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Ozone Formation by Photodissociation of Oxygen Molecule with a 193 nm Excimer Laser

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Chemical processes are studied in ozone formation by the photodissociation of oxygen molecule excited to the Schumann−Runge band at 193 nm with use of an ArF excimer laser. The experimental results at an O_2 pressure of 100−500 Torr indicate that the ozone formation $O + O_2 + O_2 \rightarrow O_3 + O_2$ is very rapid, that the predissociation $O_2 \rightarrow O + O$ is a rate-determining process. The rate constant of the predissociation $O_2 \rightarrow O + O$ is found to be 6.40×10^{-5} cm^2 J^{-1} at 22.1 °C.

Introduction

Oxygen−ozone chemistry is of great interest, especially in atmospheric chemistry.[1] For example, the basic mechanism of the stratospheric ozone chemistry is given by Chapman's theory.[2] Chemical processes with HO_x, NO_x, and ClO_x were added to the Chapman mechanism[3−5] in order to fit better the natural atmospheric chemistry. In fact, recently, an ozone hole, which is due to the chemical reactions of ozone with halocarbons, was observed in polar regions.[6] Besides, an anticorrelation between the concentrations of ozone and water vapor was found in the stratosphere in a low-latitude region,[7] suggesting that the chemical processes with HO_x are essential.

The ozone formation by the photodissociation of the oxygen molecule excited to a Schumann−Runge band is of primary importance for the atmospheric ozone chemistry. Many elementary processes will be essential for the ozone formation by the photodissociation of oxygen molecule excited at 193 nm:[8−10] radiationless transition, emission, predissociation, collisional quenching, chemical reactions, photodissociation of products, etc. Since the ozone formation is thus complicated, our understanding of the elementary processes is still insufficient. In the present paper, we study the mechanism of the ozone formation by the photodissociation of oxygen molecule excited at 193 nm with use of an ArF excimer laser.

Experimental Section

The experimental system is schematically shown in Figure 1. Ozone was formed by the irradiation of O_2, which filled a cylindrical Pyrex-glass cell (25 mm o.d. in diameter, 100 mm in length, quartz windows) at a pressure of 100−500 Torr, with use of an ArF excimer laser (Lambda-Physik LPX-105) beam. The laser repetition rate was 5 Hz. The laser power was measured with use of a power meter (SCIENTECH 38-2UV5), which was normally placed 10 cm apart from the laser output window; we call the position *the normal position*. The concentration of ozone formed in the reaction cell was observed by measuring the decrease in the intensity of the probe light, for which a 253.65-nm line emission of a low-pressure Hg lamp (Hamamatsu Photonics L973-02) was used because of the coincidence with the wavelength of the Hartley bands of O_3;[1] the probe light emitted from the Hg lamp was introduced into the reaction cell with use of a lens, thereafter dispersed with a monochromator (Jobin Yvon H20, entrance and exit slit widths of 0.5 mm), and detected with a photomultiplier (Hamamatsu Photonics, R562), whose output signal was recorded on a three-pens chart recorder. The light intensities of the laser and the Hg lamp were measured during the experiments in order to monitor their fluctuations; photodiodes and a boxcar averager (Princeton Applied Research Model 162) were used for the monitoring, as shown in Figure 1.

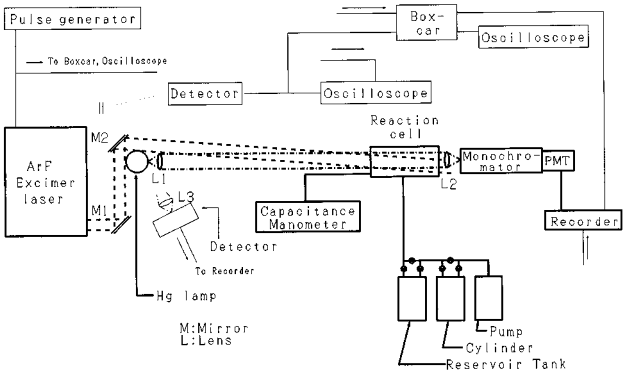

Figure 1. Schematic diagram for the experimental system.

