

Chemical markers of possible hot spots on Mars

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[1] Although there is no evidence of active volcanism on Mars today, “localized” outgassing sources, the hot spots, may not be ruled out. If outgassing does occur somewhere on Mars, water, carbon dioxide, sulfur species, methane, and to a lesser extent, halogens would be the likely molecules of outgassing, based on terrestrial analogs. The sulfur species, methane, and halogens have not been detected in the Martian atmosphere, but the observations were averaged over large areas, which could result in substantial dilution in abundances. If the interpretation of certain Mars Global Surveyor images indicating recent ground water seepage and surface runoff [Malin and Edgett, 2000] is correct, it may imply that Mars could still be active internally in some places from time to time, and outgassing of the abovementioned species may occur with or without the water seepage. Moreover, if the tentative detection of formaldehyde (CH₂O) in the equatorial region of Mars [Korablev *et al.*, 1993] is confirmed by future observations, it would imply at least local outgassing of methane, whose oxidation results in the formation of CH₂O. Considering the possibility of outgassing from some localized hot spots, we have developed a one-dimensional photochemical model that includes methane (CH₄), sulfur dioxide (SO₂), and hydrogen sulfide (H₂S), starting with their current “global average” upper limits of 0.02, 0.1, and 0.1 ppm at the surface, respectively, and then progressively increasing their abundances above possible hot spots. We find that the introduction of methane into the Martian atmosphere results in the formation of mainly formaldehyde, methyl alcohol (CH₃OH), and ethane (C₂H₆), whereas the introduction of the sulfur species produces mainly sulfur monoxide (SO) and sulfuric acid (H₂SO₄). The effect of outgassed halogens on the Martian atmosphere is found to be negligible. Depending upon the flux of outgassed molecules from possible hot spots, some of these species and the resulting new molecules may be detectable locally, either by remote sensing or in situ measurements. *INDEX TERMS:* 5405 Planetology: Solid Surface Planets: Atmospheres—composition and chemistry; 6225 Planetology: Solar System Objects: Mars; 0370 Atmospheric Composition and Structure: Volcanic effects (8409); 0317 Atmospheric Composition and Structure: Chemical kinetic and photochemical properties; 5480 Planetology: Solid Surface Planets: Volcanism (8450); *KEYWORDS:* Mars, photochemistry, hot spot, outgassing, biomarkers, sulfur dioxide

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1. Introduction

[2] Based on the record of cratering densities in the calderas and along the flanks of volcanoes, it has been suggested that the volcanoes in the Tharsis region of Mars were active in recent geologic time, perhaps within the past few hundred million years. Although there is no evidence of volcanism on Mars today, outgassing from small, localized sources, the hot spots, may not be ruled out. Typically, carbon dioxide, water vapor, sulfur dioxide (SO₂), hydrogen sulfide (H₂S), methane (CH₄), and to a lesser extent,

halogens are outgassed from terrestrial hot spots [Walker, 1997]. On Mars, sulfur and halogen species have not been detected in the atmosphere, and only a tentative detection of one hydrocarbon, formaldehyde (CH₂O, H₂CO), has been reported in the equatorial region during northern spring [Korablev *et al.*, 1993]. If the CH₂O detection is correct, its existence could imply a large flux of methane into the Martian atmosphere. Methane could either be abiotic in nature or could be released as a metabolic by-product by any subsurface bacteria that use the readily available Martian H₂ or CO as an energy source. However, methane has not yet been detected on Mars. The nondetection of methane and other possible outgassing species should be viewed with some caution, as the observations of such species

represent averages over large areas, typically the disk or the hemisphere of Mars so that small localized outgassing sources, especially if transient, could very well go undetected. Furthermore, if the suggestion of recent ground water seepage and surface runoff, particularly at the middle and high latitudes as interpreted from certain Mars Global Surveyor images [Malin and Edgett, 2000], is correct, this too may imply that even now Mars could be active from time to time at least in some places. With the above in mind, and due to considerable interest in the question of extinct or extant life on Mars, we have developed a one-dimensional photochemical model, considering the possibility that methane, sulfur dioxide, hydrogen sulfide, and halogens from any outgassing sources may be introduced into the Martian atmosphere. From this model we predict the abundances of the various new molecules that are expected to be formed in the ensuing atmospheric chemistry, in the hope of guiding future remote sensing and in situ measurements of the chemical markers of possible hot spots on Mars.

