# Mechanism for $N_2O$ Formation from NO at Ambient Temperature

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*$N_2O$ was reported to form in sample containers of flue gases containing NO and $SO_2$. This could have significant implications for the evaluation of $N_2O$ buildup in the atmosphere. Existing models are based either on liquid-phase reactions, which cannot account for $N_2O$ formation at low humidity, or on termolecular reactions, which are not likely to occur at low concentrations. In this work, we propose mechanisms for $N_2O$ formation based on gas-phase reactions, which address the effect of $SO_2$, $O_2$, and moisture. Analytical expressions of the formation rate were derived and compared to reported rates, and rate constants were estimated for limiting cases. The current analyses suggest that $N_2O_2$ could be an important precursor for $N_2O$ formation from NO, and the mechanism may be important for $N_2O$ formation in power-plant plumes.*

## Introduction

$N_2O$ is a powerful greenhouse gas, and can also cause depletion of stratospheric ozone. The concentration of $N_2O$ in the atmosphere has been increasing at a rate of about 0.2% per year. Several past studies concluded that anthropogenic sources, including emissions from combustion systems, might be large enough to account for the observed increase of atmospheric $N_2O$ (Weiss, 1981; Lyon et al., 1989; Muzio and Kramlich, 1988).

Muzio and Kramlich (1988) investigated the effects of fuel nitrogen and sulfur on $N_2O$ formation. They showed unequivocally that $N_2O$ formed in flue-gas sample vessels containing NO, $SO_2$, $O_2$, and $H_2O$. This finding had significant implications, as previous projections of the importance of fossil-fuel combustion on atmospheric $N_2O$ buildup were largely based on batch measurements of flue gases stored in containers. Since $N_2O$ forms in such sample containers, the formation attributed to combustion could be greatly overestimated (Lyon et al., 1989; Muzio and Kramlich, 1988). However, this finding also suggests that $N_2O$ could form in postcombustion flue gases, since the components just mentioned coexist in power-plant plumes, and hence significant amount of $N_2O$ might be expected to form in such plumes (Khalil and Rasmussen, 1992; Linak et al., 1990).

Lyon and Cole (1989) suggested that the formation of $N_2O$ requires liquid-phase reactions, and this view was also supported by Muzio et al. (1989). Pires and Rossi modified Lyon and Cole's model, but maintained the necessity of liquid-phase reaction (Pires and Rossi, 1997). For cases without the presence of a liquid phase, it was suggested that the reaction would take place in thin water film formed on polar surfaces. However, such models do not predict any $N_2O$ formation in the absence of water, which was observed in several studies (Muzio and Kramlich, 1988; de Soete, 1988a; Preto et al., 1999), and might serve as a stratospheric source of $N_2O$ (de Soete, 1988b). Moreover, the hypothesis that liquid water must be present is not likely to explain $N_2O$ formation under low-humidity conditions, since the amount of liquid under such conditions is probably too small for significant liquid-phase reactions.

In previous experiments at the CANMET Energy Technology Centre (CETC) gas mixtures of $N_2$, $O_2$, NO, and $SO_2$ were used to simulate power-plant plumes, while varying the moisture content. Experimental details are given elsewhere (Preto et al., 1999). It was found that $N_2O$ formed in effectively dry mixtures with low NO and $SO_2$ concentrations. With 5% relative humidity (RH) the reaction rate tripled, whereas above this RH level the humidity effect was not significant (Figure 1). These results strongly suggest $N_2O$ formation from gas-phase reactions.

$N_2O$ is known to form from the disproportionation reaction of NO (Greenwood and Earnshaw, 1989; Martin et al., 1981)

$$3NO = N_2O + NO_2. \qquad (1)$$

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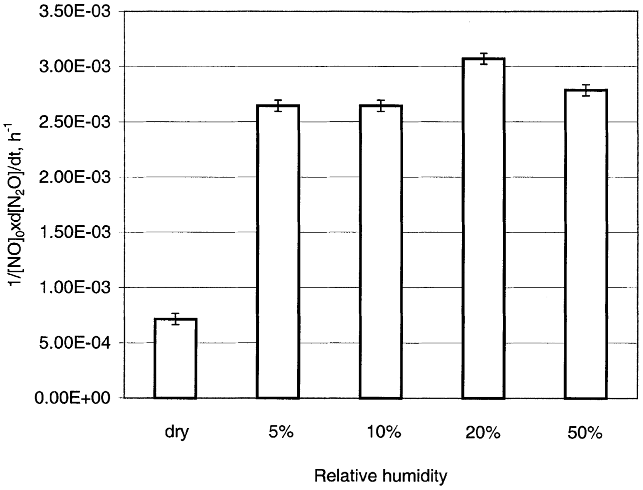


