



New insights into martian atmospheric chemistry



C.S. Boxe^{a,b,c,d,*}, J.S. Francisco^e, R.-L. Shia^f, Y.L. Yung^f, H. Nair^g, M.-C. Liang^{h,i}, A. Saiz-Lopez^j

^a Earth and Space Science Division, NASA's Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, USA

^b Medgar Evers College of the City University of New York, Brooklyn, NY 11225, USA

^c CUNY Graduate Center, Chemistry Division, Manhattan, NY 10016, USA

^d CUNY Graduate Center, Earth and Environmental Science Division, Manhattan, NY 10016, USA

^e Department of Chemistry and Earth and Atmospheric Sciences, Purdue University, West Lafayette, IN 47907, USA

^f Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA

^g Johns Hopkins Applied Physics Laboratory, Laurel, MD 20273, USA

^h Research Center for Environmental Studies, Academia Sinica, Institute of Astronomy, National Central University, Taiwan

ⁱ Institute of Astronomy and Astrophysics, Academia Sinica, Taipei, Taiwan

^j Atmospheric Chemistry and Climate Group, Institute of Physical Chemistry Rocasolano, CSIC, Madrid, Spain

ARTICLE INFO

Article history:

Received 4 May 2014

Revised 18 July 2014

Accepted 18 July 2014

Available online 4 August 2014

Keyword:

Mars

Atmospheres, chemistry

Atmospheres, composition

ABSTRACT

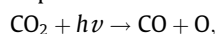
HO_x radicals are produced in the martian atmosphere by the photolysis of water vapor and subsequently participate in catalytic cycles that recycle carbon dioxide (CO₂) from its photolysis product carbon monoxide (CO), providing a qualitative explanation for the stability of its atmosphere. Balancing CO₂ production and loss based on our current understanding of martian gas-phase chemistry has, however, proven to be difficult. The photolysis of O₃ produces O(¹D), while oxidation of CO produces HOCO radicals, a new member of the HO_x family. The O(¹D) quantum yield has recently been updated, which quantifies non-zero quantum yields in the Huggins bands. In Earth's atmosphere HOCO is considered to be unimportant since it is quickly removed by abundant oxygen molecules. The smaller amount of O₂ in the Mars' atmosphere causes HOCO's lifetime to be longer in Mars' atmosphere than Earth's (3 × 10⁻⁵ s to 1.2 days from Mars's surface to 240 km, respectively). Limited kinetic data on reactions involving HOCO prevented consideration of its reactions directly in atmospheric models. Therefore, the impact of HOCO reactions on martian chemistry is currently unknown. Here, we incorporate new literature rate constants for HOCO chemistry and an updated representation of the O(¹D) quantum yield in the Caltech/JPL 1-D photochemical model for Mars' atmosphere. Our simulations exemplify perturbations to NO_y, HO_x, and CO_x species, ranging from 5% to 50%. The modified O(¹D) quantum yield and new HOCO chemistry cause a 10% decrease and a 50% increase in OH and H₂O₂ total column abundances, respectively. At low altitudes, HOCO production contributes 5% towards CO₂ production. Given recent experimentally-obtained branching ratios for the oxidation of CO, HOCO may contribute up to 70% toward the production of NO_y, where HO_x and NO_y species are enhanced up to a factor 3, which has implications for rethinking the fundamental understanding of NO_y, HO_x, and CO/CO₂ cycling on Mars. Two new reaction mechanisms for converting CO to CO₂ using HOCO reactions are proposed, which reveal that H₂O₂ is more intimately coupled to CO_x chemistry. Our simulations are in good agreement with satellite/spacecraft measurements of CO and H₂O₂ on Mars.

Published by Elsevier Inc.

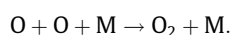
1. Introduction

Mars continues to be a test-bed for space exploration for finding extraterrestrial life. At present, finding life on Mars may not be limited by essential life nutrients, such as water and nitrogen

(Boxe et al., 2012a,b). Its atmosphere is comprised primarily of carbon dioxide (Owen et al., 1977), approximately ~95%, which is readily photolyzed by solar ultraviolet radiation below 205 nm to produce carbon monoxide (CO) and atomic oxygen (O):



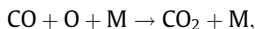
where atomic oxygen forms O₂ via the following reaction:



Once CO₂ is converted into CO and O, it is difficult to restore it. This is primarily due to the fact that the following reaction,

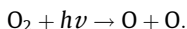
* Corresponding author. Addresses: Medgar Evers College of the City University of New York, Brooklyn, NY 11225, USA and CUNY's Graduate Center's Chemistry and Earth and Environmental Science Divisions, Manhattan, NY 10016, USA.

