Efficient Photochemical Conversion of N_2O into N_2 and O_2 by 193-nm-ArF-excimer Laser in N_2 or Air at Atmospheric Pressure

Masaharu Tsuji,*[†,††] Hiroshi Sako,[††] Kenji Noda,[††] Makoto Senda,[††] Taro Hamagami, and Takeshi Tsuji[†,††]
Institute for Materials Chemistry and Engineering, Kyushu University, Kasuga 816-8580
[†]*JST, Kawaguchi, Saitama 332-0012*
[††]*Department of Applied Science for Electronics and Materials, Graduate School of Engineering Sciences, Kyushu University, Kasuga 816-8580*

(Received March 14, 2005; CL-050343)

N_2O removal by using 193-nm-ArF-excimer laser has been studied at a low N_2O concentration of 100 ppm in N_2 or air. N_2O was decomposed into N_2 and O_2 without any NO*x* emission at atmospheric pressure. After 10 min laser irradiation, the N_2O conversion was 95% in N_2, while it was 100% in air. The decomposition mechanism of N_2O in N_2 and air was discussed from a kinetic model.

Nitrous oxide (N_2O) in the Earth's atmosphere is a major contributor to the greenhouse effect due to its long residence time of about 150 years and its relatively large energy absorption capacity per molecule. We have recently proposed a photochemical process as a new removal method of N_2O in air without using any catalysts.[1] The maximum conversion of N_2O in N_2 and air at N_2O concentrations of 9.1 and 7.7%, respectively, was 93% at a laser power of 136 mJ, a repetition frequency of 5 Hz, and an irradiation time of 30 min. The formation ratios of N_2:O_2:NO in N_2O/N_2 and $N_2O/N_2/O_2$ mixtures were 64:31:5.1% and 60:27:13%, respectively. In our previous experiments, N_2O removal was studied in the high N_2O concentration range of 2.0–9.1% because of low detection sensitivity of mass spectrometer at low N_2O concentrations. Since actual N_2O emission occurs at much lower levels of 5–200 ppm, further experiments at a low concentration were required for practical application of this method.

In this study, N_2O removal in N_2 or air (4:1 mixture of N_2/O_2) was studied at a low N_2O concentration of 100 ppm by using a high-sensitive FTIR-gas-analysis system. The decomposition mechanism of N_2O under 193 nm photolysis was discussed by comparing experimental data with calculated ones from a kinetic model.

N_2O photolysis chamber used in this study was identical to that reported previously[1] except for the use of higher sensitive analytical systems of products. Light from an unfocused ArF-excimer laser (Lambda Physik, COMPex102) was used to decompose N_2O at room temperature. The laser pulses had a duration of 15 ns and delivered an output energy of 100 mJ/pulse at a repletion rate of 5 Hz. All experiments were carried out in a closed batch system. The total pressure was kept at atmospheric pressure and the N_2O concentration diluted in N_2 or air was 100 ppm (v/v).

After 0.5–30 min laser irradiation, products were analyzed by using HORIBA gas analysis system (FG-100) equipped with an FTIR spectrometer and ANELVA gas analysis system (M-200GA-DTS) equipped with a quadrupole mass spectrometer. We determined the residual amount of N_2O, $[N_2O]/[N_2O]_0$, the conversion of N_2O, $1\text{-}[N_2O]/[N_2O]_0$, and the formation ratios of N_2, O_2, and NO, defined as $[N_2]/[N_2O]_0$, $[O_2]/[N_2O]_0$, and $[NO]/[N_2O]_0$, respectively, from gas analyses. Here, $[N_2O]_0$ is an initial concentration of N_2O.

FTIR spectra before laser irradiation in N_2 or air consisted of N_2O peaks. After laser irradiation, these N_2O peaks either became weak or disappeared. Although no peaks of NO and NO_2 were observed, strong O_3 peaks were found in air. These results suggest that N_2O is efficiently decomposed without any NO*x* emission in both N_2 and air at a low N_2O concentration of 100 ppm, and that O_3 is produced in air.