**Figure 1. Dependence of formation rate of $N_2O$ (normalized with initial NO concentration) on relative humidity.**

Experimental conditions: $[NO]_0 = [SO_2]_0 = 50$ ppm; $[O_2]_0 = 10.5\%$; $T = 25°C$. All methods were the same as those reported by Preto et al. (1999).

Muzio and Kramlich (1988) reported that 3 ppm $N_2O$ formed in an "artificial flue gas" containing $N_2$, $O_2$, $CO_2$, and 600 ppm NO in a period of 2 h, which may be attributed to this reaction (see later discussions). However, when $SO_2$ was present, the formation rate was much higher, indicating that a reaction pathway involving $SO_2$ was dominant.

The following mechanism for $N_2O$ formation from dry gas mixtures has been proposed by de Soete (1988a)

$$2NO + SO_2 = N_2O + SO_3 \tag{2}$$

$$NO + SO_3 = NO_2 + SO_2. \tag{3}$$

Reaction 2 (Eq. 2) is third-order, and hence is most likely to be a global reaction rather than a genuine termolecular reaction, especially at low reactant concentrations. This viewpoint is supported by CETC experiments, which showed that $N_2O$ was formed at 10 ppm NO and $SO_2$ concentrations, which seem to be too low for an effective termolecular reaction. Accordingly, Eq. 2 does not give information that can give rise to a rate expression. Moreover, Eq. 2 does not reflect the effect of $O_2$, which was also found to influence $N_2O$ formation. Finally, reaction 3 (Eq. 3) would most likely be overwhelmed by its reverse reaction, because the equilibrium constant is small ($5.8 \times 10^{-7}$ at 25°C).

Based on the preceding considerations, we propose an alternative mechanism for $N_2O$ formation via gas-phase reactions, which will account for the observed behavior of both dry-gas and humid-gas cases.

## Mechanisms and Discussions

### *$N_2O$ formation from dry mixtures of NO and $SO_2$*

First, for the dry mixtures of NO and $SO_2$, we considered the following reactions.

$$2NO = N_2O_2 \qquad K_4 = 1.5 \times 10^{-6} \tag{4}$$

$$N_2O_2 + SO_2 = N_2O + SO_3 \qquad K_5 = 2.2 \times 10^{30}, \tag{5}$$

where $K$ denotes the equilibrium constant (in terms of partial pressures) at 25°C, obtained from the thermochemical software package HSC Chemistry. Reaction 4 (Eq. 4), along with the reaction

$$N_2O_2 + O_2 = 2NO_2 \quad K_6 = 1.1 \times 10^{19} \tag{6}$$

was proposed for gas-phase oxidation of NO (Greenwood and Earnshaw, 1989; Atkins, 1998), which is believed to proceed by a termolecular reaction

$$2NO + O_2 = 2NO_2. \tag{7}$$

Reaction 7 (Eq. 7) is also included in the models of Lyon and Cole (1989) and Pires and Rossi (1997), for $N_2O$ formation via heterogeneous reactions. However, given that the reaction rate is known to decrease with increasing temperature, this suggests a complex reaction mechanism. With Eqs. 4 and 6, the observed reaction order and temperature dependence can be explained (Atkins, 1998). This mechanism is important for the present case because the intermediate $N_2O_2$ might be a precursor of $N_2O$ when $SO_2$ is present, and it gives Eq. 2 as an overall reaction.