[3] The photochemical model for hot spots discussed in this paper assumes the “normal” Martian atmosphere model of *Atreya and Gu* [1994] as a starting point. In general terms, the *Atreya and Gu* [1994] model is similar to the models of *Krasnopolsky* [1993] and *Nair et al.* [1994]. *Krasnopolsky* [1993] includes SO_2 in his model, but that study is preliminary and considers only a very small amount of SO_2 released from the airborne dust. In their one-dimensional, globally averaged photochemical model of Mars, *Summers et al.* [2002] consider several biogenically produced trace species including CH_4 and H_2S . In this model they calculate, for example, a methane abundance that is roughly comparable to the global average upper limit for this species. In the present work, we introduce SO_2 , H_2S , and CH_4 into the Martian atmosphere from localized outgassing sources, the hot spots. We begin with their current global average upper limits and then consider progressively larger abundances over the hot spots. We do not consider halogens in our model. The present global upper limit of hydrogen chloride (2×10^{-9}) [*Krasnopolsky et al.*, 1997], which is presumably the most abundant halogen, is already much smaller than that of other possible outgassing species. In terrestrial outgassing sources, chlorine compounds (HCl , Cl_2 , etc.) comprise a small fraction of SO_2 or the total atmospheric CH_4 [*Walker*, 1997]. In view of the likely negligible amounts of any outgassed halogens and the fact that even their photolysis would be shielded by the copious amounts of CO_2 in the Martian atmosphere, the halogens are not expected to play a significant role in the hot spot chemistry of Mars. In the following paragraphs, we describe first the photochemical model and then discuss the results of numerical computations corresponding to the hot spots.

2. Photochemical Model

[4] Photochemical models have been used previously to study the distribution of molecules in the atmosphere of Mars [*Krasnopolsky*, 1993; *Atreya and Gu*, 1994; *Nair et al.*, 1994]. In this paper we have developed a new one-dimensional photochemical model for Mars to investigate the consequence of possible hot spots. The model solves for each chemical species the steady state continuity-diffusion equations using finite-difference techniques. The density of

each species as a function of altitude is calculated from the ground up to 220 km. The solar flux, temperature profile, and eddy diffusion coefficients are all global and seasonal averaged values taken from *Atreya and Gu* [1994]. The dust optical depth is taken to be 0.4, which is typical for Mars [*Krasnopolsky*, 1993]. Water content is the global averaged value of 150 ppm or 10 μm at the surface. The pressure at the surface is 6.10 mbar, and the atmospheric density is computed assuming hydrostatic equilibrium. Concentration of CO_2 at any given altitude is held fixed. Molecular nitrogen is included as a background gas. The lower boundary conditions are mixing ratios of 2.7×10^{-2} for N_2 , 1.50×10^{-4} for H_2O , and fixed concentration of CO_2 based on surface pressure and temperature. Upper boundary conditions are H and H_2 effusion velocities of 3.1×10^3 and $3.4 \times 10^1 \text{ cm s}^{-1}$, respectively, and escape flux of atomic oxygen of $1.2 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$ [*Nair et al.*, 1994] to balance the escape rate of hydrogen. Fluxes of all other species are zero at both boundaries. Condensation of H_2O and H_2O_2 are considered; however, in the present model H_2O_2 is always found to be subsaturated. The basic photochemical reactions for the normal, i.e., non-hot spot, atmosphere are listed in Table 1.

[5] New species and reactions added for calculation of hot spot chemistry are described in the next three sections. Since the photolysis of methane is spectrally and spatially removed from the photolysis of SO_2 and H_2S , we find that there is little significant interaction between the sulfur species and the hydrocarbon species. This is further amplified by the fact the S abundance is extremely low at all altitudes to permit any appreciable product density upon reaction with the hydrocarbons, even if the (unmeasured) rate of $\text{S} + \text{CH}_3$ reaction were fast (other sulfur reactions were found to be even less important). In view of the above, we consider the hydrocarbon and the sulfur chemical schemes separately.

