

Radiation Chemical Studies on
the Electron-Beam Treatment of Exhaust
Gases

March 1980

日本原子力研究所

Japan Atomic Energy Research Institute

JAERI レポート

この報告書は、日本原子力研究所で行なわれた研究および技術の成果を研究成果編集委員会の審査を経て、不定期に刊行しているものです。

研究成果編集委員会

委員長 石川 寛 (理事)

委 員

赤石 準 (保健物理部)	田中 正俊 (核融合研究部)
朝岡 卓見 (原子炉工学部)	仲本秀四郎 (技術情報部)
今井 和彦 (環境安全研究部)	長崎 隆吉 (燃料工学部)
神原 忠則 (材料試験炉部)	橋谷 博 (原子炉化学部)
小林 岩夫 (動力試験炉部)	浜口 由和 (物理部)
栗山 将 (高崎研究所)	原 昌雄 (動力炉開発・安全性研究管理部)
佐々木吉方 (研究炉管理部)	原田吉之助 (物理部)
佐藤 一男 (安全解析部)	更田豊治郎 (企画室)
佐野川好母 (高温工学室)	三井 光 (高崎研究所)
四方 英治 (製造部)	森島 淳好 (安全工学部)

入手 (資料交換による)、複製などのお問い合わせは、日本原子力研究所技術情報部 (〒319-11 茨城県那珂郡東海村) あて、お申しこみください。なお、このほかに財団法人原子力弘済会情報サービス事業部 (茨城県那珂郡東海村日本原子力研究所内) で複写による実費頒布をおこなっております。

JAERI Report

Published by the Japan Atomic Energy Research Institute

Board of Editors

Hiroshi Ishikawa (Chief Editor)

Jun Akaishi	Masao Hara	Isamu Kuriyama	Yoshikata Sasaki
Takumi Asaoka	Kichinosuke Harada	Hiroshi Mitsui	Kazuo Sato
Toyojiro Fuketa	Kazuhiko Imai	Atuyoshi Morishima	Konomo Sanokawa
Yoshikazu Hamaguchi	Masanori Kanbara	Ryukichi Nagasaki	Eiji Shikata
Hiroshi Hashitani	Iwao Koboyashi	Hideshiro Nakamoto	Masatoshi Tanaka

Inquiries about the availability of reports and their reproduction should be addressed to the Division of Technical Information, Japan Atomic Energy Research Institute, Tokai-mura, Naka-gun, Ibaraki-ken, Japan.

編集兼発行 日本原子力研究所
印 刷 学術図書印刷株式会社

Radiation Chemical Studies on the Electron-Beam Treatment of Exhaust Gases

Masamitsu WASHINO, Okihiro TOKUNAGA, Koichi NISHIMURA
and Nobutake SUZUKI

Takasaki Radiation Chemistry Research Establishment

Received October 15, 1979

This report summarizes the radiation chemical studies on the synthetic models of exhaust gases which has been done in JAERI-Takasaki.

Radiation-induced reactions of low concentrations of SO_2 and NO was studied in dry and moist mixtures of N_2 and O_2 . SO_2 was oxidized to H_2SO_4 only in the moist mixtures. Oxidation of NO and reduction of NO_2 took place simultaneously and approached to a radiation-chemical stationary state in the dry N_2 - O_2 systems. NO was easily oxidized to NO_2 and finally to HNO_3 in the moist systems. Addition of NH_3 in the mixture enhanced the NO -removing reactions and suppressed the NO_2 - and HNO_3 -formations.

A set of reaction mechanisms deduced is proposed. The reaction proceeds by the mechanism of such indirect effect of radiation as the energies absorbed by the main components are transferred and utilized effectively to the SO_2 - and NO_x -removing reactions.

Keywords: Chemical radiation effects, Exhaust gases, Environmental protection, Nitrogen oxides, Sulfur dioxide, Ammonia, Moisture, G value.

排ガスの電子線処理に関する放射線化学的研究

鷺野正光, 徳永興公
西村浩一, 鈴木伸武

日本原子力研究所 高崎研究所

1979年10月15日 受理

高崎研究所研究部で排煙の電子線処理技術に関して行った排煙模擬ガスによる放射線化学的研究をまとめた。

即ち、低濃度の SO_2 および NO の放射線によって誘起される反応を、乾燥状態または水分を含む窒素と酸素の混合物中で研究した。 SO_2 は、水分を含む混合物中においてのみ硫酸に酸化された。 NO は、乾燥した混合物中では NO_2 への酸化および NO_2 の還元が同時に起り、放射線化学的定常状態に近づく。水分を含む系中では、 NO は容易に酸化されて NO_2 を経て硝酸を生ずる。アンモニアを混合物中に添加すると、 NO 除去反応が促進されるとともに、 NO_2 および硝酸の生成が抑制された。

この研究結果より、一連の反応機構を推定した。反応は放射線の間接効果によって起り、主成分に吸収された放射線エネルギーは効率よく移動して SO_2 および NO_x 除去反応に利用される。

Contents

1. Introduction	1
2. Experimental and analysis	3
2.1 Apparatus for flow experiments	3
2.2 Irradiation of glass ampoules.....	3
2.3 Dose rate measurement	4
2.4 Analysis	4
3. Results	5
3.1 Irradiation of SO ₂ in N ₂ -O ₂ systems	5
3.1.1 Reaction of SO ₂ in dry and moist mixtures	5
3.1.2 Effect of radical scavengers	5
3.1.3 Effect of O ₂ concentration	6
3.1.4 Effect of temperature	6
3.2 Irradiation of NO _x in various systems	7
3.2.1 Reaction of NO _x in N ₂ and in rare gases.....	7
3.2.2 Oxidation of NO and reduction of NO ₂ in dry N ₂ -O ₂ mixtures	8
3.2.3 Effect of moisture.....	9
3.2.4 Effect of CO	10
3.2.5 Effect of SO ₂ and temperature	11
3.2.6 Effect of ammonia	11
4. Discussion	12
4.1 Primary species in the radiolysis of moist N ₂ -O ₂ mixtures	12
4.2 Mechanism of SO ₂ oxidation	13
4.3 Mechanism of NO _x reactions.....	13
4.3.1 Decomposition in N ₂ and rare gases	13
4.3.2 Reaction in dry N ₂ -O ₂ mixtures	13
4.3.3 Oxidation of NO in the moist mixtures.....	14
4.3.4 Reaction of NH ₃	15
5. Conclusion.....	16
Acknowledgement	16
References.....	17

目 次

1. 序 論	1
2. 実験および分析	3
2.1 流通実験装置	3
2.2 ガラスアンプルの照射	3
2.3 線量率の測定	4
2.4 分 析	4
3. 結 果	5
3.1 N_2-O_2 系中の SO_2 の照射	5
3.1.1 乾燥系および湿った系中での SO_2 の反応	5
3.1.2 ラジカル捕捉剤の効果	5
3.1.3 酸素濃度の効果	6
3.1.4 温度の効果	6
3.2 種々の系中の NO_x の照射	7
3.2.1 窒素および希ガス中の NO_x の反応	7
3.2.2 乾いた N_2-O_2 混合系中における NO の酸化および NO_2 の還元	8
3.2.3 水分の効果	9
3.2.4 CO の効果	10
3.2.5 SO_2 および温度の効果	11
3.2.6 アンモニアの効果	11
4. 考 察	12
4.1 湿った N_2-O_2 混合系の放射線分解における初期活性種	12
4.2 SO_2 の酸化反応機構	13
4.3 NO_x の反応機構	13
4.3.1 窒素および希ガス中における分解	13
4.3.2 乾いた N_2-O_2 混合系中における反応	13
4.3.3 湿った混合系中における NO の酸化	14
4.3.4 アンモニアの反応	15
5. 結 論	16
謝 辞	16
参考文献	17

1. Introduction

The radiation treatment process for combustion gases was developed at first by collaboration of JAERI and Ebara Manufacturing Company^{1,2)}. This work was started at Takasaki Radiation Chemistry Research Establishment in 1972 using a small-scale flow irradiation apparatus for heavy oil combustion gas with the flow rate ranging 5 to 40 m³/h. The SO₂ and NO_x was found to be removed simultaneously as mist and dust containing sulfuric and nitric acids by using an electrostatic precipitator.

