The *G*-value of Nitrogen Atoms Produced in the γ-Radiolysis of Liquid Nitrogen and the Ozone Formation in the γ-Irradiated Liquid Nitrogen Solution of Oxygen

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(Received April 7, 1978)

The γ-radiolyses of liquid nitrogen solutions of nitrogen oxide and of oxygen gave nitrogen dioxide and ozone, respectively, as the main products. Over the solute concentrations from 0.01 to 0.1 mol l^{-1}, the *G*-values of both products were constants: $G(NO_2)=3.3$ and $G(O_3)\approx 7$. The *G*-value of nitrogen dioxide in the former solution probably corresponds to the *G*-value of nitrogen atoms from liquid nitrogen. For the formation of ozone in the latter solution, a possible reaction mechanism is discussed. Dinitrogen oxide was found as a minor product, the *G*-value being about 0.1 for both solutions.

The γ-radiolysis of liquid nitrogen containing a certain solute is one useful method for the investigation of the reactions of nitrogen atoms with the solute molecule or the radicals eventually produced from the solute in the solution, although this method is restricted by the solubility of the solute in liquid nitrogen. In previous papers,[1] we used several hydrocarbons as the solute and observed various nitrogen-containing compounds as the products; however, because of the complexity of the reactions occurring in the solution, we could not precisely determine the *G*-values of active species produced in the γ-irradiated liquid nitrogen.

In the study of active nitrogen in the gas phase, it is now well known that the titration using nitrogen oxide is one of the best methods for determining the concentration of nitrogen atoms.[2] We, therefore, attempted to study the γ-radiolysis of liquid nitrogen containing nitrogen oxide in the hope that the *G*-value of nitrogen atoms could be determined.

The formation of ozone in the γ-irradiated liquid nitrogen containing oxygen has long been known; however, the *G*-value of ozone did not seem to be measured. Since the technique used for the determination of the *G*-value of nitrogen dioxide can be applied for the estimation of ozone yield, the *G*-value of ozone from the liquid nitrogen solution of oxygen has also been measured.

Experimental

The dried high-purity nitrogen supplied by the Nihon Sanso Co. was used after having been passed through sulfuric acid. The research grade nitrogen oxide and oxygen were purchased from the Takachiho Shoji Co.

The procedures of preparation and of γ-irradiation at 77 K of the samples were the same as those previously reported.[1] The dose rate was 1.06×10^6 R h^{-1} and the irradiation time ranged from 20 min to 2 h. The absorbed dose was estimated by the Fricke dosimetry.

After the γ-irradiation, the inside of the sampling tube was slowly pumped out at 77 K. Usually two hours were taken for complete evacuation. When nitrogen oxide was used as the solute, the pumping was stopped at the pressure of 0.1 Torr, in order to prevent the pumping-out of nitrogen oxide. The products thus obtained were subjected to analysis.

In the case of the solution of nitrogen oxide, the observed products were nitrogen dioxide and a small amount of dinitrogen oxide. The amount of nitrogen dioxide was estimated by the optical density at 450 nm using a Hitachi Model 200-20 spectrophotometer. Since an excess amount of nitrogen oxide was present in the analyzing vessel, the following two equilibrium reactions had to be taken into account:

$$NO + NO_2 \rightleftarrows N_2O_3,$$
$$2NO_2 \rightleftarrows N_2O_4.$$

The equilibrium constants were taken from the literature.[3,4]

The analysis of dinitrogen oxide was made by a gaschromatograph equipped with a 5 m dimethyl sulfolane column of 20% w/w on celite. Before introducing the products into the gaschromatograph, nitrogen dioxide was separated by the distillation at −120 °C.

When oxygen was used as the solute, the formation of nitrogen dioxide could not be observed. The observed products were ozone and a small amount of dinitrogen oxide. Since ozone is easily decomposed at room temperature, the following procedure was used for the measurement. After the evacuation of the γ-irradiated solution at 77 K, a known amount of nitrogen oxide was introduced into the sampling tube. Then the liquid nitrogen Dewar flask was removed, so that all molecules of ozone should have been converted into nitrogen dioxide according to the stoichiometric reaction:

$$O_3 + 3NO = 3NO_2.$$

Then the amount of nitrogen dioxide was measured as stated above.

Results

Figure 1 shows the *G*-value of nitrogen dioxide as a function of the amount of nitrogen oxide introduced

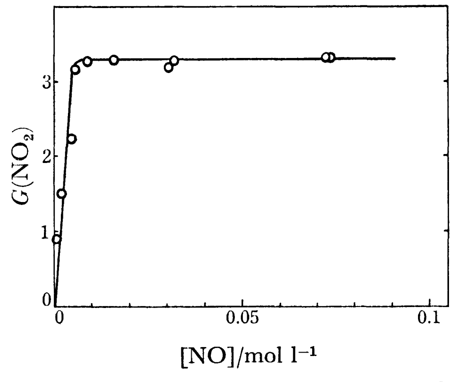

Fig. 1. The *G*-value of nitrogen dioxide as a function of the concentration of nitrogen oxide.

Table 1. The measurement of dinitrogen oxide

	Liquid N_2/cm^3	Solute/ 10^{-3} M	Irradiation time/min	$G(N_2O)$
Nitrogen oxide	30	6.6	60	0.10
	30	6.2	30	0.13
Oxygen	10	6.7	20	0.09
	20	11.4	20	0.08
	10	33.0	30	0.10

in liquid nitrogen. Below 0.01 mol l^{-1}, the yield of nitrogen dioxide was about equal to a half of the amount of nitrogen oxide introduced. At the concentrations higher than 0.01 mol l^{-1}, the following *G*-values were obtained: $G(NO_2)=3.3$ and $G(N_2O)=0.1$. Table 1 summarizes the results of the measurement of dinitrogen oxide.