3. Sulfur Chemistry

[6] *Farquhar et al.* [2000] and *Wänke and Dreibus* [1994] have speculated on the presence of SO_2 and H_2S in the atmosphere of Mars, generally in the past. In the current work, we investigate in detail the photochemistry of sulfur species in Martian atmosphere. The main reactions of sulfur chemistry and their rate coefficients are listed in Table 2. The principal reaction pathways are illustrated in Figure 1 and will be discussed later in this section.

[7] The upper limits of SO_2 and H_2S are 0.1 ppm each for globally averaged observations [*Maguire*, 1977]. In the model we first study the photochemistry of each of these two gases as independent outgassing species. We start with SO_2 as the only outgassed species, with 0.1 ppm at the surface. In subsequent model runs we increase its concentration gradually until it reaches 10 ppm above the hot spot. We do the same with H_2S outgassing by itself. Then we assume both gases outgassing from the surface together and increase the concentration of each from 0.1 ppm to 100 ppm. Since the existence and nature of hot spots are speculative, we consider enhancement by up to a factor of 1000 over outgassing sources relative to the global upper limits of H_2S and SO_2 . However, enhancement factors are necessarily arbitrary. They could be lower or even greater, depending

Table 1. Basic Set of Photochemical Reactions Along With Their Rate Coefficients and References Used in the Model

