# The heterogeneous generation of $N_2O$ from exhaust gases of combustion: A laboratory study

M. Pires and M.J. Rossi

Laboratory of Air and Soil Pollution(LPAS), Swiss Federal Institute of Technology (EPFL), Lausanne, Switzerland

**Abstract.** The heterogeneous reaction of NO, $SO_2$ and $O_2$ in the presence of condensed or adsorbed $H_2O$ results in high yields of $N_2O$ under conditions mimicking flue gas from fossil fuel combustion. We observed a strong influence of the nature of the substrate surface on the rate of $N_2O$ formation. The maximum rate of $N_2O$ formation of 350 ppm $h^{-1}$ occurred on soot and fly ash at relative humidities approaching 100% at 368K final yields of 80-100% $N_2O$. The mechanism corresponds to a complex multiphase system in which $NO_2$ seems to be a key species. The observed abundance of $NO_2$ does not correspond to the one predicted by the simple mechanism by Lyon and Cole (1988).

## Introduction

In view of the uncertainty of the origin of the secular increase of $N_2O$ (Cicerone, 1989), we have investigated the possibility whether or not $N_2O$ may be generated in a slow secondary reaction of combustion exhaust gases in the presence of airborne particulate such as soot, sulfuric acid aerosol and fly ash. The interest in the present work stems from the fact that in contrast to the well defined albeit variable biogenic origin of $N_2O$, mainly from natural processes in oceans and soil, the anthropogenic sources are not well characterized. It is thought that the increase of the $N_2O$ concentration in the atmosphere is attributable mainly to human activities such as the use of fertilizers, combustion of fossil fuel, biomass burning, and industrial production of adipic and nitric acids (Bouwman, 1990; Thiemens and Trogler, 1991). The contribution of mobile and stationary combustion sources is highly uncertain and emissions of power plants remains controversial since a $N_2O$ sampling artifact was discovered in 1988 putting into doubt the importance of combustion processes as a source of $N_2O$ (Muzio and Kramlich, 1988). However, the reactions that lead to the formation of $N_2O$ in sampling containers may occur in exhaust plumes and could contribute significantly to the nitrous oxide budget (Khalil and Rasmussen, 1992).

The goal of the present laboratory study was to investigate heterogeneous chemical processes of combustion exhaust gases taking place on the above mentioned particulate surfaces and contributing towards the formation of $N_2O$ under experimental conditions that come as closely as possible to exhaust conditions containing NO and $SO_2$, among other constituents.

## Experimental

$N_2O$ formation was studied in a static aluminum cell(1 liter) coated with halocarbon wax to avoid wall reactions, at different

temperatures between 298 to 368K. The reactants and intermediates were analyzed by UV-VIS absorption spectroscopy using a CCD camera as a detector. The absorption coefficients of $SO_2$, NO, and $NO_2$ were determined as a function of total pressure at 298K in the wavelength range of 200 to 400 nm. The spectra obtained are in good agreement with literature data (Forte and van den Bergh 1978; Manatt and Lane 1993; Bass et al. 1976). The HONO concentration was determined using the extinction coefficient at 354nm using data of Stockwell and Calvert (1978) and Bougartz et al.(1991).

The $N_2O$ measurement method was similar to that described by Ford(1990). A Dani 86.10 gas chromatograph equipped with an electron capture detector (ECD) was used for analysis. A mixture of 95% argon and 5% methane was used as carrier gas (Carbagas) without additional purification. The sampling was performed by gas syringes. The only peak observed in the chromatogram is due to $N_2O$ which appeared at a retention time of 5.20 min.. There was no interference due to $O_2$ and $H_2O$ vapor because they were separated from $N_2O$ and thus bypassed the detector. We were able to detect low $N_2O$ concentrations at a minimum detection limit of 0.2 ppm within a 2% precision.