The reaction cell was pumped at a pressure of less than 1.5×10^{-3} Torr with use of a diffusion pump and a rotary pump. After the pumping was stopped by closing a valve, the pressure in the reaction cell did not increase or decrease for 20 min, which equals a period of measurement or a period from the start to the stop of the laser irradiation. Grade-A O_2 gas (Nihon Sanso; $O_2 \geq 99.99\%$, $N_2 < 10$ ppm, $CH_4 < 30$ ppm, $Ar < 30$ ppm) was introduced into the reaction cell by measuring the pressure with a capacitance manometer (MKS Baratron Type 127A, 1000 Torr/full scale).

Results and Discussion

In Figure 2, the intensity of the Hg-lamp light which passed through the reaction cell is plotted as a function of ArF-laser irradiation time. The light intensity decreases because of the absorption by ozone formed by the laser irradia-

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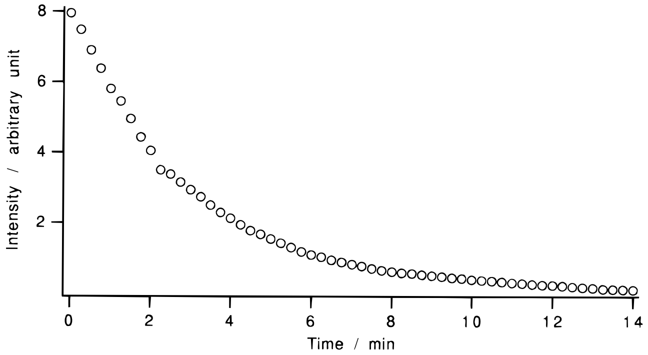

Figure 2. Hg-lamp light intensity, which passed through the reaction cell, as a function of irradiation time. The pressure of O_2 is 500 Torr. The laser power is 56 mJ pulse^{-1} at the normal position.

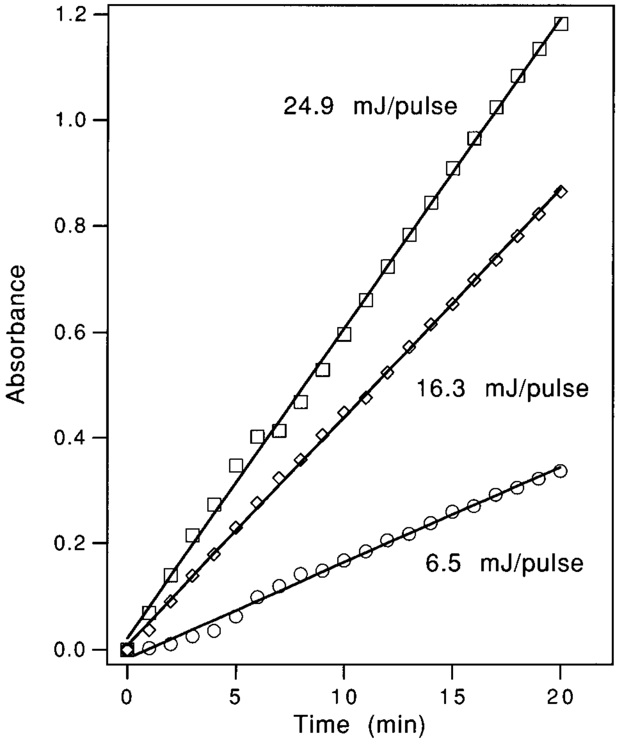

Figure 3. Absorbance of O_3 as a function of laser irradiation time. The pressure of O_2 is 200 Torr. The laser power was measured at the normal position.

tion. The application of the Beer–Lambert equation, expressed in terms of eq 1,

$$A = \ln(I_R/I)$$
$$= \epsilon cl \qquad (1)$$

gives the O_3 absorbance as a function of laser irradiation time, as shown in Figure 3. In eq 1, A is absorbance, I_R is the intensity of the Hg-lamp light before the laser irradiation of O_2 in the reaction cell, I is the Hg-lamp light intensity during the laser irradiation, ϵ is the absorption cross-section of ozone at 253.65 nm, c is the ozone concentration in the reaction cell, and l is the optical length in the reaction cell. As seen from eq 1, the absorbance is proportional to the ozone concentration in the reaction cell. In Figure 3, it is found that the absorbance, or the ozone concentration in the reaction cell, linearly increases with the time of laser irradiation and that the ozone formation increases with an increase in intensity of the laser light. The slope of the linearity in Figure 3 will be called *the rate of O_3 formation.*