	Reaction	Rate Coefficient ^a	Reference
(R1)	$\text{CO}_2 + h\nu \rightarrow \text{CO} + \text{O} \rightarrow \text{CO} + \text{O}(^1\text{D})$	$J(\text{CO}_2) = 1.4 \times 10^{-12},$ 7.9×10^{-7}	<i>Shemansky [1972], Lewis and Carver [1983], Atreya and Gu [1994]</i>
(R2)	$\text{O}_2 + h\nu \rightarrow 2\text{O} \rightarrow \text{O}(^1\text{D}) + \text{O}$	$J(\text{O}_2) = 8.9 \times 10^{-11},$ 9.0×10^{-7}	<i>Watanabe et al. [1953]</i>
(R3)	$\text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O}(^1\text{D}) \rightarrow \text{O}_2 + \text{O}$	$J(\text{O}_3) = 6.0 \times 10^{-5},$ 1.7×10^{-3}	<i>World Meteorological Organization (WMO) [1985]</i>
(R4)	$\text{H}_2\text{O} + h\nu \rightarrow \text{OH} + \text{H}$	$J(\text{H}_2\text{O}) = 2.0 \times 10^{-10},$ 1.6×10^{-6}	<i>Thompson et al. [1963]</i>
(R5)	$\text{HO}_2 + h\nu \rightarrow \text{OH} + \text{O}$	$J(\text{HO}_2) = 3.6 \times 10^{-6},$ 1.9×10^{-4}	<i>Okabe [1978]</i>
(R6)	$\text{H}_2\text{O}_2 + h\nu \rightarrow 2\text{OH}$	$J(\text{H}_2\text{O}_2) = 3.3 \times 10^{-6},$ 2.3×10^{-5}	<i>Okabe [1978]</i>
(R7)	$\text{O} + \text{O} + \text{M} \rightarrow \text{O}_2 + \text{M}$	$5.21 \times 10^{-35} e^{900/T}$	<i>Tsang and Hampson [1986]</i>
(R8)	$\text{O}(^1\text{D}) + \text{CO}_2 \rightarrow \text{O} + \text{CO}_2$	$7.41 \times 10^{-11} e^{120/T}$	<i>DeMore et al. [1997]</i>
(R9)	$\text{O}_2 + \text{O} + \text{M} \rightarrow \text{O}_3 + \text{M}$	$2.95 \times 10^{-28} T^{-2.3}$	<i>DeMore et al. [1997] for N₂</i>
(R10)	$\text{O}_3 + \text{O} \rightarrow 2\text{O}_2$	$8.2 \times 10^{-12} e^{-2060/T}$	<i>Atkinson et al. [1997]</i>
(R11)	$\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$	$5.16 \times 10^{-28} T^{-1.6}$	<i>DeMore et al. [1992]</i>
(R12)	$\text{H} + \text{O}_3 \rightarrow \text{OH} + \text{O}_2$	$1.4 \times 10^{-10} e^{-470/T}$	<i>DeMore et al. [1992]</i>
(R13)	$\text{H} + \text{H} + \text{M} \rightarrow \text{H}_2 + \text{M}$	$2.7 \times 10^{-31} T^{-0.6}$	<i>Baulch et al. [1992]</i>
(R14)	$\text{H}_2 + \text{O}(^1\text{D}) \rightarrow \text{OH} + \text{H}$	1.0×10^{-10}	<i>Gericke and Comes [1981]</i>
(R15)	$\text{H}_2\text{O} + \text{O}(^1\text{D}) \rightarrow 2\text{OH}$	2.2×10^{-10}	<i>DeMore et al. [1992]</i>
(R16)	$\text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H}$	$1.99 \times 10^{-17} T^{1.35} e^{365/T}$	<i>Larson et al. [1988]</i>
(R17)	$\text{OH} + \text{O} \rightarrow \text{O}_2 + \text{H}$	$2.2 \times 10^{-11} e^{120/T}$	<i>DeMore et al. [1992]</i>
(R18)	$\text{OH} + \text{O}_3 \rightarrow \text{O}_2 + \text{HO}_2$	$1.6 \times 10^{-12} e^{-940/T}$	<i>DeMore et al. [1997]</i>
(R19)	$\text{HO}_2 + \text{O} \rightarrow \text{OH} + \text{O}_2$	$2.9 \times 10^{-11} e^{200/T}$	<i>Atkinson et al. [1989]</i>
(R20)	$\text{HO}_2 + \text{O}_3 \rightarrow 2\text{O}_2 + \text{OH}$	$1.1 \times 10^{-14} e^{-500/T}$	<i>DeMore et al. [1997]</i>
(R21)	$\text{HO}_2 + \text{OH} \rightarrow \text{O}_2 + \text{H}_2\text{O}$	$4.8 \times 10^{-11} e^{250/T}$	<i>DeMore et al. [1997]</i>
(R22)	$\text{HO}_2 + \text{H} \rightarrow 2\text{OH}$	7.2×10^{-11}	<i>Atkinson et al. [1989]</i>
	$\rightarrow \text{H}_2 + \text{O}_2$	5.6×10^{-12}	<i>Atkinson et al. [1989]</i>
	$\rightarrow \text{H}_2\text{O} + \text{O}$	2.4×10^{-12}	<i>Atkinson et al. [1989]</i>
(R23)	$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$1.5 \times 10^{-12} e^{-12/T}$	<i>Christensen et al. [2002]</i>
(R24)	$\text{H}_2\text{O}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2$	$2.91 \times 10^{-12} e^{-161/T}$	<i>DeMore et al. [1992]</i>
(R25)	$\text{N}_2 + \text{O}(^1\text{D}) \rightarrow \text{N}_2 + \text{O}$	$1.8 \times 10^{-11} e^{110/T}$	<i>DeMore et al. [1997]</i>

^aUnits are s^{-1} for photolysis reactions, $\text{cm}^3 \text{s}^{-1}$ for two-body reactions, and $\text{cm}^6 \text{s}^{-1}$ for three-body reactions. Photolysis rate coefficients are given at 10 km and 200 km.

upon the size, strength, and the duration of the source. For example, gases released from a 1 km diameter source may be diluted by a factor of as much as 10^8 when spread uniformly over the Martian surface. The results of a few investigative runs are summarized in Table 3.

[8] Models A and B are cases with only SO_2 outgassing, with 0.1 ppm and 10 ppm mixing ratio at the surface, respectively. Models C and D are cases with only H_2S outgassing, 0.1 ppm and 10 ppm surface mixing ratio, respectively. Models E, F, and G correspond to the cases where both gases are outgassed, with 0.1 ppm, 10 ppm, and 100 ppm surface mixing ratio of each species, respectively. Only for the purpose of illustration, the result of a “nominal” case, Model G, is summarized here. The resulting mixing ratios of SO_2 , H_2S , and SO at 10 km are 1.7×10^{-4} , 1.8×10^{-5} , and 1.7×10^{-7} , respectively (see Table 3). These are the most abundant species and possibly detectable. The number densities and mixing ratios of important sulfur species are plotted in Figure 2.