Before each run the cell is connected to the vacuum system and a background pressure lower than 10 mTorr was obtained. Subsequently, the reactant gases NO (>99.9%, Carbagas), $SO_2$ (>99.9%, Matheson Inc.) and $O_2$ (>99.998%, Carbagas) are introduced into the cell. The system is maintained at atmospheric pressure adding as a balance nitrogen (>99.999%, Carbagas). The gas concentration is obtained by absolute pressure measurements. For NO and $SO_2$ the concentration and purity are also confirmed by their respective UV absorption spectra. In the experiments carried out in the presence of water vapor liquid water (0.5-2 ml) was injected into the heated cell to attain the expected relative humidity (80% to 100%). To demonstrate the influence of the condensed phase as well as the acidity/basicity of the substrate, kinetic experiments were performed using sulfuric acid solutions (95%/wt to 1 M), buffered phosphate (pH = 7), $KHC_8O_4H_4$ (pH=4), and sodium hydroxide solution (0.1 M). The liquid and solid (soot or fly ash) phases were put into a glass dish with a known surface area (10, 20 or 50 $cm^2$). Soot was produced by burning rubber and the fly ash sample is a standard reference material from NIST (ref. n°1633b). All liquid solutions were prepared from p.a. Fluka reagents. Demineralized water was used in all experiments.

## Results and discussion

We chose standard gas concentrations mimicking typical flue gas or exhaust conditions in order to compare our results. The standard conditions used throughout this work are: $[NO]_0$=650 ppm, $[SO_2]_0$=3000 ppm and $[O_2]_0$=5% balanced by $N_2$. The condensed phase consisted of 20ml sulfuric acid solution at 0.1M exposed in a sample dish of 50 $cm^2$ surface area at ambient
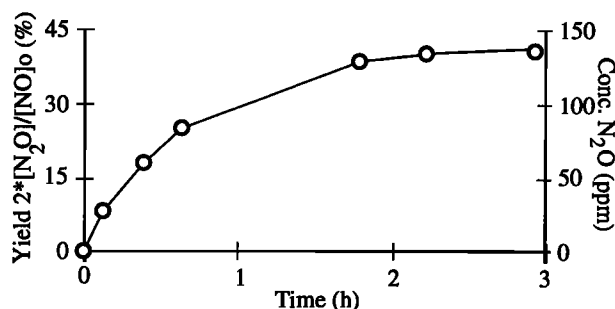
**Figure 1.** Formation of $N_2O$ in synthetic exhaust gas mixture at standard conditions (T=298K, $[NO]_0$=650ppm, $[SO_2]_0$= 3000ppm, $[O_2]_0$=5%.).

temperature (298K). Figure 1 shows the yield and concentration profile of $N_2O$ obtained under these conditions. The completion of the reaction is achieved after 2h with final yields of 40% and 10% with respect to nitrogen and sulfur, respectively. The initial rate is significant (202 ppm $N_2O$/h) and a large concentration of nitrous oxide is produced within the first hour of reaction. These results are in agreement with literature data (De Soete, 1988; Muzio and Kramlich, 1988). The variation of the initial concentration of NO and $SO_2$ affects $N_2O$ formation in different ways. While the $N_2O$ concentration scales directly with the increase of NO, the variation of $SO_2$. leads to a rate of formation of 230±20 ppm $N_2O$/h at $[SO_2]_0$=500ppm and remains unchanged upon further increases of $SO_2$ up to 6000 ppm. Most importantly, we did not observe a critical threshold of $SO_2$ for production of $N_2O$ as observed by Muzio et al.(1989). These authors found little $N_2O$ formation for $SO_2$ levels less than 500 ppm ($[NO]_0$=750ppm at T=298K).