Many attentions have been paid to this new process which has major advantages as follows :

- Simultaneous removing of SO₂ and NO_x
- Applicability to gases containing dust
- Dry process . . . no need of waste water treatment
- Relatively low temperature preferred (120°C).

Other processes for exhaust gas treatment have been examined by many institutions in this country but the only proven process among them is the SO₂-removing wet process followed by the NO_x-removing dry process which needs relatively high temperature . . . i. e. the available process needs large facilities and energies.

Our process had its own problems, on the other hand, for the realization of practical use : The electron accelerator of large power and of low construction cost had to be developed, and the radiation dose needed for treatment of exhaust gases was desirably reduced by applying optimum reaction conditions and possibly by using additives.

We can probably expect the rapid development of large accelerators that is actually stimulated by the recent development of radiation processes in various fields. As to the reduction of the necessary dose, on the other hand, it was necessary to know reaction mechanism of the irradiation of the exhaust gases which was very complicated systems in comparison with the gaseous systems ever studied radiation-chemically. We decided to start the study on the mechanism of exhaust gas irradiation from simple systems, e. g. NO-N₂ or NO-O₂-N₂ mixtures, and proceeded to complex systems with progressive elucidation of the reaction mechanisms.

Then since two pilot scale plants of this process were constructed successfully ; one for heavy oil combustion gas at the Central Laboratory of the Ebara Co.^{3,4)} and the other for the fume from a sintering furnace at the Yahata Works of the Nippon Steel Corporation ; the capacities being 1000 and 3000 m³/h respectively. The latter project was performed by the Research Association for Abatement and Removal of NO_x in the Steel Industry, in collaboration of the Ebara Co. with the partial support from the government.

In the stage of planning the second pilot scale experiment, the advantage of utilizing ammonia as an additive to the irradiating gas was realized by us⁵⁾ : ammonia was effective to solidify nitric acid and to make the product easily collected by an electrostatic precipitator. In our study, ammonia was shown also to be effective to increase removal rate of NO_x and hence to reduce the necessary dose. This method was actually employed in the pilot-scale experiments on the basis of our results and the effectiveness was demonstrated.

To support these projects, researches have been continued at JAERI-Takasaki, at the University of Tokyo and at the Tokyo Institute of Technology in the view-points of radiation chemistry, reaction- and electrical- engineering, and inorganic solid chemistry, respectively⁶⁾. This report summarizes radiation-chemical studies on the models of exhaust gases done at Takasaki and

presents a set of reaction mechanisms deduced or strongly suggested in our studies.

The aims of the study are :

- (1) To promote pilot scale experiments by giving radiation-chemical bases to the electron-beam process. In this view the reaction mechanisms were studied to prove that the process is essentially an effective one in view of energy utilization, i. e., the radiation energy absorbed in the gas is effectively used to the SO_2 - and NO_x -removal.
- (2) To study the possibility of reducing the radiation dose which is necessary to treat exhaust gases by elucidating reaction mechanisms, by choosing pertinent reaction condition, and especially by utilizing additives like ammonia.
- (3) To give the mechanistic bases to the kinetic analysis of the results of the pilot scale experiments and to contribute to the optimization of the reaction conditions.
- (4) To connect previous basic radiation-chemical studies to the application of radiation chemistry to complex systems like exhaust gases. In this view various systems from simple NO-N_2 mixture to complex $\text{NO-SO}_2\text{-H}_2\text{O-O}_2\text{-N}_2$ mixtures were studied as models of the exhaust gases. The radiation-chemical study of the moist $\text{O}_2\text{-N}_2$ system is especially important because its application is not restricted to the exhaust gas treatment but is connected to various fields of nuclear technology and because the radiation-chemical mechanism of this system is not yet established.

Radiation-chemical studies on SO_2 or NO_x in the moist $\text{N}_2\text{-O}_2$ systems, like exhaust gases, have rarely been reported except some on the formation of NO_x and nitric acid in connection with the nitrogen fixation or the metal corrosion by the action of nuclear radiations⁷⁻⁹). Jones¹⁰) studied on radiolysis of $\text{N}_2\text{-O}_2\text{-H}_2\text{O}$ system and found that the formation of nitric acid was inhibited by the presence of NO_2 , but the reaction mechanism was not studied.

2. Experimental and Analysis

2.1 Apparatus for Flow Experiments¹¹⁾

Most experiments were carried out using a flow system as shown in Fig. 1. A stainless steel box-type reaction vessel of 1 liter capacity was placed just below the electron accelerator scanning horn. The top and bottom of the reaction vessel were made of stainless steel foil (0.05 mm thick) to minimize the electron energy absorption and hence the heat evolution. On the top of the reaction vessel, a water-cooled slit (maximum aperture 40 cm × 5 cm) was placed to control the absorbed dose in the irradiated gas by varying the aperture of the slit. The temperature of the reaction vessel was controlled by a heater outside the vessel. N₂, O₂, and N₂-diluted NO, NO₂ and SO₂ were introduced separately to the temperature-controlled mixing volume (0.35 l) which was placed just before the reaction vessel. Water was also fed into the mixing volume by a volumetric pump. The gaseous mixture thus prepared was charged into the reaction vessel at a flow rate of 3.0 l/min and irradiated within 7 sec after the mixing by the electron beams from an accelerator by Hitach Co. (Cockcroft-Walton type). The irradiated gas was led into gas analyzers through stainless steel tubings heated to 110°C.

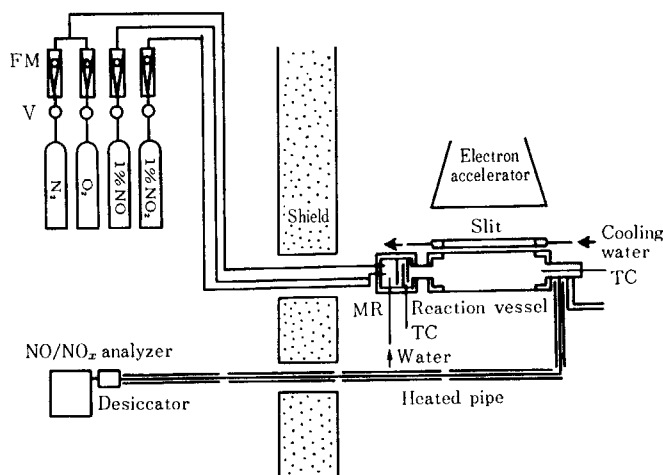


Fig. 1 Schematic diagram of the flow-experimental apparatus.
TC, thermocouple; MR, mixing room; FM, flow meter;
V, flow control valve.

2.2 Irradiation of Glass Ampoules¹²⁾

Some experiments were performed using glass ampoules when the gaseous system did not contain NO and hence the thermal oxidation was negligibly slow at the temperatures of handling and irradiation. The SO₂, H₂O, O₂, N₂ and additives were introduced into a 56 ml glass ampoule fitted with a capillary of 3 mm in diameter. The samples were then wrapped with aluminium foil to prevent possible photochemical reactions, and stored at 100°C to prevent the oxidation of SO₂ via nitrosylsulfuric acid. The samples were irradiated by electron beams in a thermostatic air bath; the cross-section is shown in Fig. 2. The air bath was moved on a conveyer with a constant speed under the scanning horn of the electron accelerator.

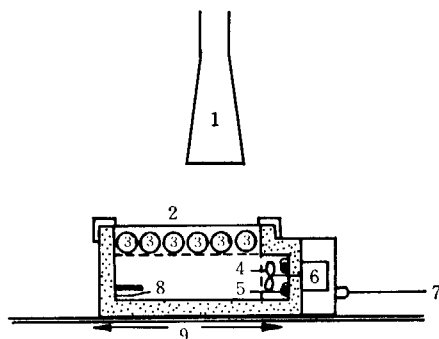


Fig. 2 Thermostatic irradiation bath; (1) scanner of electron beam accelerator; (2) stainless steel foil (SUS-27, 50 mm thickness); (3) ampoules; (4) fan; (5) heater; (6) electric motor; (7) cable (to a control box); (8) thermocouple; (9) conveyer.