[9] Once in the atmosphere, sulfur dioxide is photodissociated to produce sulfur monoxide (SO). Sulfur monoxide can be photodissociated to form sulfur atoms. The reaction of SO with O_2 or OH recycles sulfur atoms back to SO_2 (R33, R35), while the reaction with ozone (O_3) forms sulfur trioxide (SO_3 , R34). Sulfur trioxide quickly combines with water vapor to form sulfuric acid (H_2SO_4 , R39).

The saturation vapor pressure measurements of H_2SO_4 [Stull, 1947] can be fitted by the following expression: $\log_{10} P(\text{H}_2\text{SO}_4) = -3954.90/T + 9.4570$, for temperature range approximately between 420 K and 580 K, where $P(\text{H}_2\text{SO}_4)$ is the saturation vapor pressure of H_2SO_4 in mmHg. Extrapolating this expression to the lower temperatures of the Martian atmosphere, it is found that the H_2SO_4 produced from photochemistry would condense in the lower atmosphere. For example, $P(\text{H}_2\text{SO}_4) = 4.8 \times 10^{-11}$ mmHg at 200 K, an extremely low value. Without condensation, H_2SO_4 mixing ratio reaches a value of approximately 40 ppm in Model G where SO_2 and H_2S are each 100 ppm above the hot spot. Taking condensation into account, the resulting column abundance of H_2SO_4 above 10 km is $2.1 \times 10^{12} \text{ cm}^{-2}$, or approximately 0.2 ppb, too low to be plotted in Figure 2. However, the actual H_2SO_4 vapor-mixing ratio would depend on a number of factors, including the abundance of water, concentration of sulfuric acid, degree of supersaturation, and the range of validity of the saturation vapor pressure relationship.

[10] We have found that the outgassing of H_2S alone gives similar composition as the outgassing of SO_2 (see Table 3). This is due to the fact that the outgassed H_2S is rapidly converted to SO_2 (see Figure 1). After H_2S is released into the atmosphere, it undergoes photodissociation to form mercapto radical HS (R28). The photodissociation

Table 2. Photochemical Reactions of Sulfur Species Along With Their Rate Coefficients and References Studied in the Model