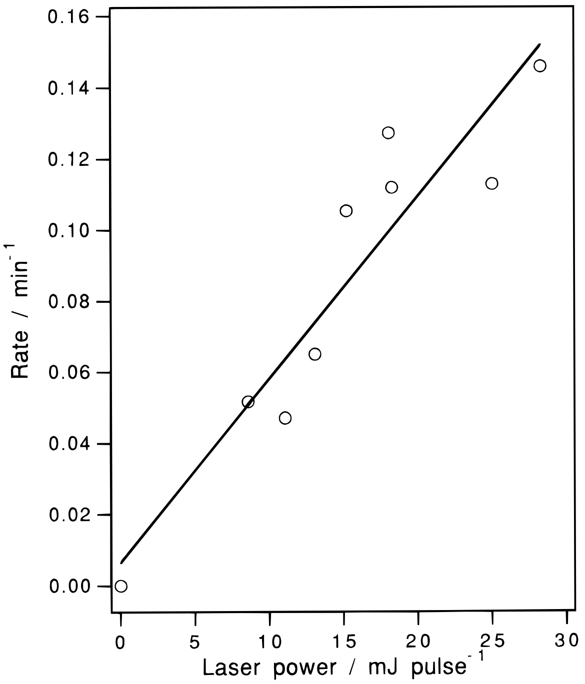

Figure 4. Rate for the O_3 formation as a function of laser power. The pressure of O_2 is 500 Torr. The laser power was measured at the normal position.

In Figure 4, the O_3 formation rate is plotted as a function of laser power. It is found that the O_3 formation rate linearly increases with the intensity of the laser light. Furthermore, in Figure 5, the O_3 formation rate at 1 mJ of laser power is plotted as a function of O_2 pressure in the reaction cell; in order to obtain Figure 5, we plot the rate of O_3 formation as a function of laser power at various pressures of O_2 and get the rates at 1 mJ from the linearities in these plots. The linearity is obtained in the plot in Figure 5.

We assume that the present reaction system is represented by the following processes:

(a) photoexcitation, $O_2 + h\nu \rightarrow O_2^*$

(b) predissociation, $O_2^* \rightarrow O + O$

(c) ozone formation,

$$O + O_2 \rightarrow O_3^{\ddagger},\ O_3^{\ddagger} + O_2 \rightarrow O_3 + O_2$$

(d) photodissociation, $O_3 + h\nu \rightarrow O_2 + O$

(e) dissociative reaction, $O + O_3 \rightarrow 2O_2$

where O_2^* denotes O_2 in the excited state, $O_3^{\ddagger}$ denotes a hot ozone molecule, and $h\nu$ denotes the photon energy of the laser. Figure 4 indicates that the photoexcitation of O_2, or process a, is a single-photon process. Furthermore we assume that process d can be omitted, since the intensity of the Hg-lamp light used for monitoring the ozone concentration is very weak, and the absorption cross-section of ozone is very small at 193 nm, and that process e can be omitted, since the O and O_3 concentrations are much less than the O_2 concentration.

For processes a–c, the ozone concentration is expressed in terms of eq 2, where k_0 is the overall rate constant for processes

$$[O_3] = k_0I_0[O_2]t - (k_0I_0/k_1[O_2])\{1 - \exp(-k_1[O_2]^2t)\} \qquad (2)$$