Using the measured values of the rate of $N_2O$ formation in a large initial excess of either NO or $SO_2$ we calculated the reaction order and the rate constant of $N_2O$ formation. We computed a rate constant of $(6.4\pm3.8)\times10^{-7}$ ppm$^{-1.88}$ h$^{-1}$ for $N_2O$ formation using a reaction order of 2 and 0.88 with respect to NO and $SO_2$, respectively, as displayed in Figure 2. The second order dependence on NO suggests that NO oxidation by $O_2$ in the gas phase, liquid or at the interface could be the rate limiting step for $N_2O$ formation (Pires et al. 1994). The fractional $SO_2$ reaction order points towards a complex mechanism involving $SO_2$. The only other data on the kinetic rate law for this system could be found in the work of De Soete(1988) who obtained fractional orders of 0.68 and 0.7 with respect to NO and $SO_2$,
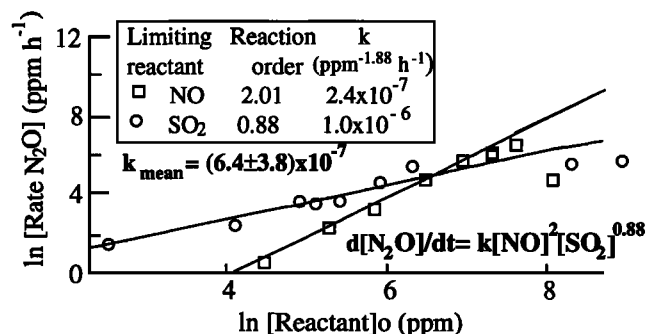
respectively. De Soete gave only values for the final rate at time scales larger by a factor of 2 or 3 compared to our work but did not control the pH which decreases during the experiment. Consequently our results can not directly be compared with De Soete's.

The presence of $O_2$ increases both the rate and the yield of $N_2O$ formation. The increase of the initial $O_2$ concentration from 0 to 5% increases the $N_2O$ yield ten times. However, an additional increase of oxygen up to 21% has little effect on $N_2O$ formation indicating that $O_2$ is not the limiting reactant. Most significant is a small, but non negligible production of $N_2O$ in the absence of $O_2$, which points to the existence of slow concurrent reactions.

The acidity of the condensed phase seemed to have an influence on both the initial rate as well as the yield of $N_2O$ with a maximum of NO consumed at pH=0 of a $H_2SO_4/H_2O$ solution Figure 3 shows the log of the rate constant as a function of pH and $H_0$(Hammett acidity function for sulfuric acid). A complex dependence of the rate constant with acidity is observed. In alkaline to neutral solutions, between pH 13 to 7, the rate constant does not change significantly. On the other hand, in acidic media a strong increase of the rate as well as the yield of $N_2O$ formation was obtained with a maximum for both at pH=0. The reaction order of $H^+$ in the rate law was found to be 0.43. For high acidities ($H_2SO_4 > 1M$) the rate of $N_2O$ formation decreases drastically and reaches a negligible value for $H_0 < -10$ (65% wt $H_2SO_4$ ). These results are in good agreement with the work of Ross et al.(1983) who studied the aqueous $SO_2/NO_x$ chemistry at high acidities. The analysis of these results in terms of elementary reactions is undoubtedly complex because the influence of the acidity is expected to be important to many reactions of the system as well as for various gas/liquid equilibria. The high $N_2O$ rate of formation under conditions where HONO is the predominant N-species and the change of slope (Figure 3) around pH=3 suggests that nitrous acid (pKa=3.3) is the active nitrogen precursor species in the system. The identification of the reactive sulfur species, one or several, is more difficult than in the case of the N(III) species. In acid solutions probably both bisulfite and sulfurous acid react with HONO to produce $N_2O$ (Martin et al. 1981). On the other hand, $N_2O$ formation in neutral and basic medium is slower and probably follows a different mechanism, perhaps involving the reaction between NO and sulfite to produce $N_2O$ (Littlejohn and Chang, 1991).
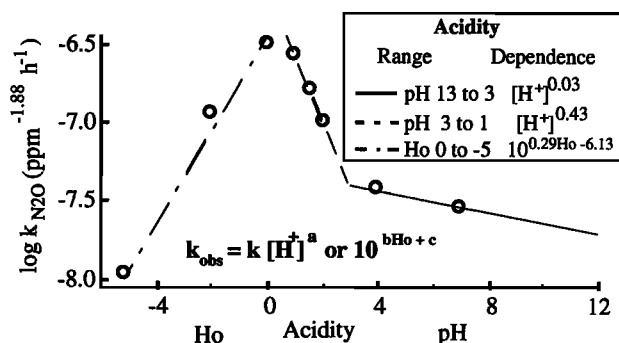


