The Ultraviolet Spectrum of Ozone Produced in the γ-Irradiated Liquid Nitrogen Containing a Small Amount of Oxygen

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Synopsis. The ultraviolet spectrum observed in γ-irradiated liquid nitrogen containing a small amount of oxygen has been ascribed to ozone. The εG value was obtained. The dose rate effect on the yield of ozone was observed. The value of $\varepsilon_m G$ was inversely proportional to the square root of the dose rate. This allowed us to discuss the formation mechanism of ozone in liquid nitrogen.

It is well-known that ozone is produced in irradiated liquid nitrogen containing a small amount of oxygen and that the decomposition of such ozone sometimes leads to incidental explosions during the irradiation with γ-rays[1] electron beams[2] or reactor radiation.[3] The yield of ozone as a function of oxygen concentration in γ-irradiated liquid nitrogen has been measured by an indirect method.[4]

Although the optical absorption spectrum of gaseous ozone was previously reported,[5,6] there is no report of the ultraviolet absorption spectrum of ozone produced in γ-irradiated liquid nitrogen as far as we are aware. In the ultraviolet region there often appear the absorption bands due to ionic species or radicals when organic substances are irradiated in liquid nitrogen. So, if one uses the same cryostat for both irradiation and optical measurement, it becomes indispensable to distinguish the ultraviolet spectrum of the species from that of ozone.

In this study we report the ultraviolet spectrum of ozone produced in γ-irradiated liquid nitrogen. We also discuss the formation mechanism of ozone in connection with the effect of dose rate on the yield of ozone.

Experimental

Liquid nitrogen supplied by the Osaka Sanso Co. was used. Oxygen concentration in liquid nitrogen was measured by a zirconia type oxygen gas sensor and a gas chromatography. Although the concentration of oxygen in liquid nitrogen stored in a 3000 dm^3 storage tank was about 0.3 ppm, it amounted to 160±30 ppm after liquid nitrogen was transferred in air from a 5 dm^3 container to an optical cryostat. This nitrogen in the cryostat was used for both γ-irradiation and optical absorption measurement. Nitrogen gas evaporated inside the cryostat was released into atmosphere after passing through silicon oil in a gas wash bottle which was attached to the cryostat. This device prevented the outside air being dissolved in liquid nitrogen.

Liquid nitrogen was irradiated by γ-rays with various dose rates (163 Gy h^{-1}—1602 Gy h^{-1}). The total dose was always 801 Gy. Optical absorption measurements were carried out with a Shimadzu double beam spectrophotometer. Optical absorption spectra were recorded in the ultraviolet region of 210 nm$<\lambda<$320 nm and in the absorbance region of $0<A<4$.

Results and Discussion

The ultraviolet spectrum of liquid nitrogen recorded after the γ-irradiation with the dose rate of 1602 Gy h^{-1} is shown in Fig. 1(A), where ε is the molar absorption coefficient ($dm^3\ mol^{-1}\ cm^{-1}$) and G is the G-value (molecules formed/100 eV absorbed). The spectrum shows the wavelength of the absorption maximum (λ_{max}) of 255 nm, the half-height width ($W_{1/2}$) of 6.6×10^3 cm^{-1} and a vibrational band structure near the absorption maximum.

The apparent absorption intensity of the spectrum increased as the amount of liquid nitrogen in the cryostat decreased owing to the natural evaporation. The reciprocal plots of the absorption intensity against the evaporation time after the irradiation were linear for an extended period of time, e.g. 4 hours. This can be explained on the assumption that liquid nitrogen in the cryostat evaporates at a constant rate and that the species responsible for the absorption does not evaporate together with nitrogen, being dissolved in the remaining liquid nitrogen.