Figure 1 shows the dependence of residual amount of N_2O and the formation ratios of N_2 and O_2 on the irradiation time of ArF laser in N_2 and air. The formation ratios of N_2 and O_2 were estimated from N and O balance before and after laser irradiation, respectively. O atoms in N_2O can be converted not

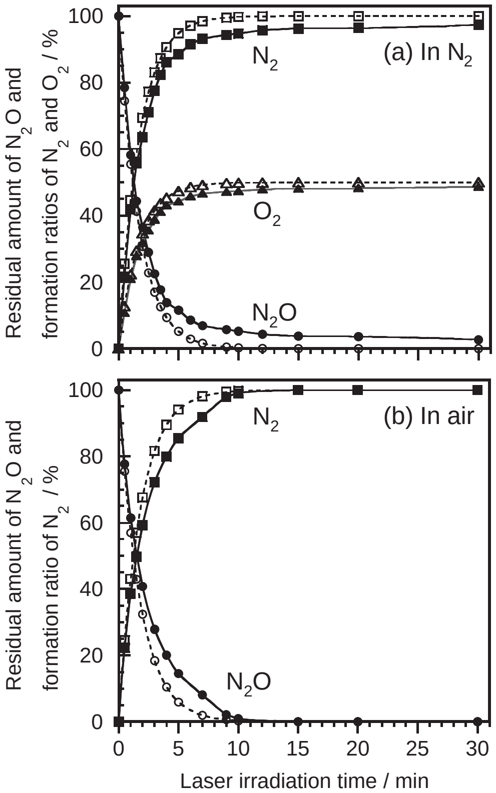

Figure 1. Dependence of the residual amount of N_2O and the formation ratios of N_2 and O_2 on the laser irradiation time in N_2 or air at an N_2O concentration of 100 ppm. ●: N_2O(Obs.), ○: N_2O(Calc.), ■: N_2(Obs.), □: N_2(Calc.), ▲: O_2(Obs.), △: O_2(Calc.).

only to O_2 but also to O_3 and dominant source of O_3 is O_2 in air. It was therefore difficult to determine the formation ratio of O_2 in air from O balance. The residual amount of N_2O in N_2 rapidly decreases to 5% after 10 min laser irradiation and becomes 2.7% at 30 min. The formation ratios of N_2 and O_2 in N_2 rapidly increase to 95 and 47% after 10 min laser irradiation and become 97 and 49%, respectively, at 30 min. On the other hand, all N_2O was decomposed in air after about 10 min laser irradiation. The formation ratio of N_2 becomes 100% after 10 min laser irradiation. The concentration of O_3 was 116 ppm at 0.5 min. It increases to 2690, 2980, and 3060 ppm at 10, 20, and 30 min, respectively. The much higher concentrations of O_3 than the $[N_2O]_0$ value suggests that O_3 dominantly arises from O_2. Similar decay curves of N_2O in the 0–7 min range in N_2 and air suggest that effects of O_2 and O_3 are insignificant for the N_2O decomposition. The N_2O conversion and the formation ratios of N_2 and O_2 increased almost linearly in the laser-power range of 40–110 mJ/pulse. It was therefore concluded that decomposition of N_2O proceeds through one photon process.

The observed data are compared with calculated values from a kinetic model,[2] which was similar to that reported, previously.[1] Five photolysis processes and eight two-body and seven three-body reactions were taken into account in the simulation, including sixteen processes used in the previous model calculation.[1] Among them, ten major photolysis and subsequent reaction processes are given in Table 1.

The calculated data are shown by dotted lines in Figure 1. A reasonable agreement between the observed and calculated data is found, though N_2O decomposition in N_2 and air in the model calculations occurs more rapidly than the experimental observation. A small discrepancy is also found between the observed and calculated data for the final conversion of N_2O in N_2. Although N_2O in N_2 is completely converted into N_2 and O_2 after 10 min laser irradiation in the model calculations, it was about 95% in the experimental observation. No NO and NO_2 formation is expected in the model calculations, which is consistent with the experimental observation.

As shown in Table 1, photolysis of N_2O by 193-nm-ArF laser starts from process (1) leading to $O(^1D) + N_2$.[8] In air, O_3 atoms are produced via photolysis of O_2 (2) followed by the three-body recombination reactions such as process (7). O_3 has a large absorption cross section at 193 nm and also provides active $O(^1D)$ atoms through process (3). The secondary reaction of $O(^1D)$ atoms with N_2O gives $N_2 + O_2$ and 2NO via processes (4a) and (4b), respectively. On the basis of above findings, there are two pathways for the N_2O decomposition: photolysis process (1) and secondary two-body reactions (4).