With a pseudo-steady-state hypothesis for $N_2O_2$ (see the Appendix), the formation rate of $N_2O$ can be derived from Eqs. 4 and 5 as

$$\frac{d[N_2O]}{dt} = \frac{k_4 k_5 [NO]^2 [SO_2]}{k_{-4} + k_5 [SO_2]}. \tag{8}$$

Hence, the formation rate of $N_2O$ is expected to be proportional to the square of the NO concentration. The second-order dependence on NO concentration was observed with the presence of condensed water (Pires and Rossi, 1997), and a global aqueous-phase reaction

$$2NO + SO_2(aq) + H_2O = N_2O + H_2SO_4, \tag{9}$$

was proposed for the $N_2O$ formation. However, it is easy to show that Eq. 9 conforms to the mechanism we have proposed. At low humidity there is no dissolved $SO_2$, and by combining Eqs. 4 and 5 with the reaction

$$SO_3 + H_2O(g) = H_2SO_4, \tag{10}$$

one obtains a global reaction with the same form as Eq. 9. The only difference is that NO is considered to react with gaseous $SO_2$ rather than dissolved $SO_2$. Moreover, when $SO_2$ concentration is low, so that $k_5[N_2O_2][SO_2] \ll k_{-4}[N_2O_2]$ or $k_5[SO_2] \ll k_{-4}$ for Eqs. 4 and 5, from Eq. 8 one gets

$$\frac{d[N_2O]}{dt} \approx K_{4c} k_5 [NO]^2 [SO_2], \tag{11}$$

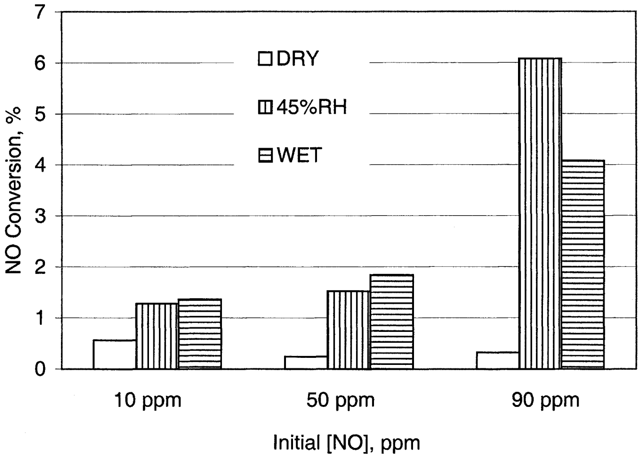


**Figure 2. Effect of relative humidity and initial NO concentration on conversion of NO (median values after 4 h).**

The experiments are described by Preto et al. (1999). In the case of the wet conditions, water was sprayed directly into the reactor.

where $K_{4c} = k_4/k_{-4}$ is the equilibrium constant for Eq. 4 in terms of concentration, and can be calculated from the partial-pressure-based $K_4$. While Eq. 11 is third-order, when $k_5[SO_2] \gg k_{-4}$, Eq. 8 reduces to

$$\frac{d[N_2O]}{dt} \approx k_4[NO]^2. \tag{12}$$

That is, under such conditions the formation rate is independent of $SO_2$ concentration. However, both Eqs. 11 and 12 suggest second-order dependence of the rate on NO concentration.

The rate constant for Eq. 9 was reported to be $1.3\times10^{-7}$ $ppm^{-2}\cdot h^{-1}$ (Pires and Rossi, 1997). Although this constant was measured in the presence of a condensed water phase, and the actual concentrations of NO and $SO_2$ were not given, we can still make use of this value. As noted earlier, once water is present, the actual amount did not affect the formation rate of $N_2O$ (de Soete, 1988a). Furthermore, the formation rate was not enhanced by the presence of condensed water (Figure 2), as was also observed in the CETC study (Preto et al., 1999). One interpretation of this behavior could be that $N_2O$ forms mostly via reactions 4 and 5, regardless of the extent of moisture. The difference between the formation rates in dry gases and wet gases can be related to the effect of oxygen, which will be discussed later. Accordingly, we can estimate the rate constants for Eq. 8 using the reported apparent rate constant. Assuming that Eq. 11 is applicable, we obtain $k_5 = 8.7\times10^4$ $ppm^{-1}\cdot h^{-1}$ or $5.4\times10^{11} cm^3\cdot mol^{-1}\cdot s^{-1}$. Moreover, using Eq. 11 and the reported rate constant, we calculated $N_2O$ formation for dry mixtures of NO and $SO_2$, and compared it with our experimental result. The calculated value is lower by about one third, which suggests that the formation rate in a mixture with condensed water is not higher than in the dry gas, when $O_2$ is not present.