After liquid nitrogen in the cryostat was completely evaporated, the absorption measurement was again carried out in order to see if there is any absorption due to the residual gas inside the cryostat. The absorption

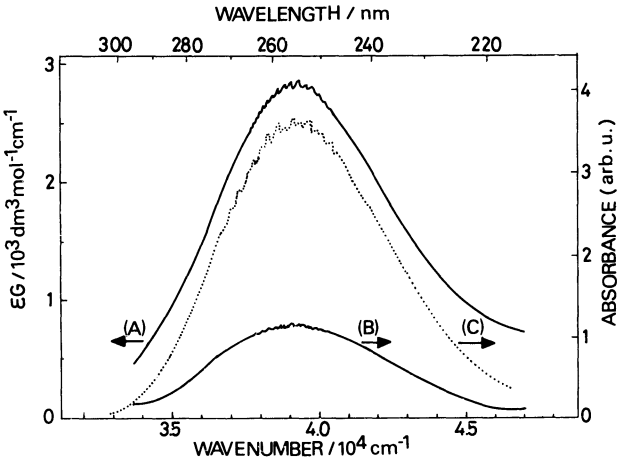

Fig. 1. The ultraviolet absorption spectra of ozone: (A) observed in γ-irradiated liquid nitrogen containing 160 ppm oxygen, (B) observed after liquid nitrogen was completely evaporated, and (C) reported spectrum of gaseous ozone (Ref. 5). The γ-irradiation was carried out at the dose rate of 1602 Gy h^{-1}. The total dose was 801 Gy.

spectrum thus recorded is shown in Fig. 1(B). The values of λ_{max} and $W_{1/2}$ of spectrum (B) were the same as those of spectrum (A). Opening the frange of the cryostat, we could smell irritatingly. The smell was characteristic of ozone. The ultraviolet spectrum of ozone at 300 K which was reported previously by other authors[6] is shown in Fig. 1(C), where the Hartley band structure is clearly seen near the absorption maximum. The values of λ_{max} and $W_{1/2}$ of spectra (A) and (B) were almost the same as those of spectrum (C). From these observations, we ascribe spectra (A) and (B) to ozone formed by γ-irradiation of liquid nitrogen containing the small amount of oxygen. The value of ε at $\lambda=\lambda_{max}$, ε_m, reported for ozone at 300 K[6] is 2900 $dm^3\ mol^{-1}\ cm^{-1}$. If we use this value for the present case, we obtain the G-value of ozone, $G(O_3)=1.0$ for the dose rate of 1602 Gy h^{-1}. It is reported, however, that the value of ε depends on temperature at temperatures higher than 300 K.[7] If this is also true at 77 K, the calculated $G(O_3)$ is not correct. Instead, if the empirical relationship between the value of ε and temperature[7] is extrapolated to 77 K, the value of ε becomes about 3500 $dm^3\ mol^{-1}\ cm^{-1}$ at 77 K so that $G(O_3)=0.83$ is obtained. Matumoto et al.[4] used the method of the stoichiometric reaction between ozone and nitrogen monoxide in order to determine $G(O_3)$. According to their results, one can estimate $G(O_3)=6.0$ under the conditions of the oxygen concentration of 160 ppm and the γ-dose rate of 1.1×10^4 Gy h^{-1}. Their value is much larger than ours. This may partly due to an enhanced reaction of oxygen atom with the quartz wall of the cryostat in our case. However, the discrepancy between the reported $G(O_3)$ and ours cannot be elucidated by the present knowledge.

A dose rate effect on the yield of ozone was observed. This is demonstrated in Fig. 2. It is seen from Fig. 2 that the plots of log ($\varepsilon_m G$) against log (dD_a/dt), where dD_a/dt is the dose rate, gave a straight line with the gradient of $-1/2$.