2.3 Dose Rate Measurement^{11,12)}

Dose rate in the reaction vessel or in the ampoule was measured using an ethylene dosimeter consisting of ethylene gas at 20–50°C. The absorbed energy in the gaseous mixture was determined from the yield of hydrogen in irradiated ethylene using the known g -value, $G(\text{H}_2)=1.31$, and corrected for stopping powers of ethylene and nitrogen. In the case of irradiation by electron beams of 1.5 MeV 2 mA, the absorbed dose rate in nitrogen was 0.29 Mrad/sec for the flow system, and 2.6 Mrad per a passage under the scanning horn for the experiments with ampoules. The absorbed dose in the flowing gas was found to be proportional to the residence time in the irradiation zone.

2.4 Analysis

The SO_2 concentration was determined by a gas chromatograph (Yanagimoto G-80) with a flame photometric detector. The column (50°C) was filled with polytetrafluoroethylene powder (40–50 mesh), treated with polyphenylether (five rings) and phosphoric acid. The carrier gas was N_2 . For the samples in ampoules, the irradiated ampoule was connected to a gas sampler heated at 100°C, and the capillary of the ampoule was broken in the sampler.

The concentrations of NO and NO_2 were measured with a chemoluminescence-type NO/ NO_x analyzer (Shimadzu CLM-201). About 1 l/min of the irradiated gas was led to the analyzer through the heated stainless steel tubings. The analyzer detects NO and the total of NO and NO_2 as NO_x . Because HNO_3 (or N_2O_5) were also detected as NO_x with a low sensitivity, concentration of NO_2 was obtained as the difference $[\text{NO}_x]-[\text{NO}]$ with a small correction for HNO_3 . Contribution of N_2O_3 is negligible in the temperature employed.

NO_x in glass ampoules were determined by the phenol-disulfonic acid method after NO and NO_2 were converted to NO_3^- ions in the solution of H_2O_2 and H_2SO_4 .

3. Results

3.1 Irradiation of SO_2 in $\text{N}_2\text{-O}_2$ Systems^{12,13)}

3.1.1 Reaction of SO_2 in dry and moist mixtures

Irradiation did not cause any decrease in SO_2 concentration in carefully dried $\text{N}_2\text{-O}_2\text{-SO}_2$ system but SO_2 was readily oxidized to H_2SO_4 in the moist mixtures as shown in Fig. 3. $G(-\text{SO}_2)$ was 5.3 in air at 100°C independent of $[\text{H}_2\text{O}]$ within the range studied (0.26–8%).

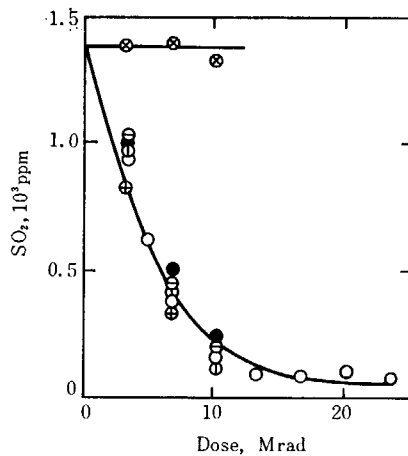


Fig. 3 Effect of moisture on the decrease of SO_2 . Initial concentration; 1400 ppm SO_2 , 20% O_2 , N_2 . Irradiation temp., 100°C . H_2O concentration (%): \otimes 0; \ominus 0.26; \oplus 0.53; \bullet 0.79; \circ 1.3; \oplus 8.0.

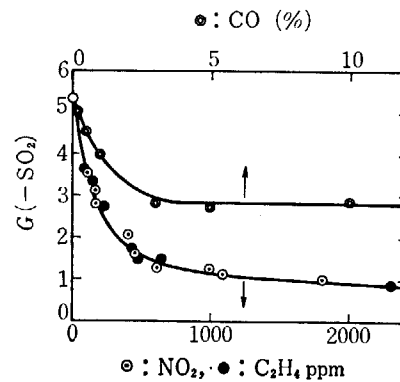


Fig. 4 Effect of CO , NO_2 and C_2H_4 on $G(-\text{SO}_2)$. $\text{SO}_2(1400 \text{ ppm})\text{-H}_2\text{O}(1.3\%)\text{-O}_2(20\%)\text{-N}_2$, 100°C .

3.1.2 Effect of radical scavengers

Figure 4 shows the $G(-\text{SO}_2)$ at low doses as function of additive concentrations. Because CO is known to react with OH radical and only very slowly with O atom, the portion of $G(-\text{SO}_2)$ which were removed by the addition of high concentration of CO can be attributed to the oxidation of SO_2 by OH . Such powerful radical scavengers as NO_2 and C_2H_4 suppressed most part of $G(-\text{SO}_2)$ at much lower concentrations in comparison with CO . Then, most part of SO_2 removal is attributable to the oxidation by OH and O . The remaining part of $G(-\text{SO}_2)$ was 0.9.

3.1.3 Effect of O₂ concentration

$G(-SO_2)$ in the moist mixture with and without CO is shown in Fig. 5 as function of O₂ concentration. $G(-SO_2)$ which was 0.9 in moist N₂ increased abruptly to 8.0 at 0.1% O₂, and decreased gradually with increasing [O₂]. The difference between the two curves was remained at constant value of 2.9 which is attributable to the oxidation by OH radical as shown in the preceding section.

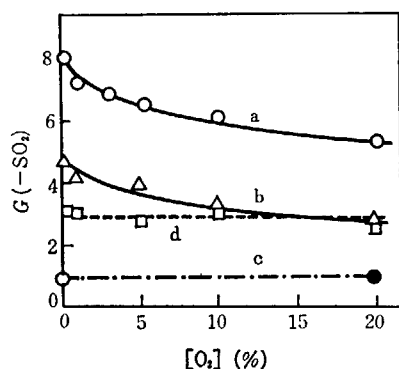


Fig. 5 Effects of O₂ on $G(-SO_2)$ in the SO₂-H₂O-O₂-N₂ mixture with and without CO.

- a ○: Mixture without CO
 b △: Mixture with 10% CO
 c ●: Mixture with 2300 ppm C₂H₄
 d □: Difference between $G(-SO_2)$ for mixtures with and without CO.
 Initial concentrations—
 SO₂: 1400 ppm, H₂O: 1.3%, N₂: 68.6~98.6%
 Irradiation temperature: 100°C

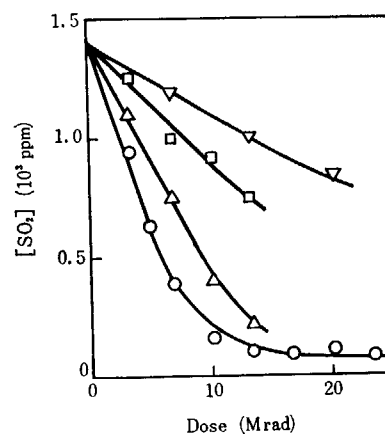


Fig. 6 SO₂ concentration as a function of dose in the SO₂-H₂O-O₂-N₂ mixtures at various irradiation temperatures.

- Irradiation temperature (°C)—
 ○: 100, △: 143, □: 200, ▽: 250
 Initial concentrations—
 SO₂: 1400 ppm, H₂O: 1.3%, O₂: 20%,
 N₂: 78.6%

3.1.4 Effect of temperature

SO₂ concentration decay curves in the moist mixture for irradiation at various temperatures are shown in Fig. 6. $G(-SO_2)$ was 5.3, 3.1, 1.7 and 1.0 at 100, 143, 200 and 250°C respectively. The apparent activation energy of the SO₂ oxidation was obtained as -4.2 kcal/mol.

