PRODUCTION OF NITROGEN OXIDES BY LIGHTNING AND CORONAE DISCHARGES IN SIMULATED EARLY EARTH, VENUS AND MARS ENVIRONMENTS

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ABSTRACT

We present measurements for the production of nitrogen oxides (NO and N₂O) in CO₂-N₂ mixtures that simulate different stages of the evolution of the atmospheres of the Earth, Venus and Mars. The nitrogen fixation rates by two different types of electrical discharges, namely lightning and coronae, were studied over a wide range in CO₂ and N₂ mixing ratios. Nitric oxide (NO) is formed with a maximum energy yield estimated to be $\sim 1.3 \times 10^{16}$ molecule J⁻¹ at 80% CO₂ and $\sim 1.3 \times 10^{14}$ molecule J⁻¹ at 50% CO₂ for lightning and coronae discharges, respectively. Nitrous oxide (N₂O) is only formed by coronae discharge with a maximum energy yield estimated to be $\sim 1.2 \times 10^{13}$ molecule J⁻¹ at 50% CO₂. The pronounced difference in NO production in lightning and coronae discharges and the lack of formation of N₂O in lightning indicate that the physics and chemistry involved in nitrogen fixation differs substantially in these two forms of electric energy.

INTRODUCTION

Nitrogen fixation by natural abiotic sources on the contemporaneous Earth has been studied with great interest since the end of the 70's. Dinitrogen is converted in the atmosphere into NO_x (NO + NO₂) and N₂O, forms known as fixed nitrogen, by energetic processes. The production of NO_x and N₂O in the atmosphere is of major environmental importance. NO_x has a key role in the photochemistry of the atmosphere leading to the production of tropospheric ozone and controlling the levels of stratospheric ozone. Moreover the removal of NO_x by acid precipitation (in the form of nitrous and nitric acids) is a source of fixed nitrogen for the biosphere (Stark *et al.*, 1996). The amount of nitrogen fixed by tropospheric processes plays a major role in the equilibrium of the biosphere. This is because nitrogen fixation requires a great deal of energy to break the N≡N bond (9.45 MJ mol⁻¹). The ability to fix nitrogen biologically is restricted to bacteria (Postgate, 1987). N₂O is a stable trace gas in the troposphere where it plays an important greenhouse effect. Its sink is its photodestruction in the stratosphere where it contributes to ozone depletion (Adema *et al.*, 1990).

Among the natural sources of atmospheric NO_x, lightning has been proposed to be significant (Von Liebig, 1827; Chameides *et al.*, 1977) and possibly the major pathway by which nitrogen is fixed to NO_x (Noxon, 1976; Zipf and Dubin, 1976; Griffing, 1977; Chameides, 1979a; Franzblau and Popp, 1989). The production yield of NO_x by lightning discharge has been estimated by field observations and measurements (Noxon, 1976, 1978; Borucki and Chameides, 1984; Chameides *et al.*, 1987; Ridley *et al.*, 1987; Franzblau and Popp, 1989; Biazar and McNider, 1995), by laboratory discharge experiments (Chameides *et al.*, 1977; Hill *et al.*, 1988; Martinez and Brandvold, 1996; Stark *et al.*, 1996; Wang *et al.*, 1998) and also by theoretical modeling (Chameides *et al.*, 1977; Chameides, 1979a; Yung and McElroy, 1979; Hill *et al.*, 1980; Chameides and Walker, 1981; Bhetanabhotla *et al.*, 1985;

Coppens *et al.*, 1998). From these results the estimated energy yield of NO_x production extends from $\sim 6 \times 10^{15}$ to $\sim 2 \times 10^{17}$ molecule J⁻¹, and the corresponding global production rate varies from $\sim 9 \times 10^7$ up to $\sim 1 \times 10^{14}$ g N yr⁻¹.

Production of N₂O has been observed in lightning (Levine *et al.*, 1981) and in coronae (Brandvold *et al.*, 1996) discharges during thunderstorms. N₂O has also been detected in laboratory discharges (Donohoe *et al.*, 1977; Levine *et al.*, 1979; Hill *et al.*, 1988; Brandvold *et al.*, 1989; Fraser *et al.*, 1990). Based on laboratory measurements and theoretical calculations (Chameides, 1979a, 1979b; Hill *et al.*, 1984; Bhetanabhotla *et al.*, 1985) it has been estimated a production efficiency from $\sim 3 \times 10^{12}$ up to $\sim 1.5 \times 10^{13}$ molecule J⁻¹ in the lightning discharge and from $\sim 3 \times 10^{15}$ up to $\sim 1 \times 10^{17}$ molecule J⁻¹ for coronae processes.