**Figure 2.** Calculated rate constant and reaction order, with respect to NO and $SO_2$, for $N_2O$ formation at T=298K in the presence of 20ml $H_2SO_4$ 0.1M with a surface area of 50 cm².



**Figure 3.** Influence of the acidity on the rate constant of $N_2O$ production at T=298K.

## Dependence of $N_2O$ formation on liquid/solid surfaces and $H_2O$ vapor

The influence of the presence of water vapor and/or active liquid/solid interfaces on the $N_2O$ production was investigated. The results are shown in Figure 4. The formation of $N_2O$ has been observed in the presence and the absence of condensed phase $H_2O$. The rate of nitrous oxide formation in a dry system is slower by a factor of 100 corresponding to a NO conversion of 0.2% compared to the analogous wet system. On the other hand, the injection of water vapor at 368K increases the initial rate and final yield by a factor of 30 to 60, respectively, when compared to a dry system. Most remarkable is the behavior of the system in the presence of solid surfaces such as a soot and fly ash surfaces. The addition of a fly ash sample of 50 cm² surface area in a dry system did not change the initial rate nor the final yield of $N_2O$ formation. On the other hand, under similarly dry conditions the presence of soot resulted in an increase of a factor of 5 in the initial rate of $N_2O$ formation at ambient temperature. With the increase of the relative humidity to 90-100% at elevated temperature (368K) and in the presence of similar soot and fly ash samples we observed yet another significant increase of both the initial rate and the final yield of $N_2O$ compared to the corresponding dry soot/fly ash systems. The maximum rate of $N_2O$ formation is observed at these conditions and the limiting final $N_2O$ yield of 100% and 80% with respect to NO for fly ash and soot surfaces, respectively. Due to the high limiting yields for $N_2O$ other forms of nitrogen oxides such as nitrate can not be formed. These results are important because the conditions of the wet soot and fly ash systems studied here approach the conditions of a real case of exhaust or flue gas from combustion such as elevated temperature, high humidity and the presence of polar surfaces.

### Additional results

The replacement of NO by an equivalent amount of either $NO_2$ or HONO as nitrogen reactant accelerates the initial rate of $N_2O$ formation at standard conditions. While the initial rate
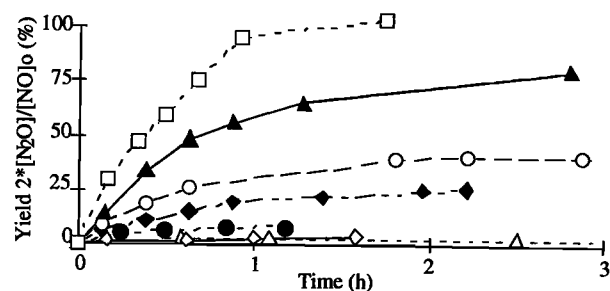
| Legend | Surface | $H_2O$ | Temp. (K) | Initial rate [ppm $N_2O$/h] | Yield (%) 2*[$N_2O$]/[NO]o |
|--------|---------|--------|-----------|-----------------------------|----------------------------|
| △ | - | dry (x10) | 298 | 2 | 0.5 |
| ◆ | - | vapor | 368 | 61 | 30 |
| ○ | $H_2SO_4$ | liquid | 298 | 202 | 40 |
| ◇ | Soot | dry | 298 | 11 | 40 |
| ▲ | " | vapor | 368 | 292 | 80 |
| ● | Fly-ash | dry (x10) | 298 | 2 | 0.7 |
| □ | " | vapor | 368 | 332 | ≈100 |