3.2 Irradiation of NO_x in Various Systems

3.2.1 Reaction of NO_x in N_2 and in rare gases^{11,17-19}

As one of bases of the kinetic study, low concentrations of NO and NO_2 were radiolysed in common inert gases, i.e. N_2 , He and Ar. NO decomposed to N_2 and O_2 with the formation of a low concentration of NO_2 in the inert gases as is shown in Fig. 7; NO_2 decomposed at first to NO and O_2 , and further to N_2 and O_2 at larger doses; N_2O was also produced in the NO_2 - N_2 system as in Fig. 8. Curves in Figs. 7 and 8 are calculated ones by computer simulation as described later.

G-values at low doses in the systems containing 500 ppm of NO or NO_2 at 100°C were as follows :

NO- N_2 ...	$G(-\text{NO})=4.0$;	$G(\text{NO}_2)=0.6$;	$G(\text{N}_2\text{O})\doteq 0.05$
NO-He...	4.4	1.1	
NO-Ar...	1.2	0.2	
NO_2 - N_2 ...	$G(-\text{NO}_2)=2.9$;	$G(\text{NO})=3.0$;	$G(\text{N}_2\text{O})=0.9$
NO_2 -He...	10.4	10.1	
NO_2 -Ar...	5.9	5.8	

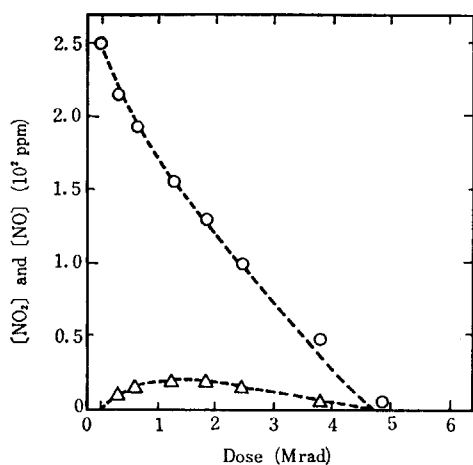


Fig. 7 NO_2 formed as function of dose in NO- N_2 mixture.

The marks and the lines represent the experimental and calculated results respectively

Δ : NO_2 concentration, \circ : NO concentration
 NO initial concentration : 250 ppm

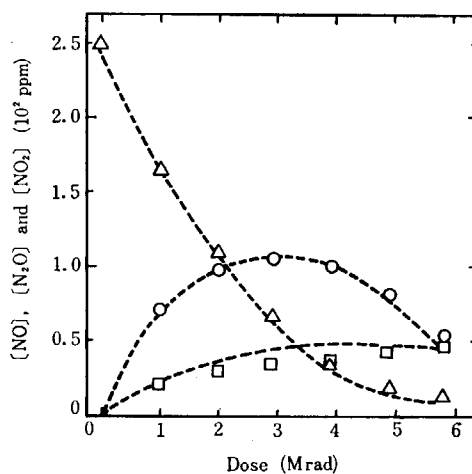


Fig. 8 NO and N_2O formed as function of dose in NO_2 - N_2 mixture.

The marks and the lines represent the experimental and calculated results respectively

\circ : NO concentration, \square : N_2O concentration
 Δ : NO_2 concentration
 NO_2 initial concentration : 250 ppm

3.2.2 Oxidation of NO and reduction of NO₂ in dry N₂-O₂ mixtures¹¹⁾

When a few percent of O₂ was present, the decomposition of NO_x was markedly suppressed and oxidation-reduction took place between NO and NO₂. Fig. 9 shows concentrations of NO, NO₂ and NO_x as functions of dose in the dry mixtures of various concentrations of NO, 3% O₂, and N₂. NO was converted in principle to NO₂ to certain extent and reached to a kinetic radiation-chemical equilibrium between NO and NO₂ where the oxidation rate of NO was balanced with the reduction rate of NO₂, although the total concentration [NO_x] gradually decreased at high concentrations and increased at low concentrations.

The relations between [NO] and [NO₂] for the mixtures shown in Fig. 9 are replotted in Fig. 10 (loci with open circles). The locus of the composition of each mixture approaches to a straight line shown in Fig. 10 with increasing dose. The analogous loci of NO-NO₂ compositions of irradiated dry N₂-O₂-NO₂ systems are also shown in Fig. 10. All the loci approach to the same straight line which gives the relation between [NO] and [NO₂] at the equilibrium :

$$[\text{NO}]/[\text{NO}_2]^2 = 0.027 \text{ ppm}^{-1}$$

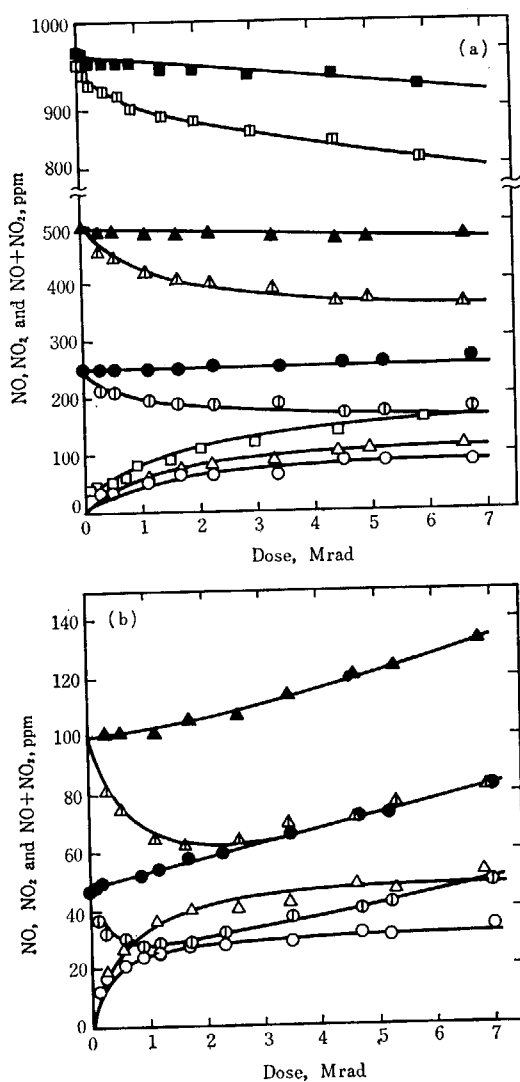


Fig. 9 Effect of dose on the concentrations of NO, NO₂ and the total in the irradiation of NO in nitrogen containing 3% oxygen.

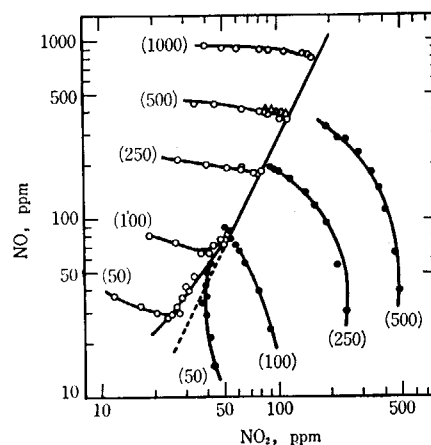


Fig. 10 Relationship between the concentrations of NO and NO₂ in the irradiation of NO or NO₂ in the mixture of nitrogen and oxygen. Oxygen concentration, 3%; number in parentheses indicates the initial concentration of NO or NO₂. ○, Irradiation of NO; ●, irradiation of NO₂; △, irradiation of the mixture of NO and NO₂.