### *Effect of $O_2$ and moisture on $N_2O$ formation*

Next we consider the effect of $O_2$. When $O_2$ concentration is high, we envisage the following pathway for $N_2O$ formation:

$$NO + O_2 = NO_3 \quad K_{13} = 6.9\times10^{-6} \tag{13}$$

$$NO_3 + NO = N_2O_4 \quad K_{14} = 2.4\times10^{18} \tag{14}$$

$$N_2O_4 + SO_2 = N_2O_3 + SO_3 \quad K_{15} = 1.3\times10^5 \tag{15}$$

$$N_2O_3 + SO_2 = N_2O_2 + SO_3 \quad K_{16} = 4.9 \tag{16}$$

$$N_2O_2 + SO_2 = N_2O + SO_3 \quad K_5 = 2.2\times10^{30}. \tag{5}$$

Reaction 13 (Eq. 13) was proposed along with the following reaction,

$$NO_3 + NO = 2NO_2 \quad K_{17} = 3.5\times10^{17}, \tag{17}$$

as a mechanism for Eq. 7 (Greenwood and Earnshaw, 1989; Atkins, 1998). Equation 14 assumes that at least a part of $NO_3$ and NO form the intermediate $N_2O_4$ first, and then dissociate into $NO_2$. Here the intermediate may not be identical to the thermodynamically stable nitrogen tetroxide, which is known to be in equilibrium with $NO_2$ at ambient temperature (Greenwood and Earnshaw, 1989). This intermediate would then be reduced by $SO_2$ to form $N_2O$, via Eqs. 15, 16, and 5. In addition to Eq. 14, the following reaction for $N_2O_4$ formation is possible

$$N_2O_2 + O_2 = N_2O_4 \quad K_{18} = 1.1\times10^{19} \tag{18}$$

However, with this pathway $O_2$ is not expected to enhance the $N_2O$ formation rate, since it reduces the concentration of $N_2O_2$, the proposed precursor of $N_2O$. If the formation of $N_2O_2$ via Eqs. 13 to 16 parallels Eq. 4, $O_2$ would enhance the formation of $N_2O$. However, in dry gases the formation rate may decline quickly as the side product $SO_3$ builds up—nitrogen oxides are well known to oxidize $SO_2$ to $SO_3$ at higher temperature, as for example, in the lead chamber process, which was used for production of sulfuric acid (Angelidis and Kruse, 2001)—and this would lead to an increasing influence of the reverse reactions, according to Eqs. 15 and 16 (particularly Eq. 16). As a result, the unstable $N_2O_3$ and $N_2O_4$ decompose:

$$N_2O_3 = NO + NO_2 \quad K_{19} = 1.9 \tag{19}$$

$$N_2O_4 = 2NO_2 \quad K_{20} = 0.15. \tag{20}$$

This behavior would evidently be unfavorable to $N_2O$ formation. On the other hand, once water is present, be it in the vapor phase or liquid phase, $SO_3$ would be removed via Eq. 10, and the forward reactions given by Eqs. 15 and 16 thus could be enhanced greatly and contribute to $N_2O$ formation. The effect of moisture on $N_2O$ formation can also be explained with this mechanism, where water is taken merely as a sink of $SO_3$. At 25°C, even with 5% RH the concentration

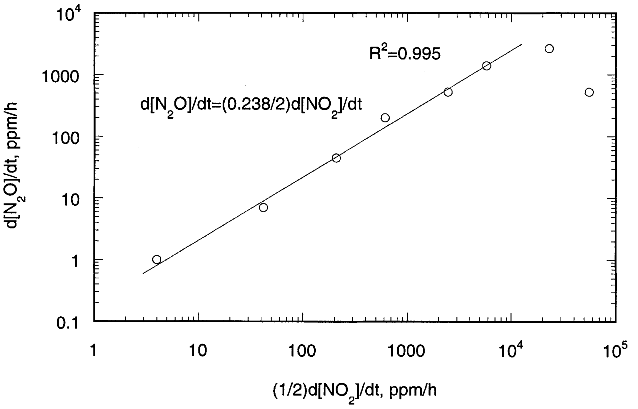


**Figure 3. Correlation of initial $N_2O$ formation rate with NO oxidation rate.**

The $N_2O$ formation rate was reported by Pires and Rossi (1997). The NO oxidation rate ($NO_2$ formation rate) was calculated in terms of Eq. 6, with $k_6 = 8\times10^9 \text{cm}^6\cdot\text{mol}^{-2}\cdot\text{s}^{-1}$.