**Figure 4.** Influence of surface type and humidity on $N_2O$ production. [NO]o= 650ppm, [$SO_2$]o=3000ppm and [$O_2$]o=5%.
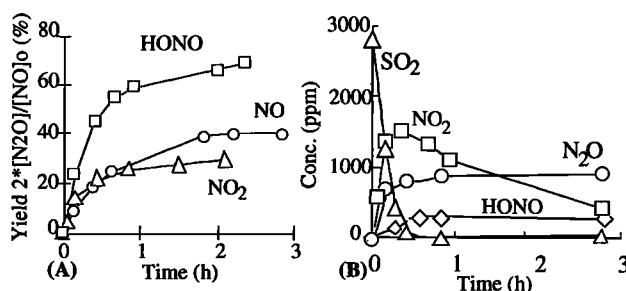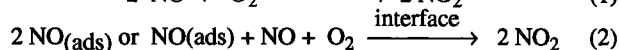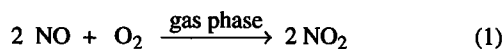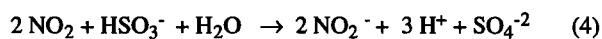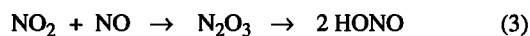
**Figure 5.** (A) Influence of replacement of NO by either $NO_2$ or HONO as reactive nitrogen compound, [N-reactant]o=650ppm; (B) concentration profiles measured by absorption spectroscopy using a CCD camera [HONO]o=650ppm (eq. in gas phase), condensed phase consisted of 20 ml 0.032 M nitrite at pH=0.8. All experiments were performed at standard conditions

increase is similar for both reactants, the final $N_2O$ yield is significantly higher in the presence of HONO(70%) compared to $NO_2$(30%) and NO(40%) (Figure 5A). These facts together with other results cited above indicates that HONO is one if not the most important of the reactive intermediates in our system. The presence of HONO in the gas phase was confirmed by UV-spectroscopy together with the presence of $NO_2$ and aqueous HONO. The concentration profiles of HONO, $NO_2$, $SO_2$ and $N_2O$ are shown in Figure 5B for the system using HONO as initial reactant. We observed the rapid appearance of HONO in the gas phase in the first few minutes of the reaction with a maximum of 300ppm at 30 min. HONO was still observable up to 3 hours after initialization of the reaction. The $SO_2$ concentration decreases rapidly, with 95% of the S(IV) consumed and/or transferred to the liquid phase (pH=1) after 30 min. of reaction. The $NO_2$ concentration profile displays a large increase with a maximum of 1500 ppm at 20 min., implying the sum of several processes of formation and destruction of $NO_2$. The $N_2O$ concentration profile presents a very rapid increase in the first minutes of reaction, implying a large initial rate of $N_2O$ formation.

Based on the results presented above we propose the following simplified mechanism for heterogeneous $N_2O$ formation from exhaust gases of combustion. Full details will be presented in a forthcoming paper (Pires and Rossi, 1995). In the first few minutes NO is oxidized by $O_2$ to $NO_2$ mainly in the gas phase, but the presence of both $H_2O$ and active surfaces accelerates the $NO_2$ production (England and Corcoran, 1975):

$$2\ NO\ +\ O_2\ \xrightarrow{\text{gas phase}}\ 2\ NO_2 \qquad (1)$$

$$2\ NO_{(ads)}\ \text{or}\ NO(ads) + NO + O_2\ \xrightarrow{\text{interface}}\ 2\ NO_2 \qquad (2)$$

Subsequently, $NO_2$ will react with excess NO to obtain HONO (reaction 3) or with S(IV) at the interface (reaction 4). $NO_2$ disproportionation (reaction 5) resulting in equivalent amounts of HONO and $HNO_3$, is too slow to compete as nitrate could not be detected under our conditions.