NO initial concn. (ppm)	NO	NO ₂	NO+NO ₂
(a) 250	○	○	●
500	△	△	▲
1000	□	□	■
(b) 50	○	○	●
100	△	△	▲

3.2.3 Effect of moisture¹⁴⁾

In the presence of moisture NO decreased nearly exponentially with increasing dose. NO is converted to NO₂ at first and then to HNO₃. A typical example is shown in Fig. 11. Fig. 12 shows the NO decay curves in N₂-O₂-NO mixtures with various concentrations of H₂O. The oxidation is accelerated by increasing [H₂O]. G(-NO) at low dose was obtained from the slope *k*, initial concentration [NO]₀, and mean molecular weight of the mixture \bar{M} , as follows:

$$\ln [\text{NO}]/[\text{NO}]_0 = -k \cdot D$$

$$G(-\text{NO}) = 0.965 k [\text{NO}]_0 / \bar{M}$$

The *k* obtained was inversely proportional to [NO]₀ giving a constant value of G(-NO):

$$G(-\text{NO}) = 7.5 \text{ (at 8.4\% H}_2\text{O, 12\% O}_2 \text{ and 120}^\circ\text{C)}$$

G(-NO) as functions of [O₂] and [H₂O] is shown in Fig. 13.

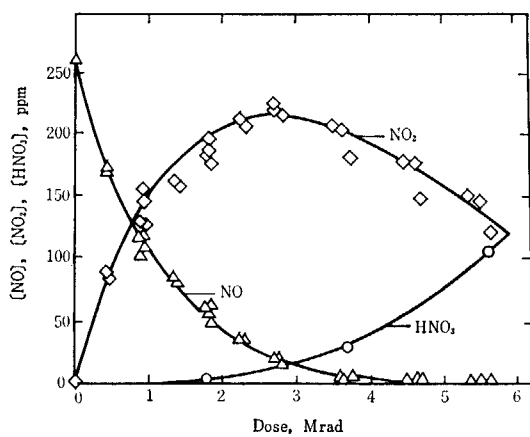


Fig. 11 Irradiation of NO in the moist mixture. NO (250 ppm)-H₂O (8%)-O₂ (12%)-N₂ (80%), 120°C

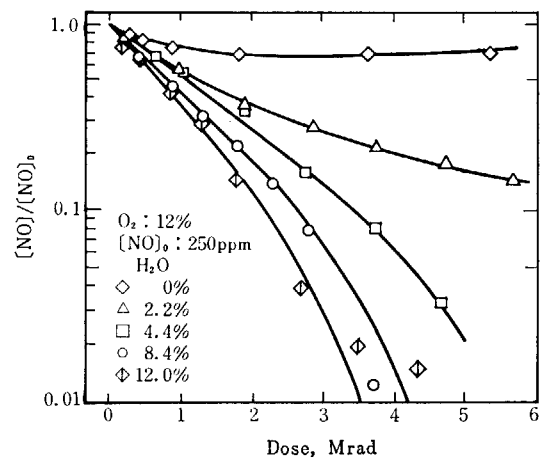


Fig. 12 Logarithmic plot of NO decay

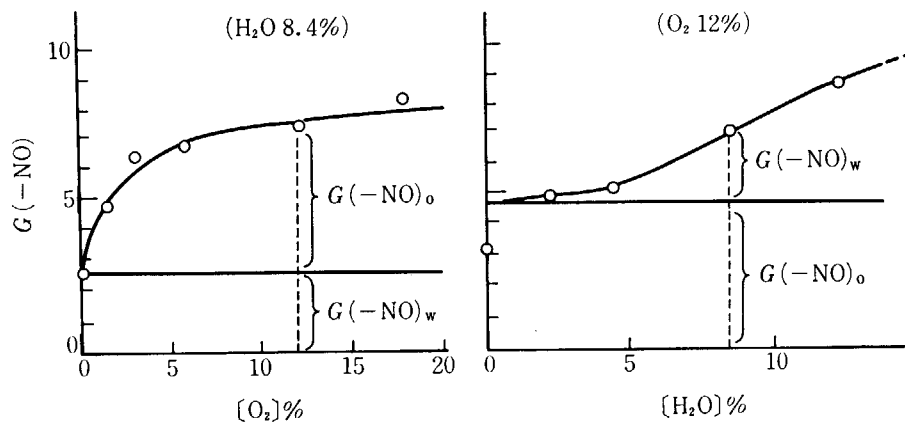
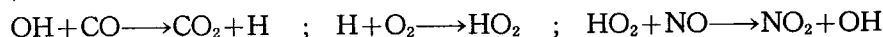


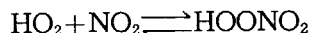
Fig. 13 Effect of [O₂] and [H₂O] on G(-NO)

3.2.4 Effect of CO¹⁶⁾

Carbon monoxide showed characteristic effect on the oxidation of NO_x in the moist mixtures of N₂ and O₂ under the irradiation. By the addition of 1% of CO, the rate of oxidation of NO to NO₂ was nearly doubled, and oxidation of NO₂ to HNO₃ was almost completely suppressed (Figs. 14 and 15). This may be due to the chain reaction as follows:



HO₂ does not react with NO₂ to give any final product:



When CO was added to NO₂-H₂O-O₂-N₂ system, a typical scavenging curve was obtained as shown in Figs. 16 and 17. From the plot of Fig. 17, a value of G(OH) and the ratio of rate constants $k(\text{OH} + \text{NO}_2)/k(\text{OH} + \text{CO})$ was obtained as follows:

$$\left\{ \frac{d[\text{NO}_2]}{dD} \right\}_{\text{OH}}^{-1} = \frac{1}{G(\text{OH})} \left\{ 1 + \frac{k(\text{OH} + \text{CO})[\text{CO}]}{k(\text{OH} + \text{NO}_2)[\text{NO}_2]} \right\}$$

$$G(\text{OH}) = 3.2 \quad ; \quad k(\text{OH} + \text{NO}_2)/k(\text{OH} + \text{CO}) = 30$$

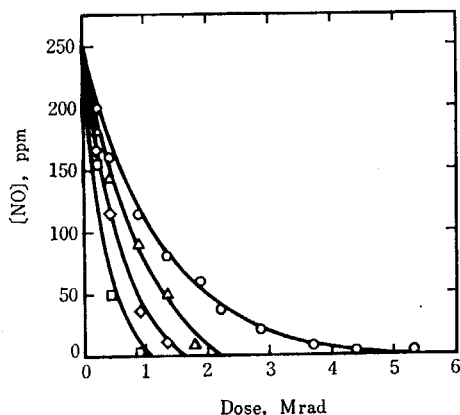


Fig. 14 NO concentrations as a function of dose in the mixture of NO, CO, H₂O, O₂ and N₂ at various CO concentrations. Initial concentrations: CO (○, 0% ; △, 0.29% ; ◇, 0.59% ; □, 1.17%). NO (250 ppm), H₂O (8.0%), O₂ (12.0%) and N₂ (78.8-80%). Irradiation temperature: 120°C.

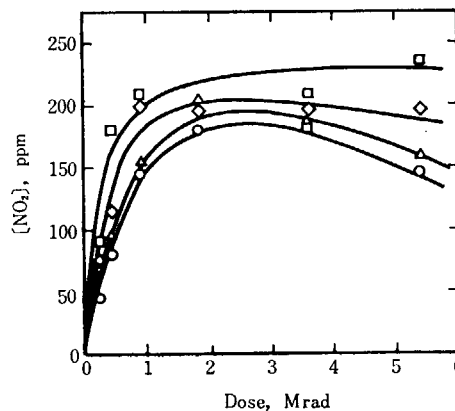


Fig. 15 NO₂ concentration as a function of dose in the mixture of NO, CO, H₂O, O₂ and N₂ at various CO concentrations. Initial concentrations: CO (○, 0% ; △, 0.29% ; ◇, 0.59% ; □, 1.17%), NO (250 ppm), H₂O (8.0%), O₂ (12.0%) and N₂ (78.8-80%). Irradiation temperature: 120°C.

