—Communication—

Kinetics of the Decomposition of Nitrous Oxide in an Ambient Pressure Plasma

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1 INTRODUCTION

Much attention has been paid to the chemistry of nitrous oxide (N_2O) in the atmosphere, since it contributes to catalytic destruction of stratospheric ozone and is also a greenhouse gas component. Lately, as one of anthropogenic sources of N_2O , chemical industries, especially ones using massive nitric acid as an oxidant were designated by Thiemens and Trogler.¹⁾ In practice, they first demonstrated the significant occurrence of N_2O as a by-product in the manufacture of nylon, specifically in the preparation of adipic acid. Generally, the waste gas from such chemical processes contains N_2O in abundance and, therefore, it should be considered to reuse N_2O as a chemical resource by converting it to more versatile species, e.g., NO_x .

From the above-mentioned viewpoint, we have undertaken to subject N_2O to gaseous plasmas, because the fission of N-N bond would be crucial for the formation of NO_x and require a quite energetic means. To our knowledge, there have been few works on the application of plasmas to the transformation of N_2O in an aspect of waste recycling. In the present paper, are described the preliminary results relevant to the kinetics of the decomposition of N_2O in an ambient pressure plasma.

2 EXPERIMENTAL

The apparatus used for the plasma reaction is illustrated in Fig. 1. The reactor was a Pyrex tube of 12 mm i.d. and ca. 200 mm in length. The pair of electrodes were copper rods (2 mm o.d.), the tips of which were gently pointed. The flow rate of N_2O was

Fig. 1 Schematic drawing of apparatus, a: reactor; b: electrode; c: neon transformer; d: electronic flowmeter; e: GC; f: NO_x analyzer; g: mass flow controller; h: gas sampler; i: three-way valve.

adjusted by a thermal mass flow controller (STEC SEC-400) and introduced into the reactor at ambient pressure. On occasion, helium was used as a diluting gas. A spindle-shaped discharge plasma was sustained in the space between electrodes as soon as a high AC voltage from a neon transformer was applied. The current was 20 mA irrespective of the reaction conditions, while the voltage was varied within 700–1300 V. The outlet gas, the flow rate of which was measured by an electronic flowmeter (J & W Scientific ADM1000), was analyzed to determine the composition by a gas chromatograph (SHIMADZU GC-8A/TCD/Molecular sieve 5A). Additionally, a NO_x analyzer (SHIMADZU NOA-7000) was employed for the precise determination of each of NO and NO_2 .

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The experimental variables were the distance between electrodes (D) and the feed rate of N_2O (F). The residence time (t) of the gas within the discharge zone was expediently defined by $t = AD/F$, where A is the internal cross section of the reactor tube.

3 RESULTS AND DISCUSSION

The decomposition of N_2O was readily carried out in an atmospheric pressure plasma to give N_2 and O_2 as major products. Both NO and NO_2 were also formed in less amounts. The stoichiometric balance was complete as to N , although that as to O was somewhat unsatisfactory. Figure 2 displays the effects of F on the output (Y) of each product at $D = 5$ mm. As F was increased, Y was proportionally enhanced. On the other hand, the relative ratio of each component was substantially unaffected. A similar dependence of Y on F was observed when D was varied within the range of 3–7 mm. The influence of D on Y at $F = 1.64$ mmol min⁻¹ are exhibited in Fig. 3. Both Y of N_2 and O_2 were augmented with an increase in D . In contrast, either Y of NO or NO_2 descended slowly at larger D . These phenomena imply that the formation of NO_x might get comparable to that of N_2 if D could be lessened without quenching the N_2O plasma.

In order to discuss the kinetics of N_2O decomposition, the effects of reaction variables on the disappearance rate of N_2O were investigated. As seen in Fig. 4, the N_2O conversion (X) gradually decreased with an increase in F and the drop was pronounced at

Fig.2 Effects of the feed rate of N_2O (F) on the output of products (Y), $D = 5$ mm, $\square$: N_2 ; $\diamond$: O_2 ; $\circ$: NO_2 ; $\triangle$: NO .

Fig.3 Effects of the distance between electrodes (D) on the output of products (Y), $F = 1.64$ mmol min⁻¹, $\square$: N_2 ; $\diamond$: O_2 ; $\circ$: NO_2 ; $\triangle$: NO .

smaller D . These results can be consistently understood by taking account of the residence time (t) of the reactant in the plasma zone. That is, the longer t should result in the higher X and vice versa. When N_2O was supplied into the reactor together with He , X was independent of N_2O content in the mixed feed at constant total flow rate. This fact strongly suggests that the decomposition of N_2O would obey the first-order rate law. Thus, the data in Fig. 4, except for

Fig.4 Effects of the feed rate of N_2O (F) on the conversion (X), D : 3 mm ($\square$); 5 mm ($\circ$); 7 mm ($\diamond$).

Fig.5 Relationship between the residence time(t) and the conversion(X).

ones of considerably high conversion, were plotted against t according to the integral rate equation for the first-order reaction. In Fig. 5, one can find an approximately linear relationship, which may be interpreted to support the foregoing assumption. A

similar kinetical conclusion has been derived in the reactions of a variety of organic and organometallic compounds in high or low pressure plasmas, where the electron bombardment onto the reactant was supposed to be a rate-determining step.²⁻⁴⁾ The more energetic electron impact could bring about the more indiscriminate bond breaking and consequently allow the formation of product which might be unlikely in terms of thermodynamics.

Further attempts to elucidate the dynamics and mechanism of the decomposition of N_2O under plasma condition are in progress.

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