E-mail addresses: boxeman3@gmail.com, cboxe@mec.cuny.edu (C.S. Boxe).



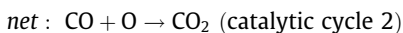
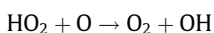
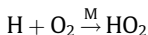
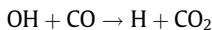
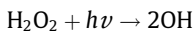
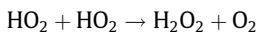
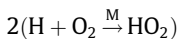
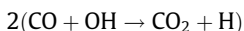
is spin-forbidden, and its three-body reaction rate coefficient is many orders of magnitude slower than the formation channel for O_2 shown above. Therefore, the net result of the of CO_2 photolysis is $2\text{CO}_2 \rightarrow 2\text{CO} + \text{O}_2$.

Within the context of a pure CO_2 atmosphere, the amounts of CO and O_2 would undoubtedly be very large, even when considering the photodissociation of O_2 :

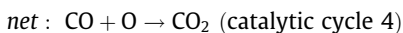
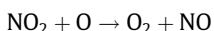
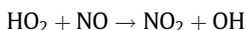
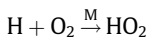
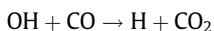
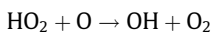
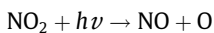
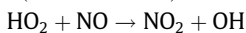
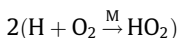
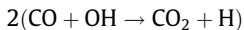


Specifically, this scenario yields CO and O_2 mixing ratios of 7.7×10^{-2} and 3.8×10^{-2} , respectively, and a CO: O_2 ratio of 2:1, which is in contradiction to the observed mixing ratios (7.0×10^{-4} for CO and 1.3×10^{-3} for O_2) and ratio of 0.5 (Yung and Demore, 1999). This suggests that another process stabilizes the observed CO_2 concentration of the martian atmosphere.

The stability of CO_2 in the martian atmosphere appeared to be a contradiction to known chemical kinetics for a pure CO_2 atmosphere, where for Mars, there was substantially smaller amounts of CO and O_2 – previously termed the CO_2 stability problem. It is well known that HO_x (H, OH, HO_2) chemistry plays an important role in stabilizing the CO_2 dominated atmosphere of Mars (McElroy and Donahue, 1972; Parkinson and Hunten, 1972). According to chemical mechanisms proposed by McElroy and Donahue (1972) (catalytic cycle 1) and Parkinson and Hunten (1972) (catalytic cycle 2), CO is then effectively converted back to CO_2 via reactions with HO_x .



McElroy and Donahue (1972) and Parkinson and Hunten (1972) recognized that the small amount of water vapor in Mars's atmosphere could play a fundamental role in atmospheric photochemical processes. Since these seminal investigations, the only significant addition involved the reaction of HO_2 with NO to yield NO_2 and OH, which introduced 2 new chemical schemes for the oxidation of CO to CO_2 (Nair et al., 1994; Yung and Demore, 1999).



Since Nair et al. (1994), there has not been any significant update on addressing the CO– CO_2 cycling on Mars. The $\text{O}(^1\text{D})$ quantum yield has recently been updated, which quantifies nonzero quantum yields in the Huggins bands (Matsumi et al., 2002). In addition, it is also known that the OH + CO reaction produces HOCO, a radical species, whose impact has never been considered in the martian atmosphere, given the once limited kinetic data on reactions involving HOCO (Petty et al., 1993; Olkhov et al., 2001; Mielke et al., 2003; Yu et al., 2005). We, therefore, utilize the Caltech/JPL 1-D photochemical model for Mars to look at the impact on the chemical state of its atmosphere via the inclusion of updated $\text{O}(^1\text{D})$ quantum yields (Matsumi et al., 2002) and HOCO chemistry (Fulle et al., 1996; Sears et al., 1992) (Table 1). Firstly, the photochemical model setup is briefly described; thereafter, the impact on NO_y , HO_x , and CO_x chemistry are discussed in Section 3.