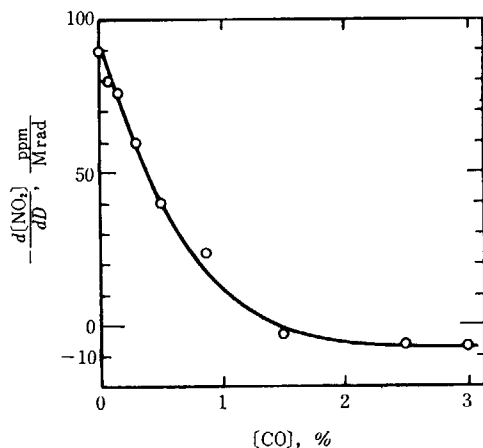


Fig. 16 Initial rate of the NO₂ removal as a function of CO concentration in the mixture of NO₂, CO, H₂O, O₂ and N₂. Initial concentrations: NO₂ (250 ppm), CO (0-3.1%), H₂O (8.4%), O₂ (12.0%) and N₂ (76.5-79.6%). Irradiation temperature: 120°C.

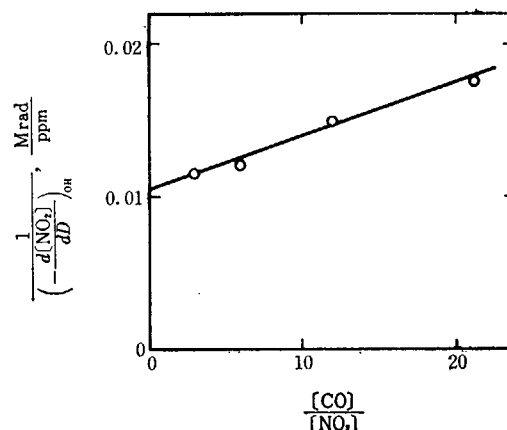


Fig. 17 Plots of reciprocal $(-d[\text{NO}_2]/dD)_{\text{OH}}$ against $[\text{CO}][\text{NO}_2]^{-1}$.

3.2.5 Effects of SO₂ and temperature¹⁴⁾

The dependences of $G(-NO)_0$ on $[SO_2]_0$ and temperature are shown in Figs. 18 and 19, respectively. $G(-NO)_0$ values were obtained from the slope of logarithmic decay curves as in the section 2.3.4.

3.2.6 Effect of ammonia¹⁵⁾

The rate of NO removal was accelerated by adding small concentration of NH₃ in the moist mixture as shown in Fig. 20, which also shows that the rate of NO₂ formation was suppressed. The effect of NH₃ on the product formation is shown in Fig. 21. Accumulation of HNO₃ is retarded considerably, though N₂O formation rate is nearly doubled.

The formation of solid NH₄NO₃ was detected but the amount was small above 70°C, suggesting the solid formation rate is relatively slow in the experimental condition.

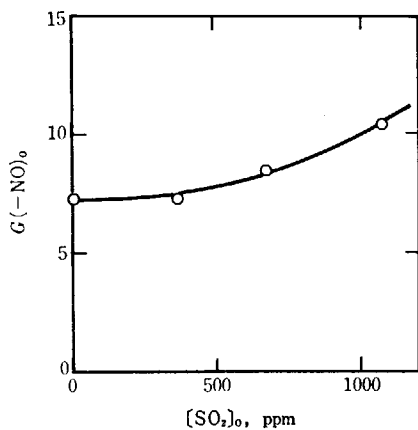


Fig. 18 $G(-NO)_0$ as function of $[SO_2]_0$. NO(250 ppm)-H₂O (8%)-O₂(12%)-N₂. 120°C.

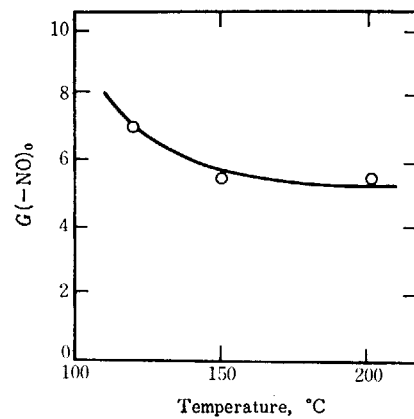


Fig. 19 $G(-NO)_0$ as function of temperature. NO(250 ppm)-H₂O(8%)-O₂(12%)-N₂.

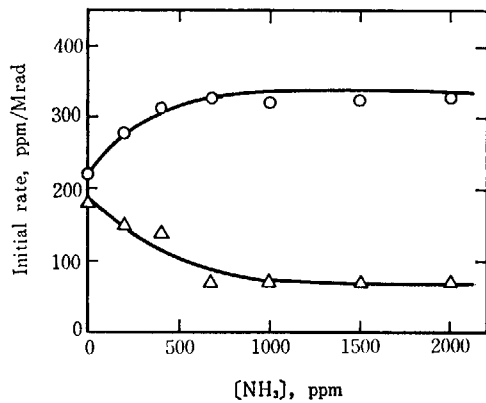


Fig. 20 Initial rates of NO removal and NO₂ formation as a function of NH₃ concentration. ○: initial rate of NO removal, △: initial rate of NO₂ formation. NO (250 ppm), NH₃ (0-2000 ppm), H₂O (8.0%), O₂ (11.6%) and N₂ (80.2%). Irradiation temperature: 120°C.

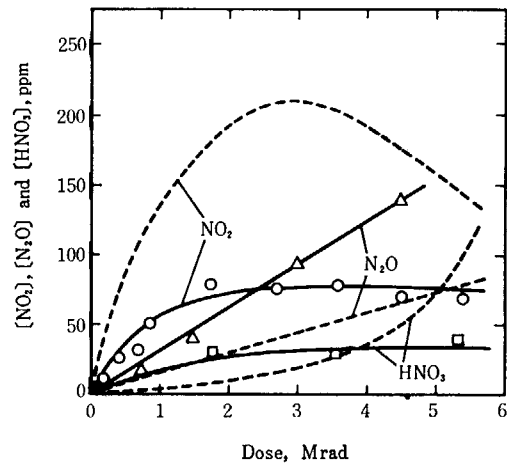
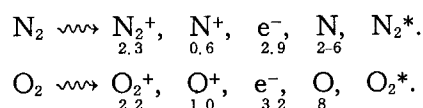


Fig. 21 NO₂, HNO₃ and N₂O concentrations as a function of dose in the mixture with and without NH₃. ---: mixture without NH₃; NO (250 ppm), N₂O (8.0%), O₂ (11.6%) and N₂ (80.4%). —: mixture with NH₃; NO (250 ppm), NH₃ (1500 ppm), H₂O (8.0%), O₂ (12.0%) and N₂ (79.8%). Irradiation temperature: 120°C.

4. Discussion

4.1 Primary Species in the Radiolysis of Moist N₂-O₂ Mixtures

The active species which induce SO₂- or NO_x-removing reactions are produced directly or indirectly from the ionization and excitation of the main component of the gaseous mixture, i. e. N₂ and O₂.



G-values of primary active species in pure N₂ or O₂ are shown above. There are discrepancies in the reported values of G(N) in N₂.

G(N) was estimated by the computer simulation of the NO- and NO₂-decay curves in the NO(500 ppm)-N₂ and NO₂(250 ppm)-N₂ mixtures at 100°C. In Fig. 22, the calculated results obtained by using values of 1.5, 2.0 and 2.5 as G(N) are shown by dotted, solid and dashed lines respectively as a function of dose. The experimental results were in good agreement with the calculated results obtained by using 2.0 as G(N). This is in accordance with the lower values in the literature. The reaction model employed in this simulation is shown in TABLE 1, and results for the production of NO₂ in NO-N₂ and of NO and N₂O in NO₂-N₂ mixtures were shown in Figs. 7 and 8 where G(N)=2.0 was assumed.