Table 1. Major photolysis of N_2O and subsequent reaction processes under 193-nm-ArF-laser irradiation

Processes	Number	Coefficients (Refs. 3–7)
$N_2O + h\nu \rightarrow O(^1D) + N_2$	(1)	8.95×10^{-20}
$O_2 + h\nu \rightarrow 2O(^3P)$	(2)	3.2×10^{-22}
$O_3 + h\nu \rightarrow O_2 + \alpha O(^1D) + \beta O(^3P)$ $\alpha:\beta = 0.87:0.13$	(3)	4.34×10^{-19}
$O(^1D) + N_2O \rightarrow N_2 + O_2$	(4a)	4.4×10^{-11}
$\rightarrow 2NO$	(4b)	7.2×10^{-11}
$\rightarrow O(^3P) + N_2O$	(4c)	4.8×10^{-12}
$O(^1D) + N_2 \rightarrow O(^3P) + N_2$	(5)	2.6×10^{-11}
$O(^1D) + O_2 \rightarrow O(^3P) + O_2$	(6)	4.0×10^{-11}
$O(^3P) + O_2 + N_2 \rightarrow O_3 + N_2$	(7)	5.7×10^{-34} $[N_2]$
$O(^1D) + O_3 \rightarrow 2O_2$	(8a)	2.4×10^{-10}
$\rightarrow O_2 + 2O(^3P)$	(8b)	2.4×10^{-10}
$O(^3P) + O(^3P) + N_2 \rightarrow O_2 + N_2$	(9)	4.82×10^{-33} $[N_2]$
$O(^3P) + O(^3P) + O_2 \rightarrow O_2 + O_2$	(10)	1.0×10^{-32} $[O_2]$

Units of coefficients are $cm^2\ molecule^{-1}$ for (1)–(3) and $cm^3\ molecule^{-1}\ s^{-1}$ for (4)–(10).

In our previous study in N_2 or air at high NO concentrations of 2.0–9.1%,[1] NO was produced with formation ratios of 5–13%. An outstanding finding in the present study at a low N_2O concentration of 100 ppm is the lack of NO emission. This indicates that application of 193 nm photolysis to N_2O removal is more effective at a low practical concentration level of N_2O. The secondary $O(^1D) + N_2O \rightarrow 2NO$ reaction (4b) competes with collisional quenching of $O(^1D)$ to $O(^3P)$ such as processes (5) and (6). With decreasing N_2O concentration, the relative importance of process (4b) to processes (5) and (6) decreases. Therefore, NO emission via process (4b) is suppressed at the low N_2O concentration.

Another outstanding finding in this study is that the N_2O removal by 193-nm-ArF laser in air is more effective than that in N_2. A complete conversion of N_2O into N_2 and O_2 without any NO*x* emission is achieved in air at atmospheric pressure. In our model calculation, N_2O is completely decomposed in N_2 and air. The slow decomposition of N_2O in N_2 indicates that some reproduction process exists in N_2. Such an N_2O reproduction can not be explained by taking all possible formation processes of N_2O into consideration.[6] We have recently found that vibrationally excited NO molecules play significant role in the ArF-laser photolysis of NO_2 at 200 ppm.[9] Similar vibrationally excited molecular products may also contribute to the reproduction of N_2O at 100 ppm in N_2.

In summary, N_2O could be efficiently decomposed by 193-nm-ArF-laser photolysis in N_2 or air at a low N_2O concentration of 100 ppm without any NO*x* emission. A further detailed study for N_2O photolysis by 193-nm-ArF laser in N_2 or air is in progress in order to obtain optimum experimental conditions for N_2O removal and to clarify the decomposition mechanism.

The authors acknowledge financial support from a Grant-in-Aid for Scientific Research Number 15310059 from the Japanese Ministry of Education, Culture, Sports, Science, and Technology.

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Published on the web (Advance View) May 14, 2005; DOI 10.1246/cl.2005.812