

Atmospheric chemistry of nitrogen on Mars: A link between oxidants in the soil and chlorine cycling

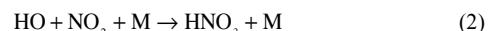
D. C. Catling (1), M. L. Smith (1), M. W. Claire (2), K. J. Zahnle (3)

(1) University of Washington, Dept. Earth and Space Sciences, Seattle WA, USA (dcatling@uw.edu) (2) University of St. Andrews, Dept. Earth & Environmental Sciences, Scotland. (3) NASA Ames Research Center, Moffett Field CA, USA.

NO and NO₂, collectively denoted NO_x, are generated in the Earth's atmosphere mainly from the photochemistry of biogenic nitrogen-containing gases whereas on Mars they form through the oxidation of products derived from ionospheric dissociation of N₂. NO_x disappears from both atmospheres when acids form from further oxidation and deposit to the surface. We show that peroxy nitric acid (PNA), HO₂NO₂, dominates the removal of NO_x from the atmosphere of Mars in contrast to nitric acid, HNO₃, in the Earth's atmosphere because PNA is stable against thermal decomposition at the colder temperatures of Mars. Following the dry deposition of PNA, peroxy nitrate or peroxy nitrite minerals are possible, while a proportion of PNA may also decompose and recycle NO_x back to the atmosphere. Deposition of PNA must have been delivering nitrogen to the martian surface since at least ~3 Ga (during the Amazonian) when Mars has been predominantly cold and dry. In aqueous solution, peroxy nitrates or peroxy nitrites decompose and release O₂. Thus, their inevitable formation from atmospheric chemistry could explain the release of O₂ when water was added to the martian soil in the Viking Lander (VL) Gas Exchange experiment. Furthermore, PNA could interact with chlorides to liberate chlorine volatiles, enabling cyclic oxidation of chlorine compounds into perchlorate even in the absence of volcanic chlorine volatiles.

1. Introduction

The oxidation of nitric oxide (NO) and nitrogen dioxide (NO₂) (together called NO_x) produces acid species in the atmospheres of Earth and Mars. NO₂ reacts with hydroxyl radicals (OH) to form nitric acid (HNO₃) or it can react with hydroperoxy radicals (HO₂) to form peroxy nitric acid, PNA (HO₂NO₂) [1]. Key reactions are as follows:



On Earth, NO_x are present mostly because of biogenic emissions of nitrogen gases, both natural and anthropogenic. There is also a source of NO from lightning, while stratospheric NO_x is mixed downward, derived from the oxidation of biogenic N₂O. On Earth, an ionospheric source of NO is very minor. However, on Mars the ionosphere is the ultimate source of nitrogen oxides [2]. NO and N are transported into the lower atmosphere where they are oxidized via eq. (1) to NO₂.

On Earth, the dominant loss of NO_x is the formation of nitric acid (eq. (2)) and its wet or dry deposition (eq. (4)). PNA deposition is usually unimportant because its formation (eq. (3)) is reversed by rapid thermal decomposition in Earth's lower troposphere. However, the thermal decomposition rate declines by orders of magnitude as the temperature drops tens of degrees below 273 K [3, 4]. So, while PNA forms in the Earth's upper troposphere and stratosphere, HNO₃ rather than PNA is the dominant nitrogen species that dry deposits onto the Earth's surface, except at the South Pole, where PNA deposition is comparable to that of nitric acid [5].

The coldness of Mars combined with the observation that PNA deposition is important at the Earth's South Pole, means that PNA should dominate the dry deposition of nitrogen on the martian surface. Our model results show that PNA is indeed dominant, which has implications for the surface chemistry.

2. Method

We used a photochemical model described by Zahnle et al. [6], which accurately reproduces the known composition of Mars's atmosphere. In brief, the

model is 1-D (vertical dimension) and has vertical transport by molecular and eddy diffusion, a standard temperature profile, and humidity fixed to match typical water column abundance. NO and N fluxes from the ionosphere (an upper boundary condition) are consistent with other models.

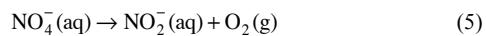
3. Results

The imposition of different temperature profiles in the model (with other parameters being equal) shows that the relative formation rates of HNO_3 and PNA reverse going from warm Earth-like temperatures to cold Mars-like temperatures. At Earth-like temperatures, the column-integrated formation rate of HNO_3 is $\sim 10^4$ times larger than PNA, whereas at Mars-like temperatures, the column-integrated formation rate of PNA is $\sim 10^3$ times larger than HNO_3 . PNA is lost to photolysis and reaction with OH, but at colder temperatures the column-integrated production of OH also declines because of less absolute water vapor. The result is that the PNA deposition rate on modern Mars is $\sim 10^5$ molecules $\text{cm}^{-2} \text{ s}^{-1}$. This is small compared to nitric acid deposition on Earth, $\sim 10^8$ molecules $\text{cm}^{-2} \text{ s}^{-1}$ [7] but on Mars this flux has significance when integrated since ~ 3 Ga.

3. Discussion

Peroxynitrites might explain the oxidant puzzle from the Viking Lander (VL) biology experiments: The Gas Exchange Experiment (GEx) found that martian soil releases O_2 when moistened [8]. This has generally been attributed to superoxides and peroxides [9], although Plumb et al. [10] proposed peroxy nitrites. They argued that UV acting on surface crystalline nitrates would decompose into nitrites and O_2 trapped in micropores. In their scenario, the O_2 was liberated by the GEx. However, they required a 10-15 wt.% nitrates plus O_2 trapping.

A simpler explanation is that the atmosphere dry deposits PNA and so creates surficial peroxy nitrites or peroxy nitrates. In aqueous solution, peroxy nitrate decomposes at a neutral or alkaline pH:



An alkaline pH was measured by the Wet Chemistry Laboratory (WCL) experiment on the Phoenix Lander [11].

If peroxy nitrate is responsible, liberation of ~ 770 nmol of O_2 per cm^{-3} soil from the GEx implies only ~ 0.005 wt% NO_4^- , assuming a soil density of

$1.15 \pm 0.15 \text{ g/cm}^{-3}$ [12]. Possibly, much peroxy nitrate or derived nitrate or nitrite is destroyed through reactions and UV decomposition that recycles nitrogen volatiles back to the atmosphere. Also, dry deposition of any volcanic SO_2 during the Amazonian would destroy nitrates, releasing nitrogen oxides [13].

PNA releases halogen volatiles when it reacts with halides [14]. In the atmosphere, chlorine volatiles liberated from chlorides could be oxidized into perchlorates. Over geologic time, such a cycle might catalyze the conversion of chloride to perchlorate and allow a build up of perchlorate, even in the absence of volcanic chlorine gases.

4. Conclusions

The dry deposition of PNA (HO_2NO_2) dominates the removal of nitrogen species from the atmosphere of Mars. The formation of peroxy nitrates and its products might explain the presence of thermally labile oxidants in the martian soil. Furthermore, the interaction of PNA with chloride minerals might release chlorine volatiles, allowing their cyclic atmospheric oxidation to perchlorates even in the absence of volcanic chlorine gases.

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