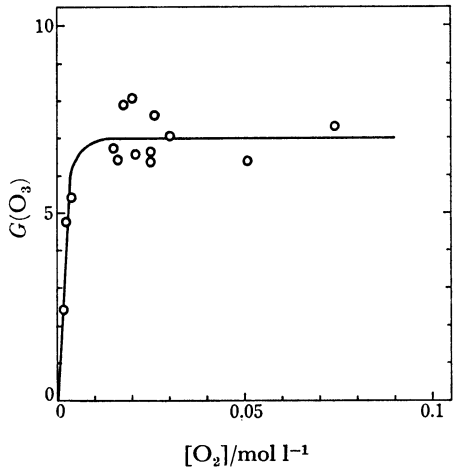

Fig. 2. The *G*-value of ozone as a function of the concentration of oxygen.

Figure 2 shows the *G*-value of ozone as a function of the amount of oxygen introduced in liquid nitrogen. Although the data are a little scattered, the following *G*-values were obtained at the concentrations higher than 0.01 mol l^{-1} of oxygen: $G(O_3)=7.0\pm0.5$ and $G(N_2O)=0.1$.

Discussion

The formation of nitrogen dioxide in the γ-irradiated liquid nitrogen containing nitrogen oxide can be simply explained by the following reactions:

$$N + NO \longrightarrow N_2 + O, \qquad (1)$$

$$O + NO \longrightarrow NO_2. \qquad (2)$$

This reaction mechanism is consistent with the fact that at the concentrations lower than 0.01 mol l^{-1}, the yield of nitrogen dioxide is equal to a half of the amount of nitrogen oxide introduced in liquid nitrogen. If the above mechanism is the only process for the formation of nitrogen dioxide, the value of 3.3 is the *G*-value of nitrogen atoms from liquid nitrogen.

Since the ionization potential of nitrogen oxide is lower than that of nitrogen, a charge transfer from nitrogen molecule ion to nitrogen oxide is possible; the neutralization reaction of the nitrogen oxide ion thus produced may form nitrogen and oxygen atoms. These atoms will produce nitrogen dioxide through Reactions 1 and 2. However, if the neutralization of nitrogen molecule ions and the charge transfer from nitrogen molecule ion to nitrogen oxide are in competition, a very high concentration of the positive ion interceptor, nitrogen oxide in the present case, must be necessary to suppress the neutralization completely.$^{5)}$ According to Fig. 1, only 0.01 mol l^{-1} is enough to saturate the *G*-value of nitrogen dioxide. This is incompatible with the formation of nitrogen dioxide through the charge transfer from nitrogen molecule ion to nitrogen oxide.

Another possible mechanism is the energy transfer reaction from excited nitrogen molecules to nitrogen oxide. However, this reaction is believed not to occur even in the gas phase reaction of active nitrogen at room temperature.$^{2)}$

Consequently it may be concluded that the *G*-value of nitrogen atoms from liquid nitrogen is 3.3.

In the γ-radiolyses of liquid nitrogen solutions of hydrogen and of various hydrocarbons,$^{1)}$ the sum of the *G*-values of nitrogen containing products we could observe did not exceed 1.5, while the present experiment suggested $G(N)=3.3$. This difference may be due to the fact that back reactions, such as

$$NH + NH \longrightarrow N_2 + H_2, \qquad (3)$$

$$RN + NH \longrightarrow N_2 + RH, \qquad (4)$$

$$RN + RN \longrightarrow N_2 + R_2, \qquad (5)$$

are important processes when hydrogen and hydrocarbons are used as solutes. Here, R stands for hydrocarbon radicals.

For the formation of ozone in the γ-irradiated liquid nitrogen containing oxygen, we tentatively considered the following reaction mechanism:

$$N_2 \rightsquigarrow N_2^+ + e^-, N_2^*, \qquad (6)$$

$$N_2^* + O_2 \longrightarrow N_2 + 2O, \qquad (7)$$

$$e^- + O_2 \longrightarrow O_2^-, \qquad (8)$$

$$N_2^+ + O_2^- \longrightarrow N_2 + 2O, \qquad (9)$$

$$O + O_2 \longrightarrow O_3. \qquad (10)$$

Here, N_2^* is the excited state of nitrogen molecule, probably $^3\Sigma_u^+$ state.$^{1)}$ The direct participation of nitrogen atoms was ignored because the reaction between nitrogen atoms with oxygen molecule to form nitrogen oxide is known to be a slow reaction.$^{6)}$ This is consistent with the experimental result that no nitrogen dioxide formation could be observed in this solution.

It may be worthwhile to mention here that the bond dissociation energy of O_2 (5.15 eV) is much smaller than that of NO (6.54 eV) and also smaller than the excitation energy of the lowest excited state $^3\Sigma_u^+$ of nitrogen (6.17 eV).

Although an oxygen molecule is a good electron scavenger, 0.01 mol l^{-1} of oxygen concentration is not high enough to scavenge all the electrons ejected into the solution.$^{7)}$ Consequently, the main process of the ozone formation probably consists of Reactions 7 and

10 at low concentrations of oxygen. If so, the *G*-value of N_2^* becomes 3.5. As possible origins of N_2^*, the following three processes have to be considered: the direct formation due to the γ-irradiation, the neutralization reaction of nitrogen molecule ions, and the recombination reaction of nitrogen atoms. The specific allotment of each contribution is beyond our present knowledge.

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