CHEMISTRY LETTERS, pp. 1465-1468, 1988.

Experimental Evidence of N_2 Formation from NO in Simulated Coal-fired Flue Gas by Electron Beam Irradiation

Hideki NAMBA,* Yasushi AOKI, Okihiro TOKUNAGA,
Ryoji SUZUKI,† and Shinji AOKI†
Takasaki Radiation Chemistry Research Establishment, JAERI,
Watanuki-machi, Takasaki, Gunma 370-12
†Environmental Plant Development Dept., Ebara Co.,
1-6-27 Kohnan, Minato-ku, Tokyo 108

Nitrogen molecule formation was first observed experimentally in simulated coal-fired flue gas ($NO-SO_2-H_2O-O_2-N_2$) with the electron beam-ammonia treatment method in flow system. The increase of $^{29}N_2$ was detected by mass-spectrometers in the flue gas containing N-15 labeled NO. The fraction of the ^{15}NO converted to $^{29}N_2$ was determined to be 23% at 14 kGy.

An air pollution caused by combustion flue gases from industrial plants has become serious problem in many countries for these years. The reactions of the emitted toxic gases, SO_x and NO_x, are thought to cause "acid rain". The research of electron beam treatment of combustion flue gases was first performed in Japan about 15 years ago;1,2) we have been continuing the research, and the results have attracted world wide attention, especially with the success of the pilot scale test for treatment of flue gas from a steel-sintering-furnace.3) The air pollution from the coal-fired combustion gas has been a current problem. The electron beam-ammonia treatment method is regarded as a promising method to solve the problem with many advantages.4) Pilot scale tests are now performing in Federal Republic of Germany5) and have just finished in the United States of America.6)

However, more precise knowledge of the reaction mechanisms of de-NO_x and de-SO_x is needed in electron beam treatment of coal-fired flue gas. Using a small scale flow system in JAERI, we found the difference of NO_x removal between in coal-fired flue gas and in steel-sintering-furnace flue gas. In the case of steel-sintering-furnace test,3) almost all the NO_x removed by electron beam irradiation was converted to ammonium nitrate. On the other hand, in coal-fired flue gas, the amount of ammonium nitrate was less than the amount expected from the amount of removed NO_x. We considered that a part of the NO_x must be converted to nitrogen molecule, and started this study. Since ammonium nitrate, the by-product, is possible to use for a fertilizer, this study is useful not only for the scientific interest of the reaction mechanism but also for the practical use of the electron beam treatment of flue gas.

All the experiments were done in a flow system shown in Fig. 1. All the vessels and the pipes of the apparatus were made of stainless-steel and the temperature of these parts were kept at 80 °C. The simulated coal-fired flue gas was prepared with mixing water vapor and standard gases in a mixing vessel. The concentration and the purity of the standard gases were almost the same as we used previously[7)] except for nitrogen monoxide (NO). Nitrogen-15 labeled NO (Shoko Trade Co.; isotopic purity :99.7%) was degassed by pump-and-thaw and condensed into a cylinder at liquid N_2 temperature on a vacuum line evacuated less than 10^{-4} Pa. The pressure of NO in the cylinder was 3.3 atm at room temperature. This NO was fed into the mixing vessel by a mass flow controller. Three percent NH_3 containing N_2 gas was mixed with the simulated flue gas just before irradiation. The concentrations of the components measured in "dry base" were as follows; NO: 400 ppm, SO_2: 1720 ppm, O_2: 6.9%, NH_3: 3840 ppm, N_2: 92.5%. The concentration of H_2O was 13% in "wet base". The pressure of the system was set at 1 atm and the pressure difference of each part of the system was less than 0.01 atm. The gas was irradiated in an irradiation vessel with electron beam (1.5 MeV, 2.3 mA) from a Cockcroft-Walton type electron accelerator. Stainless-steel foils of 50-μm thickness were put on the front and rear sides of the irradiation vessel as windows. Water-cooled jackets and heaters were put on the top and the bottom sides of the vessel to control the temperature at 80 °C regardless of irradiation. A water-cooled plate was set between the front window of the vessel and a scanning horn of the accelerator to irradiate only the window part. The dose rate at 2.3 mA was determined to be 5.8 kGy/s by a gas phase dosimeter.[8)] The flow rate of the