NO appears to be produced in a large extent inside the lightning channel with NO₂ being formed mostly as a secondary product generated outside the lightning channel with the reaction of NO with ozone. Ozone and N₂O seem to be formed preferentially in the corona sheath surrounding the lightning channel (Hill *et al.*, 1980) or in point discharges in the ground (Brandvold *et al.*, 1996).

Electrical discharges have also been proposed to be a relevant source of fixed nitrogen in the early Earth's troposphere (Yung and McElroy, 1979; Chameides and Walker, 1981; Kasting and Walker, 1981; Mancinelli and McKay, 1988). In these theoretical studies, it has been concluded that, in the absence of biological perturbation, lightning could have provided a source of fixed nitrogen necessary for the emergence of life. The only experimental report on the abiotic nitrogen fixation rate by lightning in a primitive terrestrial-type atmosphere is that of Levine *et al.* (1982). The experimental NO production was estimated to be $3.7 (\pm 0.7) \times 10^{15}$ molecule J⁻¹ in an atmosphere composed of 95.9% CO₂, 3.97% N₂, 180 ppm SO₂, 50 ppm Ar, and 30 ppm CO that simulated the present atmosphere of Venus. Another related experimental study is that of Navarro-González *et al.* (1998b) for the production of nitric oxide by lightning inside explosive volcanic clouds of the early Earth.

The purpose of this work is to provide the first comprehensive experimental study of the nitrogen fixation rate by lightning and coronae discharges under conditions relevant to the early Earth, Venus and Mars in atmospheres containing various mixing ratios of CO₂ and N₂ as the main constituents.

EXPERIMENTAL PROCEDURE

Two electrical discharge processes were simulated in the CO₂-N₂ primitive atmospheres: cloud-to-ground lightning discharge and point discharges occurring on the ground (corona discharge). Cloud-to-ground lightning was simulated in the laboratory by a laser-induced plasma (LIP) that has been shown to be a good analog of the return-stroke of a lightning flash (Borucki *et al.*, 1985; Borucki and McKay, 1987; Scattergood *et al.*, 1989; Jebens *et al.*, 1992) without introducing contamination from the electrodes as when simulated with arcs and sparks (Borucki *et al.*, 1988). The laser used was a Q-switched Neodymium-YAG operating at a wavelength of 1.06 μm, a pulse energy of up to 0.6 J, a pulse repetition rate of 10 Hz, and a pulse duration of 5-7 ns. The temperature of the plasma has been determined to be about 20,000 K after 1 μs from ignition. A beam with 0.3 J per pulse was focused inside a closed 1.08 liter Pyrex flask with a plano-convex optical glass lens with a focal length of 5 cm, expected to have a focal aberration of ~ 10 μm. The power deposited into the system was determined calorimetrically. The energy dissipated per unit length in this simulated lightning was estimated to be $\sim 10^4$ J m⁻¹, in close agreement with that from natural lightning (Hill, 1979).

The corona discharge was induced in a coaxial Pyrex reactor composed of a central tungsten rod (internal electrode) surrounded internally by a grounded stainless steel cylinder (ground electrode). The internal electrode was connected to a regulated high voltage DC power that allows for both positive and negative DC operation. The high power supply delivers a maximum current of 3 mA and a maximum voltage of 30 kV. The power dissipated through the system was determined electrically (Navarro-González *et al.* 1998a).