In the presence of moisture a series of ion-molecule reactions are known to result into the

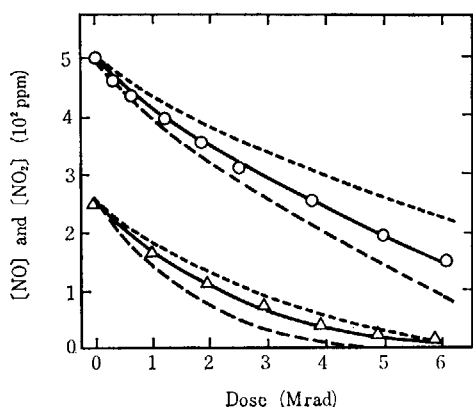


Fig. 22 NO and NO₂ concentrations as function of dose in NO-N₂ and NO₂-N₂ mixtures

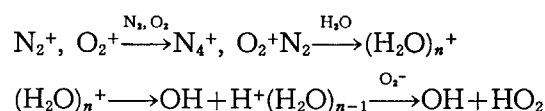
The circles and the triangles represent the experimental results obtained in the NO (500 ppm)-N₂ and NO₂(250 ppm)-N₂ mixtures respectively. The dotted, solid and dashed lines represent the calculated results obtained by using 1.5, 2.0 and 2.5 as G(N) respectively.

TABLE 1 Ion and radical reactions in irradiated NO-N₂ and NO₂-N₂ mixtures

No.	Reaction	Rate constant* (cm ³ ·molecule ⁻¹ ·s ⁻¹)
Radiolysis of N ₂		
(1)	N ₂ → N ₂ ⁺ , e, N	
Ion reactions		
(2)	N ₂ ⁺ + NO → NO ⁺ + N ₂	5 × 10 ⁻¹⁰
(3)	N ₂ ⁺ + e → 2N	1 × 10 ⁻⁷
(4 a)	NO ⁺ + e → N + O	4 × 10 ⁻⁷
(4 b)	NO ⁺ + e → NO + hν	1 × 10 ⁻¹²
(5)	NO ₂ + e + N ₂ → NO ₂ ⁻ + N ₂	8 × 10 ^{-28a)}
(6)	NO ⁺ + NO ₂ ⁻ → NO + NO ₂	3 × 10 ⁻⁷
Radical reactions		
(7)	N + NO → N ₂ + O	2.2 × 10 ⁻¹¹
(8 a)	N + NO ₂ → 2NO	5.9 × 10 ⁻¹²
(8 b)	N + NO ₂ → N ₂ O + O	7.7 × 10 ⁻¹²
(8 c)	N + NO ₂ → N ₂ + O ₂	1.8 × 10 ⁻¹²
(8 d)	N + NO ₂ → N ₂ + 2O	2.3 × 10 ⁻¹²
(9)	N + N ₂ O → NO + N ₂	1 × 10 ⁻¹²
(10)	N + N + N ₂ → 2N ₂	3.8 × 10 ^{-33a)}
(11)	O + NO + N ₂ → NO ₂ + N ₂	5.4 × 10 ^{-32a)} **
(12)	O + NO ₂ → NO + O ₂	7.7 × 10 ^{-12**}
(13)	O + O + N ₂ → O ₂ + N ₂	1.6 × 10 ^{-33a)} **

* Rate constant at room temperature, ** Rate constant at 100°C
a) Three body rate constant, units cm⁶·molecule⁻²·s⁻¹.

formation of radicals as follows :

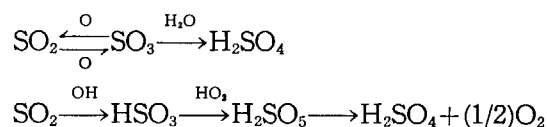


O_2^- is produced by electron capture of O_2 .

O atom and OH radical are powerful oxidizing agents and HO_2 may oxidize NO and some oxidation products of SO_2 and NO_x . Some precursors of these radicals, i. e. cations, electron and excited molecules, may be scavenged by NO_x or SO_2 (see below).

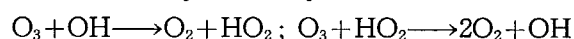
4.2 Mechanism of SO_2 Oxidation

SO_2 is oxidized presumably by O, OH and HO_2 as follows :



According to this mechanism and the scheme of OH-forming ion-molecule reactions shown in the preceding section, the contribution of OH to $G(-\text{SO}_2)$ should correspond to the G-value of ionization, i. e. 2.9-3.0 in the mixture. This is consistent with the fact that the decrease in $G(-\text{SO}_2)$ was constantly 2.9 when OH was scavenged by high concentration of CO in the mixtures containing various concentrations of O_2 (Fig. 5). The abrupt increase in $G(-\text{SO}_2)$ by the addition of slight moisture in the dry system reflects the production of OH and HO_2 as well as the removal of SO_3 producing H_2SO_4 and preventing the back reaction ($\text{SO}_3 + \text{O} \longrightarrow \text{SO}_3 + \text{O}_2$).

The difference between curves b) and c) in Fig. 5 can be regarded as the contribution of O atom in $G(-\text{SO}_2)$. This contribution decreases with increasing O_2 concentration presumably because O reacts with O_2 to form O_3 , which does not react with SO_2 rapidly but decomposes on the surface of the vessel or by the catalytic reaction of OH and HO_2 :



The "initial" G-value of O atom is obtained as $G(\text{O})=4.2$ by extrapolating the curve b) to low $[\text{O}_2]$ side. This means the energy transfer from N_2 to O_2 is important to the O atom production (see below).

The active species contributing to the remaining part of $G(-\text{SO}_2)$, $G=0.9$, are not known, though N^+ or $\text{N}_2^*(B^3\Pi_g)$ might be possible.

4.3 Mechanism of NO_x Reactions

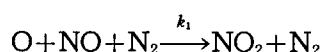
4.3.1 Decomposition in N_2 and in rare gases

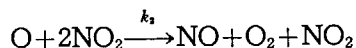
The reaction model is already shown in Table 1. It is shown by the computer simulation that the ion reactions are not contribute to the final products because reactions (2), (5) and (6) are more important than (3) and (4) in the experimental conditions.

The differences of the G-values in N_2 , He, and Ar can be attributed to the differences in the probabilities of dissociative charge transfer and dissociative excitation transfer reactions.

4.3.2 Reactions in dry N_2 - O_2 Mixtures

The "radiation-chemical equilibrium" between NO and NO_2 can be expressed by following reactions :



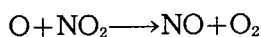


$$[\text{NO}]/[\text{NO}_2]^2 = k_2/k_1[\text{N}_2] = 0.027 \text{ ppm}^{-1} = 5.8 \times 10^{-14} \text{ cm}^3/\text{molecule}$$

$$k_2/k_1 = 2.7 \times 10^4 \quad ([\text{N}_2] = 2.0 \times 10^{19} \text{ molecule/cm}^3)$$

Then k_2 can be estimated as $1.4 \times 10^{-27} \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}$ from a reported value of k_1 .

At the low $[\text{NO}_2]$ side, however, the well known bimolecular reaction should be important :



The slope of the line of equilibrium in Fig. 10 tends in fact to decrease at the low $[\text{NO}_2]$ side.

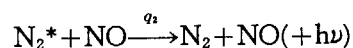
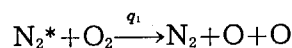
4.3.3 Oxidation of NO in the moist mixtures

As shown in Fig. 13, $G(-\text{NO})$ in the moist mixtures of NO, O₂ and NO can be divided into two parts, i.e. $G(-\text{NO})_o$ which depends on $[\text{O}_2]$ and $G(-\text{NO})_w$ which depends on $[\text{H}_2\text{O}]$. The reciprocals of each part increase linearly with $[\text{NO}]/[\text{O}_2]$ and with $[\text{H}_2\text{O}]^{-2}$, respectively, giving extrapolated values :

$$G(-\text{NO})_o \text{ (at high } [\text{O}_2]) = 5.5$$

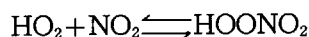
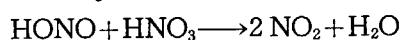
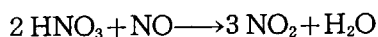
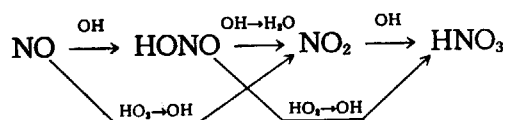
$$G(-\text{NO})_w \text{ (at high } [\text{H}_2\text{O}]) \doteq 4.6$$

$G(-\text{NO})_o$ can be attributed to the reaction of O atom as in the case of the dry systems. The reason for steep diminution at low $[\text{O}_2]$ side is presumed to the quenching of the precursor of O atom by NO. The precursor of O can be assumed to be excited N₂ molecules.