a and b, k_1 is the overall rate constant for process c, $[O_3]$ is the

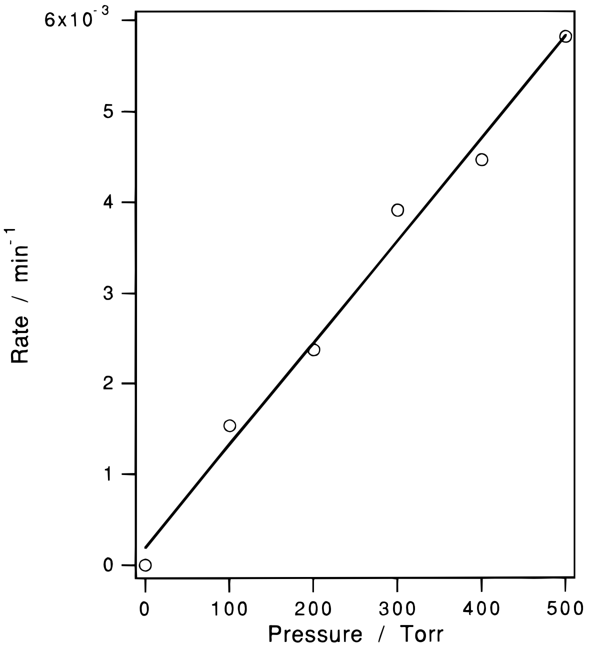

Figure 5. Rate for the O_3 formation as a function of O_2 pressure in the reaction cell. The laser power is 1 mJ pulse^{-1} at the normal position.

ozone concentration, $[O_2]$ is the oxygen molecule concentration, I_0 is the net intensity of the excimer laser light used for the irradiation of O_2 at 193 nm, and t is the laser-irradiation time.

As described above, it is found that $[O_3]$ linearly increases with t, as shown in Figure 3, and that $[O_3]/t$ linearly increases with I_0 and $[O_2]$, as shown in Figures 4 and 5, respectively. These facts indicate that the first term is essential and the second term can be omitted in eq 2 in the present experimental condition. This result is due to the relation of $k_0I_0 \ll k_1[O_2]$, or $k_0I_0[O_2] \ll k_1[O_2]^2$; process c is very rapid, since $[O_2]$ is very large. Thus, eq 2 is rewritten as

$$[O_3] = k_0I_0[O_2]t \tag{3}$$

In eq 3, the relation of $[O_3]/t$ with I_0 or $[O_2]$ gives k_0.

In order to calculate k_0, we have to obtain the exact value of I_0 that is the net absolute intensity of the laser light used for the irradiation of oxygen molecules in the reaction cell. Thus, we have done the following correction: (A) a decrease in the laser light intensity during the propagation from the laser output window to the entrance window of the reaction cell, (B) a decrease in the laser light intensity after the reflection by two mirrors placed between the laser output window and the entrance window of the reaction cell, (C) optical-path analysis in the reaction cell, and (D) an effect of the entrance window of the reaction cell on the intensity and the optical path of the penetrating laser light. In correction A, we measure, as a function of optical length, how much the laser light intensity is decreased by (A1) the absorption by the atmospheric O_2 and (A2) the scattering by the atmospheric molecules. In correction B, we measure (B1) the reflectivities of the mirrors, and (B2) the cuts in the cross-section areas of the laser beam on the mirrors. In correction C, we measure the geometric volume of the laser irradiation in the reaction cell. In correction D, (D1) we measure the transmittance of the entrance window of the reaction cell, and (D2) we calculate the refraction of the laser beam passing through the entrance window of the reaction cell. The details of the correction will be described elsewhere. All of these items of the correction have been measured with the accuracy sufficient to calculate I_0, and the items except for (A2) and (D2) turn out be significant.

By using the results of the correction for I_0, we obtain $k_0 = 6.28 \times 10^{-5}$ cm^2 J^{-1} at 21.6 °C from the relation of $[O_3]/t$ with I_0 in Figure 4 and $k_0 = 6.51 \times 10^{-5}$ cm^2 J^{-1} at 22.6 °C from the relation of $[O_3]/t$ with $[O_2]$ in Figure 5. Hence, the average of these rate constants is $(6.39_5 \pm 0.11_5) \times 10^{-5}$ cm^2 J^{-1} at 22.1 °C.