$$NO_2\ +\ NO\ \rightarrow\ N_2O_3\ \rightarrow\ 2\ HONO \qquad (3)$$

$$2\ NO_2 + HSO_3^-\ + H_2O\ \rightarrow\ 2\ NO_2^-\ + 3\ H^+ + SO_4^{-2} \qquad (4)$$

$$2\ NO_2\ +\ H_2O\ \rightarrow\ HONO\ +\ HNO_3 \qquad (5)$$

Thus HONO reacts with S(IV), probably $HSO_3^-$ under our conditions, to ultimately form $N_2O$ and $H_2SO_4$ through a complex reaction sequence following the Raschig mechanism (Scheme I),(Littlejohn and Chang, 1991).

$$HONO \xrightarrow[H^+ \downarrow]{HSO_3^-} NOSO_3^- \xrightarrow{S(IV)} HON(SO_3^-)_2$$

$$HNO + HSO_4^- + H^+$$
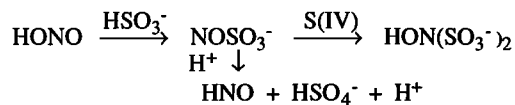
Scheme 1        $N_2O$ ⌐

Lyon and Cole (1988) proposed a simplified kinetic mechanism for $N_2O$ formation in flue gas that is similar to the model presented above. The application of the model of Lyon and Cole to our results at standard conditions showed good agreement with respect to $N_2O$ formation for the first hour of reaction. However, the model overpredicts the final $N_2O$ yield by 30% after 3 hours of reaction. On the other hand, the concentration of $NO_2$ in the gas phase as observed in our experiments is 200 times larger than predicted by the model of Lyon and Cole. It seems that the $NO_2$ concentration versus time profile is a sensitive indicator of the overall mechanism compared to the time-dependent observation of $N_2O$ and $SO_2$. As a conclusion we state that an additional source of $NO_2$, presumably according to reaction(2) has to be included in our model in order to fit the observations of $SO_2$ disappearance as well as the appearance of HONO and $NO_2$. Furthermore, the complex reaction can be subdivided into two regimes: the first is controlled by NO oxidation and uptake of NO and $SO_2$ into the liquid phase, the second is dominated by reactions displayed in Scheme I involving HONO.

## Conclusion

There is a significant heterogeneous rate of $N_2O$ formation at conditions that mimic exhaust gases from combustion processes. The simultaneous presence of NO, $SO_2$, $O_2$ and condensed phase water in the liquid or adsorbed state has been confirmed to be necessary. The presence of solid surfaces increases both the rate and the yield of $N_2O$ obtained in a dry system. The simultaneous presence of high humidity (90-100% at 368K) and internal surfaces results in the maximum rate and final yield of $N_2O$ approaching 60 and 100% conversion after 1h in the presence of soot and fly ash, respectively, leaving no room for nitrate formation.

The influence of the acidity, studied over a very wide range, showed a maximum of both the initial rate as well as the yield of $N_2O$ relative to NO consumed at pH = 0 of $H_2SO_4/H_2O$ solution. The replacement of NO by an equivalent amount of either $NO_2$ or HONO accelerates the initial rate of $N_2O$ by a factor of 1.5 and 2, respectively. These results and the absence of nitrate under the present conditions point towards HONO as the reactive nitrogen species, which is generated in the rapid reactions (3) and (4) that compete with the $NO_2$ disproportionation (reaction 5). The observation of $NO_2$ and HONO in the gas phase presents a powerful clue to the overall reaction mechanism which is dominated by homogeneous and heterogeneous (interfacial) NO oxidation in the beginning as indicated by the observed rate law.

Subsequently HONO interacts with S(IV) to result in $N_2O$ formation.

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M. Pires and M.J. Rossi, Laboratory of Air and Soil Pollution Studies (LPAS), Swiss Federal Institute of Technology (EPFL), 1015 Lausanne, Switzerland.