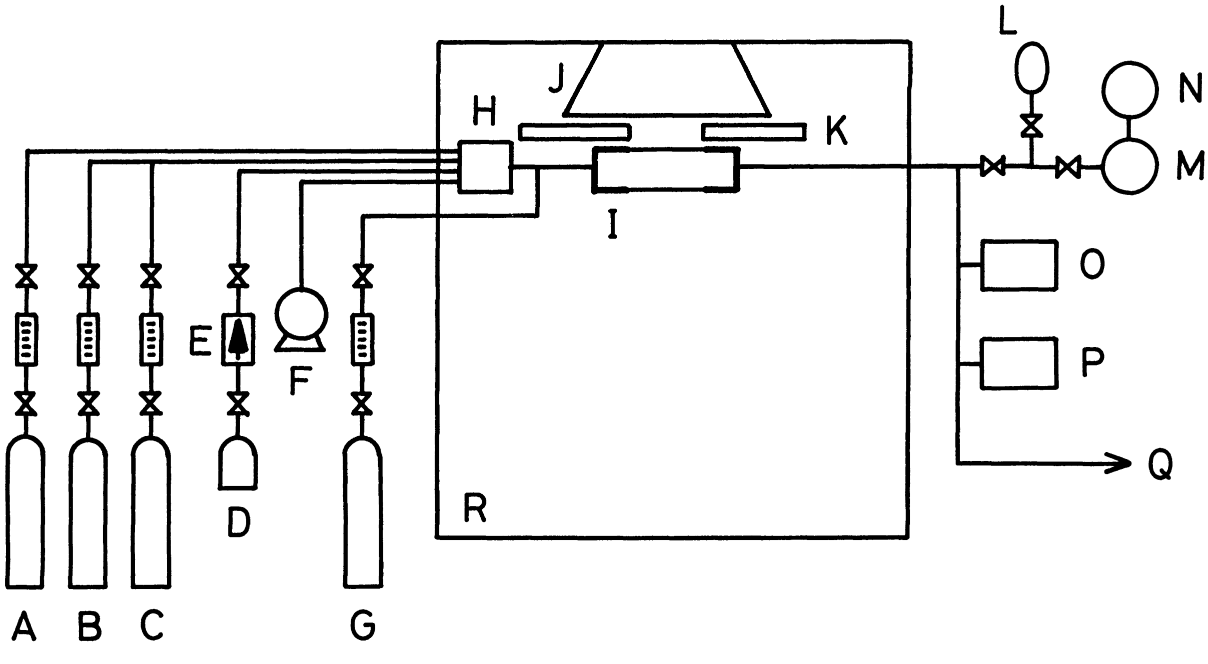

Fig. 1. Experimental apparatus for flow experiments.
A: SO_2(3%)-N_2 gas, B: N_2 gas, C: O_2 gas, D: ^{15}NO gas, E: Mass flow controller F: H_2O feeder, G: NH_3(3%)-N_2 gas, H: Mixing vessel with heaters I: Irradiation vessel with water-cooled jackets and heaters, J: Scanning horn of the accelerator, K: water-cooled plate, L: Sampling cell, M: Diffusion pump, N: Rotary pump, O: NO_x detector, P: SO_2 detector, Q: Exhaust, R: Irradiation room

Table 1. Concentrations of $^{29}N_2$ before and after electron beam irradiation in simulated coal-fired flue gas containing 400 ppm ^{15}NO

	Mass-spectrometer	Before irradiation		After irradiation		Formed
		$^{29}N_2/^{28}N_2$ (%)	$[^{29}N_2]$ (ppm)	$^{29}N_2/^{28}N_2$ (%)	$[^{29}N_2]$ (ppm)	$[^{29}N_2]$ (ppm)
I	Hitachi	0.7313±0.0053	6752±48	0.7423±0.0054	6853±49	101±97
	Finnigan Mat	0.7283±0.0004	6724±4	0.7366±0.0003	6800±3	76±7
II	Finnigan Mat	0.7277±0.0003	6719±3	0.7374±0.0002	6808±2	89±5
III	Finnigan Mat	0.7279±0.0003	6721±3	0.7384±0.0005	6817±5	96±8
	Average					89±9

simulated flue gas was 19.4 L/min at 80 °C. The volume of the irradiation vessel was 0.759 L. The irradiation time was 2.4 s and the dose absorbed in the gas was 14 kGy. The experimental conditions (composition of the gas, temperature and dose) were set close to the standard treatment condition of the pilot plant performed in the United States.[6)]

The concentrations of NO and NO_2 were measured continuously during the experiments. No NO_2 was detected before irradiation. After the electron beam irradiation, the concentrations of NO and NO_2 were 50±10 ppm and 20±10 ppm, respectively.

Gaseous samples were fed both before and after irradiation in sampling cells, which were evacuated less than 10^{-2} Pa by pumps just before sampling. Experiments were done for three times independently. The samples were collected in eight to fourteen cells on each experiment. More than ten runs of the measurements on the ratio of the peak height of M/e = 29 and 28 were done for each sample by special mass-spectrometers suitable for gaseous samples (Finnigan Mat delta, Hitachi RMU-6).