The simulated primitive atmospheres composed of CO₂ (99.99% purity) and N₂ (99.999% purity) were prepared at various mixing ratios using a measuring and control gas blending system equipped with fast response mass flow control modules of 20 cm³ min⁻¹ capacity. The reactor was evacuated to 10⁻⁷ bar and flushed twice with the gas mixture before filled up at 1 bar total pressure. The samples were irradiated at 20°C from 5 to 30 min for lightning discharge experiments and from 8 min to 2 hours for corona discharge experiments. After irradiation, the gas mixtures were analyzed using a gas chromatograph interfaced in parallel with a FTIR-detector and a quadrupole mass spectrometer equipped with electron impact and chemical ionization modes. The gases were injected into the gas chromatograph by an automatic six-port gas-sampling loop of 2 ml. Two capillary chromatographic columns were used for the separation of the products, a PoraPLOT Q fused-silica (25 m × 0.32 mm I.D.) and an Alumina/KCl (50 m × 0.32 mm I.D.). The temperatures at the GC-MS and GC-FTIR interfaces

and in the FTIR flow cell were 260°C. The column program temperature was isothermal at 30°C for 4 min, and then a rate of 13°C min⁻¹ up to 240°C, and finally isothermal for 5.62 min. The carrier gas used was helium with a flow of 2 ml min⁻¹.

RESULTS AND DISCUSSION

Analyses of the gas mixtures after irradiation showed the formation of nitric oxide in significant quantities in both lightning and corona discharge experiments. Nitrogen dioxide and ozone, if formed, were not detected by our analytical instrumentation since these reactive gases decomposed during gas chromatographic analysis when using PoraPLOT columns. NO₂ is visually observed only if the sample is significantly overexposed to LIPs. An interesting result is the production of nitrous oxide only in the cold plasma discharge. This observation is consistent with the theoretical (Hill *et al.*, 1980, Hill and Rinker, 1981; Hill *et al.*, 1984) and experimental studies (Donohoe *et al.*, 1977) of nitrogen fixation in the contemporaneous Earth which demonstrated that N₂O was produced in large extent in the corona regions and not in the lightning channel. Simultaneously carbon monoxide and molecular oxygen were detected in the samples after exposure to both electrical energy sources. These results are in agreement with Chameides *et al.* (1979c), who suggested that lightning might be a significant source of CO, NO and free oxygen on Venus. The detection of CO indicates that carbon dioxide is readily dissociated into carbon monoxide and oxygen by both forms of electrical energy: lightning and coronae discharges.

Fig. 1. Variation of nitrogen oxide yield as a function of the CO₂ mixing ratio in lightning (a) and coronae (b) discharges in CO₂-N₂ atmospheres: ○ Nitric oxide, and □ Nitrous oxide. For comparison, the experimental result from Venusian lightning (△) obtained by Levine *et al.* (1982) is given.

The variations of the production rates of NO and N₂O as a function of the CO₂ mixing ratio (χ_{CO_2}) for lightning and coronae discharges are shown in Figure 1. Our results indicate that the energy yields of NO and N₂O are very sensitive to the CO₂ mixing ratios. In the case of lightning discharge, the NO yield increases from $\sim 1.9 \times 10^{15}$ molecule J⁻¹ at $\chi_{\text{CO}_2} \sim 0.98$ to $\sim 1.3 \times 10^{16}$ molecule J⁻¹ at $\chi_{\text{CO}_2} \sim 0.80$. This yield does not vary remarkably down to about $\chi_{\text{CO}_2} \sim 0.50$. This value is in good agreement with the theoretical estimations of Mancinelli and McKay (1988) and Chameides and Walker (1981) who estimated a NO production efficiency in the range of $1\text{--}3 \times 10^{16}$ molecule J⁻¹ for χ_{CO_2} between 0.5 and 0.8. At lower mixing ratios our experimental NO yield drastically decreases to $\sim 2.4 \times 10^{14}$ molecule J⁻¹ at $\chi_{\text{CO}_2} \sim 0.20$ and then slowly diminishes to $\sim 1.1 \times 10^{14}$ molecule J⁻¹ at $\chi_{\text{CO}_2} \sim 0.025$. Any further decrease in the atmospheric CO₂ content has little impact at this point since the water vapor present in the atmosphere contributes with oxygen atoms for the production of NO, stabilizing it at about 7.0×10^{13} molecule J⁻¹. In the case of the corona discharge experiments, the maximum NO yield is