	Reaction	Rate Coefficient ^a	Reference
(R26)	$\text{SO} + h\nu \rightarrow \text{S} + \text{O}$	$J(\text{SO}) = 7.4 \times 10^{-9}$ 8.6×10^{-5}	Phillips [1981]
(R27)	$\text{SO}_2 + h\nu \rightarrow \text{SO} + \text{O}$	$J(\text{SO}_2) = 6.1 \times 10^{-18}$ 4.5×10^{-5}	Okabe [1971], Welge [1974]
(R28)	$\text{SO}_3 + h\nu \rightarrow \text{SO}_2 + \text{O}$ $\rightarrow \text{SO}_2 + \text{O}(^1\text{D})$	$J(\text{SO}_3) = 1.2 \times 10^{-7}$ 2.1×10^{-4}	Okabe [1978]
(R29)	$\text{H}_2\text{S} + h\nu \rightarrow \text{HS} + \text{H}$	$J(\text{H}_2\text{S}) = 1.7 \times 10^{-6}$ 7.2×10^{-5}	Okabe [1978]
(R30)	$\text{S} + \text{O}_2 \rightarrow \text{SO} + \text{O}$	2.3×10^{-12}	DeMore et al. [1997]
(R31)	$\text{S} + \text{O}_3 \rightarrow \text{SO} + \text{O}_2$	1.2×10^{-11}	DeMore et al. [1997]
(R32)	$\text{SO} + \text{O} + \text{M} \rightarrow \text{SO}_2 + \text{M}$	5.10×10^{-31}	Singleton and Cvetanovic [1988]
(R33)	$\text{SO} + \text{O}_2 \rightarrow \text{SO}_2 + \text{O}$	2.6×10^{-13}	DeMore et al. [1997]
(R34)	$\text{SO} + \text{O}_3 \rightarrow \text{SO}_3 + \text{O}_2$	3.6×10^{-12}	DeMore et al. [1997]
(R35)	$\text{SO} + \text{OH} \rightarrow \text{SO}_2 + \text{H}$	8.59×10^{-11}	DeMore et al. [1997]
(R36)	$\text{SO} + \text{SO} \rightarrow \text{SO}_2 + \text{S}$	$5.8 \times 10^{-12} e^{-1760/T}$	Yung and DeMore [1999]
(R37)	$\text{SO}_2 + \text{O} + \text{M} \rightarrow \text{SO}_3 + \text{M}$	$1.61 \times 10^{-42} T^{3.6}$	DeMore et al. [1997]
(R38)	$\text{SO}_2 + \text{OH} + \text{M} \rightarrow \text{HSO}_3 + \text{M}$	$4.39 \times 10^{-23} T^{-3.3}$	DeMore et al. [1997]
(R39)	$\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$	1.20×10^{-15}	Reiner and Arnold [1994]
(R40)	$\text{SO}_3 + \text{SO} \rightarrow 2\text{SO}_2$	1.99×10^{-15}	Chung et al. [1975]
(R41)	$\text{HSO}_3 + \text{O}_2 \rightarrow \text{SO}_3 + \text{HO}_2$	$1.3 \times 10^{-12} e^{-330/T}$	DeMore et al. [1997]
(R42)	$\text{HS} + \text{O} \rightarrow \text{SO} + \text{H}$	1.60×10^{-10}	DeMore et al. [1997]
(R43)	$\text{HS} + \text{O}_3 \rightarrow \text{HSO} + \text{O}_2$	$9.00 \times 10^{-12} e^{-280/T}$	DeMore et al. [1997]
(R44)	$\text{HS} + \text{H} \rightarrow \text{S} + \text{H}_2$	2.16×10^{-11}	Nicholas et al. [1979]
(R45)	$\text{HS} + \text{HO}_2 \rightarrow \text{HSO} + \text{OH}$	1.0×10^{-11}	Stachnik and Molina [1987]
(R46)	$\text{HS} + \text{HS} \rightarrow \text{H}_2\text{S} + \text{S}$	4.00×10^{-11}	Stachnik and Molina [1987]
(R47)	$\text{H}_2\text{S} + \text{O} \rightarrow \text{HS} + \text{OH}$	9.21×10^{-12}	DeMore et al. [1997]
(R48)	$\text{H}_2\text{S} + \text{H} \rightarrow \text{HS} + \text{H}_2$	$1.96 \times 10^{-17} T^{2.10} e^{-352/T}$	Yoshimura et al. [1992]
(R49)	$\text{H}_2\text{S} + \text{OH} \rightarrow \text{HS} + \text{H}_2\text{O}$	$6.00 \times 10^{-12} e^{-75/T}$	DeMore et al. [1997]
(R50)	$\text{HSO} + \text{O}_2 \rightarrow \text{SO}_2 + \text{OH}$	1.7×10^{-15}	Bulatov et al. [1986]
(R51)	$\text{HSO} + \text{O}_3 \rightarrow \text{HS} + 2\text{O}_2$	$2.54 \times 10^{-13} e^{-384/T}$	Wang and Howard [1990]

^aUnits are s^{-1} for photolysis reactions, $\text{cm}^3 \text{s}^{-1}$ for two-body reactions, and $\text{cm}^6 \text{s}^{-1}$ for three-body reactions. Photolysis rate coefficients are given at 10 km and 200 km.