of water molecules will be 1,500 ppm, which far exceeds the $SO_2$ concentration used in an earlier study (10–90 ppm) (Preto et al., 1999). Therefore it is apparent that there is enough water to absorb $SO_3$ and hence, increasing RH would not have a large effect. This mechanism may even account for the results of Lyon and Cole (1989) and Pires and Rossi (1997), who carried out the experiments with condensed phase and 2,000 and 3,000 ppm $SO_2$, respectively. At 100% RH and 25°C the concentration of water is 30,000 ppm—enough to remove all $SO_3$ and facilitate the gas-phase formation of $N_2O$. Given these assumptions, the existence of condensed water is therefore immaterial. While the liquid-phase and interface reactions proposed by Lyon and Cole (1989), Pires and Rossi (1994, 1997) and Pires et al. (1996) are quite plausible, the gas-phase reactions could contribute largely to $N_2O$ formation, at least at lower humidity.

It is interesting to note that Pires and Rossi (1997) observed the second-order dependence of the initial rate of $N_2O$ formation on NO concentration, although their experiments were carried out in the presence of acidic solutions. Pires and Rossi suggested that NO oxidation by $O_2$ is a rate-limiting step in their system. Consequently, the formation rate of $N_2O$ would be limited by $NO_2$ concentration. However, our calculation showed that under their experimental conditions, the gas-phase formation rate of $NO_2$, which is the product of NO oxidation, far exceeds the formation rate of $N_2O$. In Figure 3 the initial formation rate of $N_2O$ observed by Pires and Rossi is plotted against the calculated $NO_2$ formation rate in terms of their assumed Eq. 7, using the reported value of rate constant $k_7 = 8\times10^9$ $\text{cm}^6\cdot\text{mol}^{-2}\cdot\text{s}^{-1}$. It can be seen that there is a good correlation between the $N_2O$ formation rate and the calculated $NO_2$ formation rate below the $4\times10^4$ ppm/h $N_2O_4$ formation rate, which corresponds to 4,000 ppm $[NO]_0$. In this range the initial formation rate of $N_2O$ is proportional to the calculated $NO_2$ formation rate. The slope of the plot, which could be interpreted as the portion of $NO_2$ converted to $N_2O$, is about 0.24. Therefore, it seems unlikely that the $NO_2$ formation or NO oxidation is rate limiting. On the other hand, based on the gas-phase reactions we proposed earlier, we can derive an expression for $N_2O$ formation rate (see the Appendix)

$$\frac{d[N_2O]}{dt} = \frac{k_5 k_{14} K_{13} K_{15} [NO]^2 [O_2][SO_2]}{k_{-4} + k_5 [SO_2]}, \qquad (21)$$

which is second order in [NO]. The order in $[SO_2]$ for this expression is not an integer, which agrees with the observations of Pires and Rossi, who reported an empirical value of 0.9.

It should be noted that for the sake of simplicity, in the derivation of Eq. 21 other possible reactions involving $O_2$, such as Eq. 18, and $N_2O$ formation via Eqs. 1 and 4 have not been included. This can result in overestimation of the dependence on $O_2$. In fact, the dependence of $N_2O$ formation on $[O_2]$ observed by Pires and Rossi (1997) is weaker than the first-order dependence suggested by Eq. 21.

The decrease of the $N_2O$ formation rate in Figure 3 under high $[NO]_0$ could not be explained by the mechanism of Pires and Rossi (1997), because, as they pointed out, all possible reactions they proposed would suggest increasing $N_2O$ formation with increasing initial [NO]. We suggest that $N_2O$ was destroyed at high [NO] by some other gas-phase reaction.

### *$N_2O$ formation without the presence of $SO_2$*

The preceding discussions show that $N_2O_2$ may play an important role in $N_2O$ formation. It may also account for $N_2O$ formation without the presence of $SO_2$. As has been mentioned earlier, Muzio and Kramlich (1988) observed that 3 ppm $N_2O$ formed in an artificial combustion product containing $N_2$, $O_2$, $CO_2$, and 600 ppm NO in a period of 2 h. According to these earlier discussions, other components besides NO are unlikely to contribute to the formation, and we consider the following mechanism for this system:

$$2NO = N_2O_2 \qquad (4)$$

$$N_2O_2 + NO = N_2O + NO_2 \quad K_{22} = 1.3\times10^{24}. \qquad (22)$$

The overall reaction would be the disproportionation reaction of NO

$$3NO = N_2O + NO_2 \quad K_1 = 1.9\times10^{18}, \qquad (1)$$

which has been observed at high pressures (Greenwood and Earnshaw, 1989). Using the result of Muzio and Kramlich, we can estimate the reaction rate. Similarly to the derivation of Eq. 8, with the pseudo-steady-state hypothesis for $N_2O_2$ we obtain

$$\frac{d[N_2O]}{dt} = \frac{k_4 k_{22} [NO]^3}{k_{-4} + k_{22}[NO]} \qquad (23)$$

from Eqs. 4 and 22. Since [NO] is low and the $N_2O$ formation rate is low, we assume that $k_{22}[\mathrm{NO}] \ll k_{-4}$, and then

