (9) is responsible for this deviation because k_{obs} is not a constant value. As k_{obs} is a function of the O_2 concentration [Eq. (13)], the initial concentration of O_2 in the UV cell ($[O_2]_0'$) can be estimated from the value of instantaneous k_{obs} at t = 0 (denoted as $k_{obs,0}$) using Eq. (12).

$$[O_2]_0' = \frac{2k_1 \cdot k_3}{k_2 \cdot k_{obs,0}} \quad (14)$$

The first two points in *Fig.* 2 denote the first two O_3 concentrations in the sample, representing the initial decomposition of O_3. Therefore the slope between the first two points (dashed line, 1.22 × 10^{-22} molecules^{-1}

·cm^3·s^{-1}) is assumed to be equal to $k_{obs,0}$. By applying the literature values for k_1, k_2, and k_3 (4.38×10^{-26} $molecules^{-1}$·cm^3·s^{-1},[10] 5.92×10^{-34} $molecules^{-2}$·cm^6·s^{-1},[11] and 8.34×10^{-15} $molecules^{-1}$·cm^3·s^{-1},[12] respectively) to Eq. (14), $[O_2]_0'$ was estimated to be 1.01×10^{16} molecules·cm^{-3}, which is approximately 36.9 % of $[O_3]_0'$. This implies that the overestimation of $[O_3]_0'$, when measured from the pressure values, was partially due to the existence of initial O_2 (O_2 at the moment the O_3 transfer was completed) in the sample. Considering that the major component in the output flow from the ozone generator was O_2, the ratio of $[O_2]_0/[O_3]_0$ in the O_3 sample (and in the UV cell) showed that O_2 was efficiently removed from the O_3 sample by the purification process.

3.4. Stability of O_3 stored under various conditions

The k_{obs} and $t_{1/2}$ of the O_3 samples stored under four different conditions (Conditions 1-4) are summarized in *Table* 1.

The decomposition of O_3 was faster for the sample stored at 50 °C than that at room temperature, which resulted in a higher decomposition rate and reduction of the half-life to 4.0 days.

Unlike the sample stored under Condition 1, different irradiation environments were applied to the samples stored under Conditions 3 and 4. O_3 in the presence of UV light (λ < 320 nm) is decomposed by the following mechanism:[1]

$$O_3 \xrightarrow{k_4} O_2 + O^* \quad \text{(by radiation of } \lambda < 320 \text{ nm)} \qquad (15)$$

$$O_2 + O^* + M \xrightarrow{k_5} O_3 + M \qquad (16)$$

Table 1. k_{obs} and $t_{1/2}$ for the O_3 samples stored under various conditions

	k_{obs} ($molecules^{-1}$·cm^3·s^{-1})	$t_{1/2}$ (day)
Condition 1	4.47 [±0.64]×10^{-23}	9.5[±1.4]
Condition 2	1.06 [±0.04]×10^{-22}	4.0 [±0.2]
Condition 3	4.22 [±0.10]×10^{-20}	0.0100 [±0.0006]
Condition 4	3.71 [±0.66]×10^{-23}	11 [±2]

The numbers in parentheses indicate expanded uncertainty, $U = k \times u_c$, where u_c is the combined uncertainty and $k = 2$ with approximately 95 % confidential level.

$$O_3 + O^* \xrightarrow{k_6} 2O_2 \qquad (17)$$

Therefore, Eq. (12) (the expression of O_3 decomposition rate) is rewritten as follow:

$$\frac{d[O_3]}{dt} = \frac{-2k_4k_6[O_3]^2}{k_5[O_2][M]} = -k'_{obs}[O_3]^2 \qquad (16)$$

where, k'_{obs} is the observed rate constant of the O_3 decomposition in presence of UV light. This implies that the decomposition of O_3 in presence of UV light also follows the 2nd order reaction rate. Since k_4 and k_6 are much greater than k_1 and k_3, respectively, and k_5 is smaller than k_2 (ie, $k_4 > k_1$, $k_6 > k_3$, and $k_5 < k_2$),[11,13] k'_{obs} is considerably greater than k_{obs} as shown in *Table* 1. Consequently, half of the O_3 in the UV cell stored under Condition 3 decomposed within ~840 s. In contrast, no significant differences in the observed rate constant and half-life were observed under Conditions 1 and 4, based on the independent *t*-test with equal variance. This implies that LED light did not affect O_3 decomposition, and covering the samples with aluminum foil is not required even if the laboratory has an LED lighting system. However, blocking external light is still recommended to avoid any possibility of irradiation with indirect sunlight.

4. Conclusions

O_3 samples with high purity were prepared for studying the heterogeneous reactions of O_3 with tropospheric aerosols. To prepare purified O_3 samples, O_3 from an ozone generator was selectively adsorbed on refrigerated silica gel placed in a cold trap and then collected in an O_3 sample bulb.

The O_3 samples were characterized using a UV-Vis spectrophotometer to determine the actual $[O_3]$ in the samples and evaluate the stability of the samples. The consistent overestimation of $[O_3]$ calculated using the pressure values compared to that determined using the absorbance values was due to the presence of impurities, including O_2, which were not removed during the purification process. This implies that a correction factor of 0.48 must be applied to $[O_3]$ calculated using the pressure values. The observed

rate constant of the O_3 decomposition and the half-life of O_3 in the samples were determined as 4.47 [±0.64]×10^{-23} molecules^{-1}·cm^3·s^{-1} and 9.5 [±1.4] days at room temperature, respectively. The evaluation of O_3 stability under various conditions indicated that special care should be taken to prevent the exposure of O_3 samples to high-temperature environment and/or UV radiation.

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