From the slope of the reciprocal plot of $G(-\text{NO})_o$ with $[\text{NO}]/[\text{O}_2]$, the ratio of quenching rate constants q_2/q_1 was estimated as 40, which is in agreement with the values for N₂(A³Σ_u⁺) reported recently by the pulse radiolysis work²⁰⁾.

$G(-\text{NO})_w$ is attributed to the reactions of OH and HO₂ produced cations as mentioned in section 4.1. They oxidize NO and NO₂ by the following reactions :



This mechanism is consistent with the effect of CO on the oxidation of NO and NO₂ in the moist N₂-O₂ system (see section 3.2.4). The reason for the diminution at the low $[\text{H}_2\text{O}]$ side is probably that the cationic precursors of OH and HO₂ are scavenged by NO and stabilized by non-dissociative charge neutralizations especially when the water concentration is low. Reaction pass ways are shown in Fig. 23 together with reported rate constants and rate expressions.

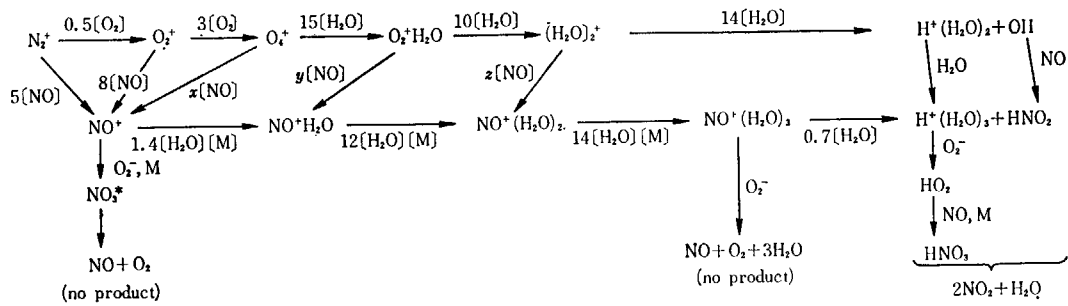
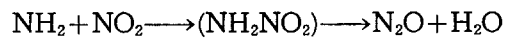
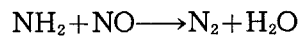
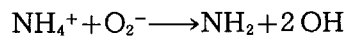
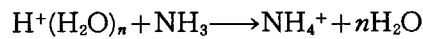
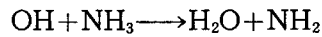


Fig. 23 Reaction pathways of cations in the presence of moisture and NO. Known rate constants are shown in $10^{-10} \text{ cm}^3/\text{s}$ or in $10^{-28} \text{ cm}^6/\text{s}$.

4.3.4 Reaction of NH_3

Besides oxidation mechanisms discussed above, NO and NO_2 are reduced in the presence of NH_3 by the following reactions :



The observed enhancement in NO removal and in N_2O formation as well as the suppression of NO_2^- and HNO_3 -formations are consistent with this reduction mechanism which works usefully together with the oxidation reactions in the viewpoint of NO_x -removing.

5. Conclusion

In connection with the initial aims of this study, following conclusions are deduced :

- (1) The electron-beam process is essentially effective because the radiolysis of SO_2 and NO_x proceeds by the mechanism of "indirect effect of radiation" in which the energies absorbed by the main component of the exhaust gas, N_2 and O_2 , are transferred and utilized effectively to the SO_2 - and NO_x -removing reactions.
- (2) The addition of a small amount of ammonia is useful to reduce the radiation dose needed to remove SO_2 and NO_x . The addition of ammonia is also effective in solidifying and hence facilitating to collect the reaction product. Although the production rate of gaseous N_2O is somewhat enhanced by the addition of ammonia, the pollution problem does not likely to occur because the concentration of N_2O in the natural atmosphere is relatively high (about 0.5 ppm) and toxicity of N_2O is fairly low.
- (3) Both SO_2 - and NO_x -removing reactions are attributed to the action of O atoms and OH- and HO_2 -radicals produced by the radiolysis of the moist $\text{N}_2\text{-O}_2$ system. The reaction mechanism which is consistent with the experimental results is deduced.
- (4) The radiation-chemical yields of the active species produced by the initial stages of radiolysis of the moist $\text{N}_2\text{-O}_2$ system is deduced at various reaction conditions and the precursors of the radicals are suggested.

For the realization of practical use of the radiation treatment process of exhaust gases, there remains three important problems :

- (1) The development of the electron accelerator of large power to apply this process to large facilities like a scintering furnace or an electric power station. Recent progress of the accelerator technology gives bright prospects to the realization with a good economic aspects.
- (2) The solution of the product wasting problem. The utilization of produced ammonium sulfate/nitrate as fertilizer may be possible, though some purification process have to be developed to remove heavy metals from the product.
- (3) Reduction of the necessary dose of radiation is desirable especially for the application to the fumes from electric power stations where coal or heavy oil is used, because these fuels contain high levels of sulfur- and nitrogen-compounds which causes higher concentrations of SO_2 and NO_x and hence higher radiation dose is necessary.

A study on the line of the third problem is now in progress with the utilization of powdery additives. The progress in the radiation chemistry of moist $\text{N}_2\text{-O}_2$ system may also be expected by the stimulation of this work.

Acknowledgement

The authors wish to thank Drs. S. Machi, W. Kawakami and M. Takehisa of Takasaki Radiation Chemistry Research Establishment for their helpful discussions and comments during the course of this work.

References

- 1) Kawamura K. et al. : "Radiation for a clean environment" IAEA, 621 (1975).
- 2) Washino M. et al. : *ibid.*, 633 (1975).
- 3) Machi S. et al. : *Radiat. Phys. Chem.*, **9**, 371 (1977).
- 4) Kawamura K. et al. : *J. At. Energy Soc. Japan*, **20**, 359 (1978).
- 5) Washino M. et al. : Japan. Pat. Kōkai 50-57064 (1975).
- 6) Masuda S. et al. : "Special Project Research on Detection and Control of Environmental Pollution" Vol. 2 (1979) pp. 249.
- 7) Wright J. et al. : Proc. 1st Intern. Conf. Peaceful Uses Atomic Energy, Geneva, 1955, **7**, 560 (1956).
- 8) Veselovsky V. I. : *ibid.*, 599 (1956).
- 9) Hardeck P. and Dondes S. : *Nucleonics*, **14**, (7) 22 (1956).
- 10) Jones A. R. : *Radiat. Res.*, **10**, 655 (1959).
- 11) Tokunaga O., Nishimura K., Machi S. and Washino M. : *Int. J. Appl. Radiat. Isotopes*, **29**, 81 (1978).
- 12) Tokunaga O., Nishimura K. and Washino M. : *ibid.*, **28**, 87 (1978).
- 13) Tokunaga O., Nishimura K., Suzuki N. and Washino M. : *J. Chem. Soc. Japan, Chem & Ind. Chem.*, 1977, 1582.
- 14) Tokunaga O., Nishimura K., Suzuki N. and Washino M. : *Radiat. Phys. Chem.*, **11**, 117 (1978).
- 15) Tokunaga O. et al. : *ibid.*, **11**, 299 (1978).
- 16) Tokunaga O. et al. : *Int. J. Appl. Radiat. Isotopes*, **30**, 19 (1979).
- 17) Suzuki N. et al. : *J. Nucl. Sci. Technol.*, **15**, 597 (1978).
- 18) Suzuki N. et al. : *ibid.*, **16**, 278 (1979).
- 19) Nishimura K. et al. : *ibid.*, 596 (1979).
- 20) Dreyer J. W. et al. : *J. Chem. Phys.*, **61**, 3161 (1974).