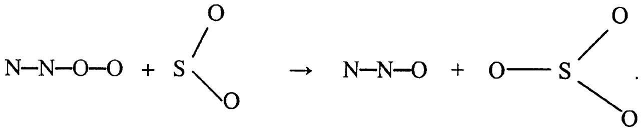
$$\frac{d[\mathrm{N_2O}]}{dt} \approx K_{4c} k_{22} [\mathrm{NO}]^3. \qquad (24)$$

Thus, the overall reaction 1 (Eq. 1) would appear to be third-order. With the relation $[\mathrm{NO}] = ([\mathrm{NO}]_0 - 3[\mathrm{N_2O}])$, one gets

$$[\mathrm{N_2O}] = \frac{1}{3}[\mathrm{NO}]_0 \left( 1 - \frac{1}{\sqrt{1 + 6K_{4c}k_{22}[\mathrm{NO}]_0^2 t}} \right) \qquad (25)$$

from Eq. 24. With $[\mathrm{NO}]_0 = 600$ ppm, $t = 2$ h (Muzio and Kramlich, 1988) and $K_{4c} = K_4/10^6 = 1.5 \times 10^{-12}$ ppm$^{-1}$, from Eq. 25 we obtain $k_{22} = 4.7 \times 10^3$ ppm$^{-1} \cdot$h$^{-1}$ or $2.9 \times 10^{10}$ cm$^3 \cdot$mol$^{-1} \cdot$s$^{-1}$. This value is about 1/20 of the rate-constant value that we estimated for reaction 5. As a consequence, for a mixture containing NO and $SO_2$, $N_2O$ would be formed predominantly via the reaction of $N_2O_2$ with $SO_2$, unless $[\mathrm{NO}]_0$ is much higher than $[\mathrm{SO_2}]_0$.

When $O_2$ is present, $N_2O_2$ may still be important, as can be seen from the discussion of Eqs. 13–16 for the $N_2O$ formation route. Theoretical studies have predicted several $N_2O_2$ isomers that have asymmetric structures (Chaban et al., 1997; Nguyen et al., 1993, 1994). One of them has a particularly unstable structure N–N–O–O. It is easy to envisage the following scheme for $N_2O$ formation



If a large portion of such unstable $N_2O_2$ isomers are formed as a result of Eqs. 13–16, the formation rate of $N_2O$ would increase substantially.

### *Temperature dependence of $N_2O$ formation*

$N_2O$ formation from dry mixtures of NO and $SO_2$ at 125°C was reported previously (Preto et al., 1999). The data show that the formation rate is about 1.5 times higher than the rate at 25°C. With Eq. 11 we can estimate the activation energy for $k_5$. The value of $K_{4c}$ at 125°C is calculated by the HSC Chemistry software to be 0.36 of the value at 25°C. Accordingly, the activation energy in terms of the Arrhenius equation is calculated to be 14.2 kJ/mol. Moreover, based on the preceding data, the apparent activation energy for the overall reaction of $N_2O$ formation (represented by Eq. 2) is only about 4 kJ/mol. A weak temperature dependence for $N_2O$ formation was also suggested by experimental data in the range of 800–1,000°C for the selective noncatalytic reduction of NO (SNR) with injection of $NH_3$ (Hulgaard and Dam-Johansen, 1992).

This weak temperature dependence implies that $N_2O$ formation by the discussed mechanism would be more significant for flue gases in the plume than in the stack, because their residence time in the stack is relatively short, whereas the time for the reactants to exist in significant concentrations in a plume is much longer (Karamchandani et al., 2000).