2. Photochemical model setup

We utilize the Caltech/JPL one-dimensional (1-D) photochemical kinetics model for a latitude of 30° versus season, which is similar to that used by Yung et al. (1988) and Nair et al. (1994) to study the, overall, photochemical state of the martian atmosphere. A detailed description of the 1-D photochemical model can be found in Nair et al. (1994); we, therefore, only provide a short description of the model. Specifically, it incorporates Mars atmospheric O_x , CO_x , HO_x , and NO_y chemistry in the presence of vertical diffusive transport and allows for time-dependent calculations. This model is an update of the Nair et al. (1994) model. It solves the 1-D continuity equation,

$$\frac{\partial n_i}{\partial t} + \frac{\partial \Phi_i}{\partial z} = P_i - L_i,$$

(n_i , Φ_i , P_i , and L_i are the concentration, vertical diffusive flux, and chemical production and loss terms, respectively, for species i (Allen et al., 1981) for 29 species (O, $\text{O}(^1\text{D})$, O_2 , O_3 , N, $\text{N}(^2\text{D})$, N_2 , N_2O , NO, NO_2 , NO_3 , N_2O_5 , HNO_2 , HNO_3 , HO_2NO_2 , H, H_2 , H_2O , OH, HO_2 , H_2O_2 , CO, CO_2 , O^+ , O_2^+ , CO_2^+ , and CO_2H^+) in 177 reactions from the surface to the exosphere at 240 km (with 2 km resolution) in 121 levels. In the diurnally-averaged 1-D photochemical model, the steady-state solution is solved after allowing $\frac{\partial n_i}{\partial t} \rightarrow 0$. The vertical flux is given by

$$\Phi_i = -D \left(\frac{dn_i}{dz} + \frac{n_i}{H_i} + \frac{n_i(1 + \alpha)}{T} \frac{dT}{dz} \right) - K \left(\frac{dn_i}{dz} + \frac{n_i}{H_i} + \frac{n_i}{T} \frac{dT}{dz} \right),$$

where D_i is the molecular diffusion coefficient of species i through the background atmosphere, H_i is the scale height of species i , T is the temperature, α is the thermal diffusion factor (which we take to be zero), K is the eddy diffusion coefficient, and H is the scale height of the background atmosphere.

Table 1

New reactions included in the JPL/Caltech 1-D Photochemical Mars Model. Rate coefficients are given in $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ for bimolecular and $\text{cm}^6 \text{molecule}^{-2} \text{s}^{-1}$ for termolecular reactions.

Reaction	Rate coefficient	Reference
R_1 OH + CO + M \rightarrow M + HCO ₂	$k_0 = 5.90\text{E}-33$ $(T/300)^{-1.4}$	Sander et al. (2006)
R_2 HCO ₂ + O ₂ \rightarrow HNO ₂ + CO ₂	2.00×10^{-12}	Sander et al. (2006)
R_3 HCO ₂ + HO ₂ \rightarrow H ₂ O ₂ + CO ₂	5.80×10^{-11}	Yu et al. (2008)
R_4 HCO ₂ + HO ₂ \rightarrow 2O ₂ + CO ₂	6.50×10^{-12}	Yu et al. (2008)
R_5 HCO ₂ + H \rightarrow H ₂ + CO ₂	1.00×10^{-10}	Yu and Francisco (2008)
R_6 HCO ₂ + H \rightarrow H ₂ O + CO	4.00×10^{-12}	Yu and Francisco (2008)
R_7 HCO ₂ + OH \rightarrow H ₂ O + CO ₂	1.00×10^{-11}	Yu et al. (2005)
R_8 HCO ₂ + NO \rightarrow HNO ₂ + CO	2.00×10^{-12}	Olkhov et al. (2001)

Download English Version:

<https://daneshyari.com/en/article/8137591>

Download Persian Version:

<https://daneshyari.com/article/8137591>

[Daneshyari.com](https://daneshyari.com)