The results obtained in the present study are summarized in Table 1. The ratios of the number of $^{29}N_2$ molecules to that of $^{28}N_2$ molecules ($^{29}N_2/^{28}N_2$) before and after electron beam irradiation are shown in Table 1. Based on the reported values[9)] of the natural abundance of the ^{15}N, the ratio of $^{29}N_2/^{28}N_2$ is calculated to be between 0.727% and 0.753%; typically 0.735%. The calculated value is close to the experimentally obtained values of before irradiation shown in Table 1 and no $^{14}N \rightarrow {}^{15}N$ exchange is indicated between N_2 and NO without irradiation at 80 °C. Electron beam irradiation increased the ratio, $^{29}N_2/^{28}N_2$. The concentration of $^{29}N_2$ ($[^{29}N_2]$) in the sample gas measured by "dry base" are calculated easily. The amount of $^{29}N_2$ formed by electron beam irradiation is obtained by subtraction. The average value of the formed $[^{29}N_2]$ is 89 ± 9 ppm in the simulated coal-fired flue gas containing 400 ppm ^{15}NO at 14 kGy. This indicates that about 23% of ^{15}NO was converted to $^{29}N_2$.

Since the main component of the flue gas is nitrogen, the production of N atom takes place in irradiated flue gas; $N_2 \xrightarrow{\text{WW}} 2N$.

The N atom reacts with NO to form N_2.

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

Theoretical studies[10] mentioned the importance of the reaction (1), because this reaction is fast enough[11] to take place in comparison with other reactions. However, there was no experimental evidence of N_2 formation in irradiation of flue gas because of the experimental difficulty; the amount of formed $^{29}N_2$ (≈ 90 ppm) detected in this study is about 1% of the natural abundance of $^{29}N_2$.

A study on $^{29}N_2$ formation was reported[12] in simple mixtures of $^{28}N_2$ (containing natural abundance $^{29}N_2$) and ^{15}NO (1.3 to 3.6%) by Co-60 γ-ray irradiation in static system; the G value of the N_2 formation was 2.57 and reaction (1) was suggested for the formation mechanism. In the present study, the value of $G(^{29}N_2)$ is 2.2 which is close to the reported value.

Nevertheless, the real mechanisms of the nitrogen formation in flue gas will be more complicated because reaction (1) must be in competition with other reactions. We also need to consider other $^{29}N_2$ formation reactions such as $NH_2 + {}^{15}NO \longrightarrow {}^{29}N_2 + H_2O$. Further studies on the reaction mechanisms using N-15 labeled compounds are in progress.

We wish to express our thanks to Mr. Shoujirou Hirosawa for his technical assistance.

References

1) K. Kawamura and S. Aoki, Nippon Genshiryoku Gakkaishi, 14, 597 (1972).
2) S. Machi, H. Namba, and N. Suzuki, IAEA-TECDOC-428, 13 (1987).
3) K. Kawamura et al., Environ. Sci. Technol., 14, 288 (1980).
4) Consultants meeting of electron beam processing of combustion flue gases, 27-29 Oct. 1986 (Karlsruhe); Advisory group meeting on radiation processing of stack gases, 16-19 Nov. 1987 (Bologna).
5) P. Fuchs, B. Roth, and U. Schwing, IAEA-TECDOC-428, 119 (1987).
6) N. W. Frank, K. Kawamura, and G. A. Miller, IAEA-TECDOC-428, 97 (1987).
7) H. Namba, O. Tokunaga, and N. Suzuki, J. Environ. Pollut. Control, 21, 629 (1985); O. Tokunaga, H. Namba, and N. Suzuki, Int. J. Appl. Radiat. Isotopes, 36, 807 (1985).
8) H. Namba, O. Tokunaga, and N. Suzuki, Int. J. Appl. Radiat. Isotopes, in press.
9) M. Lederer and V. S. Shirley, "Tables of Isotopes," 7 th ed, Wiley Interscience, N.Y. (1978).
10) C. Willis and A. W. Boyd, Int. J. Radiat. Phys. Chem., 8, 71 (1976); K. Nishimura and N. Suzuki, J. Nucl. Sci. Technol., 18, 56 (1981); S. Jordan and W. Schikarski, IAEA-TECDOC-428, 135 (1987).
11) D. L. Baulch et al., J. Phys. Chem. Ref. Data, 9, 295 (1980).
12) D. H. Dawes and R. A. Back, J. Phys. Chem., 69, 2385 (1965).

(Received May 17, 1988)