In order to discuss k_0, eq 3 can be written as

$$\frac{\partial[O_3]}{\partial t} = [O_2]\int_{\Delta\lambda}\phi_i(\lambda)\,\sigma_i(\lambda)\,I(\lambda)\,d\lambda \tag{4}$$

$$\cong [O_2]\phi_i(\lambda{=}193\text{nm})\,\sigma_i(\lambda{=}193\text{nm})\int_{\Delta\lambda}I(\lambda)\,d\lambda \tag{5}$$

$$= [O_2]k_0I_0 \tag{6}$$

where

$$k_0 = \phi_i(\lambda{=}193\text{nm})\,\sigma_i(\lambda{=}193\text{nm}) \tag{7}$$

$$I_0 = \int_{\Delta\lambda}I(\lambda)\,d\lambda \tag{8}$$

In eq 4, $\phi_i(\lambda)$ is the quantum yield of the ozone formation from O_2 by the irradiation with the laser beam at a wavelength of λ, and $\sigma_a(\lambda)$ is the absorption cross-section of O_2 at a wavelength of λ. The integrals in eqs 4, 5, and 8 are calculated over the entire wavelength range of the laser band, i.e., $\Delta\lambda$. Since the spectral width of the excimer laser at 193 nm is ~0.33 nm as a Gaussian width, or is so narrow that $\phi_i(\lambda)$ and $\sigma_a(\lambda)$ are put outside the integral as constants $\phi_i(\lambda{=}193\text{nm})$ and $\sigma_a(\lambda{=}193\text{nm})$, respectively, eq 4 is substituted by eq 5. We rewrite eq 7 as

$$\phi_i(\lambda{=}193\text{nm}) = k_0/\sigma_a(\lambda{=}193\text{nm}) \tag{9}$$

If we assume that the quantum yield of the ozone formation from O_2 by the irradiation with the laser beam at a wavelength of 193 nm, $\phi_i(\lambda{=}193\text{nm})$, equals 2 (molecule cm^{-3} s^{-1})/(photon cm^{-3} s^{-1}), or 2 molecules photon^{-1}, we obtain $\sigma_a(\lambda{=}193\text{nm}) = 3.19_8 \times 10^{-22}$ cm^2 molecule^{-1} with $k_0 = (6.39_5 \pm 0.11_5) \times 10^{-5}$ cm^2 J^{-1} at 22.1 °C. While it is difficult to get the exact absorption cross-section $\sigma_a(\lambda{=}193\text{nm})$ from the spectrum in the ref 1, we obtain $\sigma_a(\lambda{=}193\text{nm}) \cong (3.2 \pm 0.2) \times 10^{-22}$ cm^2 molecule^{-1} for the Schumann−Runge band ($v' = 4$) and $\sigma_a(\lambda{=}193\text{nm}) \cong (1.2 \pm 0.1) \times 10^{-23}$ cm^2 molecule^{-1} for the Schumann continuum. Thus, the present result agrees well with the absorption cross-section of the Schumann−Runge *band* at 193 nm, and it is more than 1 order greater than the absorption cross-section of the Schumann *continuum*. Therefore it is found that the predissociation of O_2 occurs through the Schumann−Runge band. Since the quantum yield discussed above is the product of the quantum yields of the O_2 predissociation (processes a and b) and the ozone formation (process c). The quantum yield of process c can be considered to be 1 under the present experimental condition. Hence, the quantum yield of the predissociation of O_2 excited through the Schumann-Runge band turns out to be much higher than those of emission and radiationless transitions.

Since the predissociation of O_2 is the rate determining process of the present ozone formation reaction under the present experimental condition, the second term of eq 2 was omitted. Hence, the rate constant of the ozone formation (process c) cannot be obtained in the present experiment. We need an experiment at a much lower pressure of O_2. We will pursue that in the future, while the chemical processes will be more complicated at a much lower pressure of O_2; the complication originates from the decrease in the O_2 concentration relative to those of O and O_3.

Conclusion

Chemical processes have been studied in ozone formation by the photodissociation of oxygen molecule excited to the Schumann−Runge band at 193 nm with use of an ArF excimer laser. The following conclusions have been derived from the results.

(1) At an O_2 pressure of 100−500 Torr, the predissociation of O_2 is the rate determining process in the ozone formation. As a result, the ozone concentration $[O_3]$ is proportional to the ArF-laser intensity I_0, the concentration of oxygen molecule $[O_2]$, and the laser irradiation time t. From this relation, the rate constant of the predissociation of O_2 has been obtained to be 6.40×10^{-5} cm^2 J^{-1} at 22.1 °C.

(2) The rate constant indicates that the predissociation occurs through the Schumann-Runge *band* with a very high quantum yield.

(3) The predissociation of O_2 is a single-photon process.

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