## Conclusions

The mechanism based on gas-phase reactions can account for $N_2O$ formation in dry or low-humidity mixtures of NO, $SO_2$, and $O_2$. $N_2O_2$ could be an important precursor of $N_2O$. It would react with NO and $SO_2$ to form $N_2O$, but the reaction rate would be much faster with $SO_2$. The effect of $O_2$ would be important only when $SO_2$ and water are present. Since it was observed that condensed water did not increase $N_2O$ formation significantly, gas-phase reactions may contribute largely to the formation, and the mechanism we proposed might also be operative in the systems with high humidity or condensed water.

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## Appendix: Derivation of Rate Expression for $N_2O$ Formation

### *Mixture of NO and $SO_2$ without $O_2$*

According to Eqs. 4 and 5, the net formation rate of $N_2O_2$ can be given as

$$\frac{d[N_2O_2]}{dt} = k_4[NO]^2 - k_{-4}[N_2O_2] - k_5[N_2O_2][SO_2]. \tag{A1}$$

With the pseudo-steady-state hypothesis for $N_2O_2$

$$\frac{d[N_2O_2]}{dt} \approx 0, \tag{A2}$$

we obtain

$$[N_2O_2] = \frac{k_4[NO]^2}{k_{-4} + k_5[SO_2]}. \tag{A3}$$

The formation rate of $N_2O$ is

$$\frac{d[N_2O]}{dt} = k_5[N_2O_2][SO_2] = \frac{k_4k_5[NO]^2[SO_2]}{k_{-4} + k_5[SO_2]}. \tag{A4}$$

### *In the presence of $O_2$*

Equations 13 and 14 would be operative. The net formation rate of the intermediate $NO_3$ can be given as

$$\frac{d[NO_3]}{dt} = k_{13}[NO][O_2] - k_{-13}[NO_3] - k_{14}[NO_3][NO]. \tag{A5}$$

With the pseudo-steady-state assumption for $NO_3$, we get

$$[NO_3] = \frac{k_{13}[NO][O_2]}{k_{-13} + k_{14}[NO]}. \tag{A6}$$

When water is also present, the gas phase $[SO_3]$ in Eqs. 15 and 16 would be negligible. Applying pseudo-steady-state assumptions to intermediates, for $N_2O_2$ we have

$$\frac{d[N_2O_2]}{dt} = k_{16}[N_2O_3][SO_2] - k_5[N_2O_2][SO_2] - k_{-4}[N_2O_2] \approx 0. \tag{A7}$$

Therefore,

$$[N_2O_2] = \frac{k_{16}[N_2O_3][SO_2]}{k_{-4} + k_5[SO_2]}. \tag{A8}$$

For $[N_2O_3]$ in Eq. A8, we have

$$\frac{d[N_2O_3]}{dt} = k_{15}[N_2O_4][SO_2] - k_{16}[N_2O_3][SO_2] \approx 0. \tag{A9}$$

Therefore,

$$[N_2O_3] = \frac{k_{15}}{k_{16}}[N_2O_4]. \tag{A10}$$

For $N_2O4$ in Eq. A10, we have

$$\frac{d[N_2O_4]}{dt} = k_{14}[NO_3][NO] - k_{15}[N_2O_4][SO_2] \approx 0. \tag{A11}$$

From Eqs. A11 and A6, we obtain

$$[N_2O_4] = \frac{k_{13}k_{14}[NO]^2[O_2]}{k_{15}(k_{-13} + k_{14}[NO])[SO_2]}. \tag{A12}$$

Accordingly, the formation rate of $[N_2O]$ under such conditions is

$$\frac{d[N_2O]}{dt} = k_5[N_2O_2][SO_2] = \frac{k_5k_{13}k_{14}K_{15}[NO]^2[O_2][SO_2]}{(k_{-13} + k_{14}[NO])(k_{-4} + k_5[SO_2])}. \tag{A13}$$

When the concentration of NO is low so that $k_{14}$ $[NO] \ll k_{-13}$, the rate can be given as

$$\frac{d[N_2O]}{dt} = \frac{k_5k_{14}K_{13}K_{15}[NO]^2[O_2][SO_2]}{k_{-4} + k_5[SO_2]}. \tag{A14}$$

Equation A14 predicts that the apparent reaction order with respect to $SO_2$ would decrease as the concentration of $SO_2$ increases. The dependence on $[SO_2]$ depends on the values of $k_{-4}$ and $k_5$. At large $SO_2$ concentrations, $k_5[SO_2] \gg k_{-4}$, the observed formation rate of $N_2O$ would appear to be independent of $SO_2$ concentration.

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