$\sim 1.32 \times 10^{14}$ molecule J^{-1} for $\chi_{CO_2} \sim 0.5$. N_2O has also a maximum production of $\sim 1.16 \times 10^{13}$ molecule J^{-1} at this mixing ratio. Our results clearly demonstrate that lightning is more efficient than coronae discharges in the synthesis of NO by about two orders of magnitude. For contemporaneous Earth, the lightning dissipation rate is about a factor of two higher than the coronae dissipation rate (Chyba and Sagan, 1991). If we assume that this ratio was similar for the early terrestrial planets, we could conclude that nitric oxide production by electrical processes in the early terrestrial planets was dominated by lightning discharge. This substantial discrepancy of the efficiency of NO synthesis by the two electrical energy sources can be explained by the physical differences encountered in lightning and corona discharges. Coronal discharges produce cold plasmas of highly superthermal electrons but the ions, neutral molecules and molecular fragments in the background gas remain near the ambient temperature. Therefore this system is not in thermal equilibrium. On the contrary, lightning discharges as simulated by LIPs produce hot plasmas in which the kinetic and excitation temperatures of all species are very high and are all in thermochemical equilibrium (Chyba and Sagan, 1991). Consequently, the chemistry occurring in hot plasmas appears to differ substantially from that in cold plasmas.

In this frame, we propose a reaction scheme for NO production in lightning discharge and in corona discharge. In addition we suggest a chemical mechanism to account for the production of N_2O in corona discharge.

In the lightning discharge, nitrogen fixation is governed by high temperatures chemical reactions (Borucki and Chameides, 1984; Navarro-González *et al.*, 1998b). The initial plasma temperature is higher than 30,000 K. As the gas cools down, the ions and electrons recombine leading to free radicals and stable molecules. As these species further cool down, they lead to the final products. The chemical mechanism needed to explain the formation of the final products is exclusively determined by radicals and/or stable molecule reactions occurring at high temperature. In CO_2 - N_2 mixtures, the thermal dissociation of carbon dioxide occurs leading to the formation of atomic oxygen and carbon monoxide according the reaction 1. The main fate of atomic oxygen is its recombination to molecular oxygen *via* a third body (reaction 2).

A small fraction of atomic oxygen reacts with molecular nitrogen leading to the formation of NO via a chain reaction (reactions 3 and 4). This reaction occurs only at temperatures above 1500°C.

In mixtures where N_2 dominates, the reduction in the NO production is attributed to the efficient nitrogen recombination (reaction 5) making reaction 3 a negligible channel:

The following reactions destroy NO:

In corona chemistry, it is recognized that the energy input leads to ionization and excitation and that most of species involved in the reactions are charged species and free radicals (Hill *et al.*, 1984; Bhetanabhotla *et al.*, 1985). Below we propose a chemical scheme that involves principally positive charged species.

In CO_2 dominated mixtures, CO_2 can be dissociated by the corona electrons by the following reaction:

Then O^+ can react with nitrogen to form NO^+ that lead to neutral NO via the reaction chain:

N_2O can be formed by reaction of NO^+ with nitrogen atoms via the reactions 12 and 13:

In addition to reactions 8 to 12, reactions 1, 2, and 4 to 7 can also take part in corona discharges. Reaction 3, however, does not participate in corona processes because, in order for the rate constant to be significantly fast, the temperature of the gas must be higher than 1500°C.

It is important to note that the above mechanism is only given as an illustration of the possible chemical processes that occur in both lightning and corona discharges and that it is important to develop a detail kinetic model to explain quantitatively the observed rates of nitrogen fixation. Nowadays there are still great uncertainties about the chemical mechanism of formation of NO and N_2O by corona discharges.

CONCLUSION

We have experimentally examined the nitrogen fixation rate by thunderstorm lightning and coronae in the primitive atmospheres of the Earth, Venus and Mars. We conclude that nitric oxide could have been significantly produced in the primordial atmospheric environments by electrical discharges. Nitrous oxide is a minor product formed exclusively by coronae processes. This is the first report on the production of N_2O in simulated experiments of the early telluric planets. Further studies are needed to determine its role in the atmosphere.

Currently, we are assessing the importance of nitrogen fixation by lightning on the global nitrogen cycle of the early telluric environments and its impact to the origin and evolution of life. Part of this work as it refers to the early Earth has been published elsewhere (Navarro-González *et al.*, 2001). These results suggest that the development of biological nitrogen fixation arose in response to changes in atmospheric composition that resulted in a reduction in the production of abiotically fixed nitrogen by lightning.

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