It was reported that N_3^+ ion is one of the major radiolytic products of nitrogen gas and that N_3^+ ion reacts with O_2 to give rise to oxygen atom.[8,9] On this basis, we put forward the following reaction mechanism for the formation of ozone in the γ-irradiated liquid nitrogen containing a small amount of oxygen:

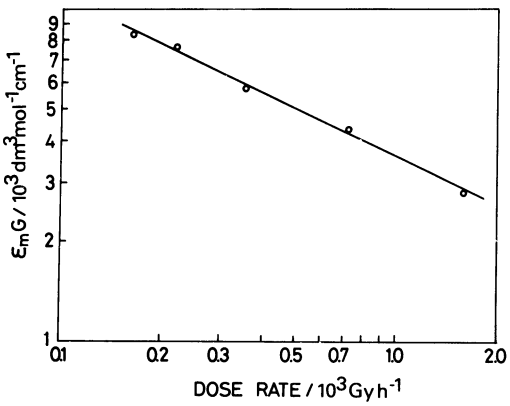

Fig. 2. Effect of the dose rate on $\varepsilon_m G$ of ozone produced in liquid nitrogen. The total dose was 801 Gy.

$$N_2 \longrightarrow N_3^+ \quad (1)$$

$$N_3^+ + e^- \longrightarrow \text{neutralization} \quad (2)$$

$$N_3^+ + O_2 \longrightarrow O + NO^+ + N_2 \quad (3)$$

$$O + O_2 + N_2 \longrightarrow O_3 + N_2 \quad (4)$$

$$O + \text{wall} \longrightarrow 1/2O_2 + \text{wall} \quad (5)$$

The formation rate of N_3^+ ion is given by $\{G(N_3^+)/100N_0\}(dD_a/dt)$, where $G(N_3^+)$ is the G-value of N_3^+ ion, N_0 the Avogadro constant and dD_a/dt is the dose rate in the unit of eV $dm^{-3}\ s^{-1}$. During γ-irradiation the steady-state conditions of $d[N_3^+]/dt=d[e^-]/dt=d[O]/dt=0$ must be satisfied, where $[N_3^+]$, $[e^-]$, and [O] are the concentration of N_3^+ ion, the excess electron, and oxygen atom. The rate constants of the Reactions 2 and 3, k_2 and k_3, are in the ranges of 10^{-6} and 10^{-10} $cm^3\ s^{-1}$ respectively.[10,11] The values of $\{G(N_3^+)/100N_0\}(dD_a/dt)$ and [O] are in the ranges of 10^{-7} mol $dm^{-3}\ s^{-1}$ and 10^{-3} mol dm^{-3}, respectively in the present case. These values result in $\{G(N_3^+)/100N_0\}(dD_a/dt) \gg \{k_2[O^2]\}$.[2] Under this condition we obtain

$$G(O_3) = \{G(N_3^+)\}^{1/2} f([O_2], k_2, k_3, k_4, k_5)(dD_a/dt)^{-1/2}, \quad (6)$$

where k_4 and k_5 are the rate constants of the Reactions 4 and 5, respectively and $f([O_2], k_2, k_3, k_4, k_5)$ is given by

$$f = (100N_0)^{1/2} k_3 k_4 [O_2]^2 / \{(2k_2)^{1/2}(k_4[O_2] + k_5)\}. \quad (7)$$

Equation 6 shows that the yield of ozone is inversely proportional to the square root of the dose rate. Thus the observed dependence of log ($\varepsilon_m G$) on log (dD_a/dt) is explained by the proposed mechanism.

Matumoto et al.[4] investigated the effect of oxygen concentration on the yield of ozone in liquid nitrogen and proposed a mechanism for the formation of ozone in liquid nitrogen. According to their mechanism, the excited state of nitrogen molecule undergoes the reaction with oxygen molecule to produce oxygen atom. However, they did not discuss the mechanism in detail, since they did not investigate other effects e.g. the dose rate effect.

It may be instructive to mention the following. If the excited nitrogen molecules react with themselves or with other transient species which concentration is proportional to that of the excited nitrogen molecules and if the reaction is competitive to the reaction with oxygen molecule, one can obtain an equation which is essentially the same as Eq. 6. In this context it is beyond our present knowledge whether N_3^+ ion or an excited state of nitrogen is responsible for the formation of ozone in liquid nitrogen.

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