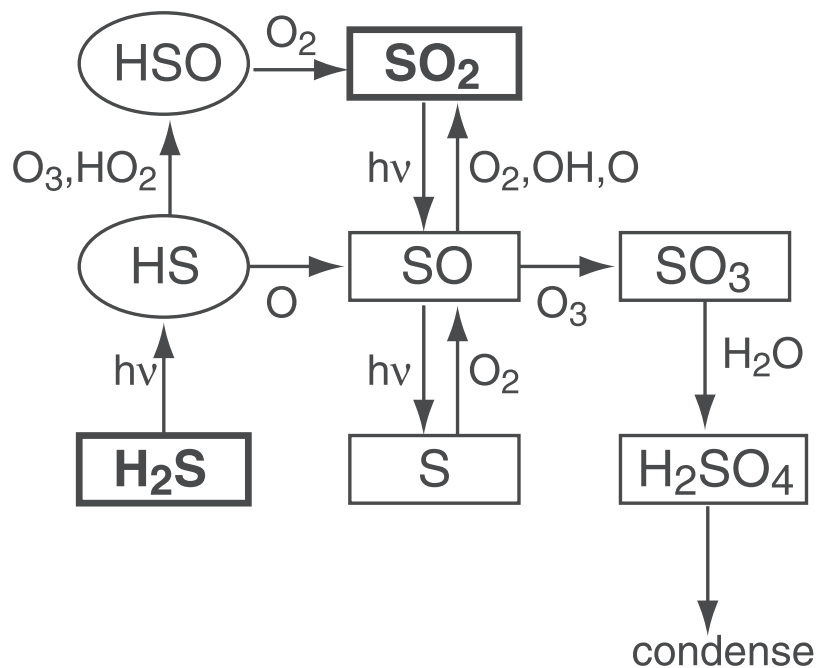


Figure 1. Schematic diagram illustrating the important reaction pathways of sulfur species in the Martian atmosphere. Stable species are in rectangles, radicals are in ovals, and outgassing species are in bold.

Table 3. Model Results for Sulfur Chemistry in the Martian Atmosphere^a

Model	Outgassing Species		Major Photochemical Products						
	Surface Mixing		SO ₂		H ₂ S		SO		
	SO ₂	H ₂ S	Mixing	Column	Mixing	Column	Mixing	Column	
A	10 ⁻⁷	0	7.4 × 10 ⁻⁸	5.4 × 10 ¹⁵	0	0	7.1 × 10 ⁻¹⁰	9.6 × 10 ¹⁴	
B	10 ⁻⁵	0	9.1 × 10 ⁻⁶	7.2 × 10 ¹⁷	0	0	1.7 × 10 ⁻¹⁰	2.4 × 10 ¹⁶	
C	0	10 ⁻⁷	6.0 × 10 ⁻⁸	5.4 × 10 ¹⁵	2.1 × 10 ⁻⁸	7.4 × 10 ¹⁴	6.7 × 10 ⁻¹⁰	1.1 × 10 ¹⁵	
D	0	10 ⁻⁵	6.7 × 10 ⁻⁶	7.7 × 10 ¹⁷	2.9 × 10 ⁻⁶	1.3 × 10 ¹⁷	9.1 × 10 ⁻⁹	3.1 × 10 ¹⁶	
E	10 ⁻⁷	10 ⁻⁷	1.4 × 10 ⁻⁷	1.1 × 10 ¹⁶	2.3 × 10 ⁻⁸	7.9 × 10 ¹⁴	1.3 × 10 ⁻⁹	2.0 × 10 ¹⁵	
F	10 ⁻⁵	10 ⁻⁵	1.7 × 10 ⁻⁵	1.7 × 10 ¹⁸	3.0 × 10 ⁻⁶	1.3 × 10 ¹⁷	9.1 × 10 ⁻⁹	4.1 × 10 ¹⁶	
G	10 ⁻⁴	10 ⁻⁴	1.7 × 10 ⁻⁴	1.8 × 10 ¹⁹	1.8 × 10 ⁻⁵	7.4 × 10 ¹⁷	1.7 × 10 ⁻⁷	7.8 × 10 ¹⁶	
Photochemical lifetime			1.4 × 10 ⁷ s (180 days)			7.9 × 10 ⁵ s (9 days)		1.7 × 10 ⁴ s (4.6 hours)	

^aMixing ratios (labeled “mixing”) and the column abundances (in cm⁻², labeled “column”) are compared at 10 km in this listing. Lifetime of a species indicates the time to destroy all of that species in the atmosphere photochemically.

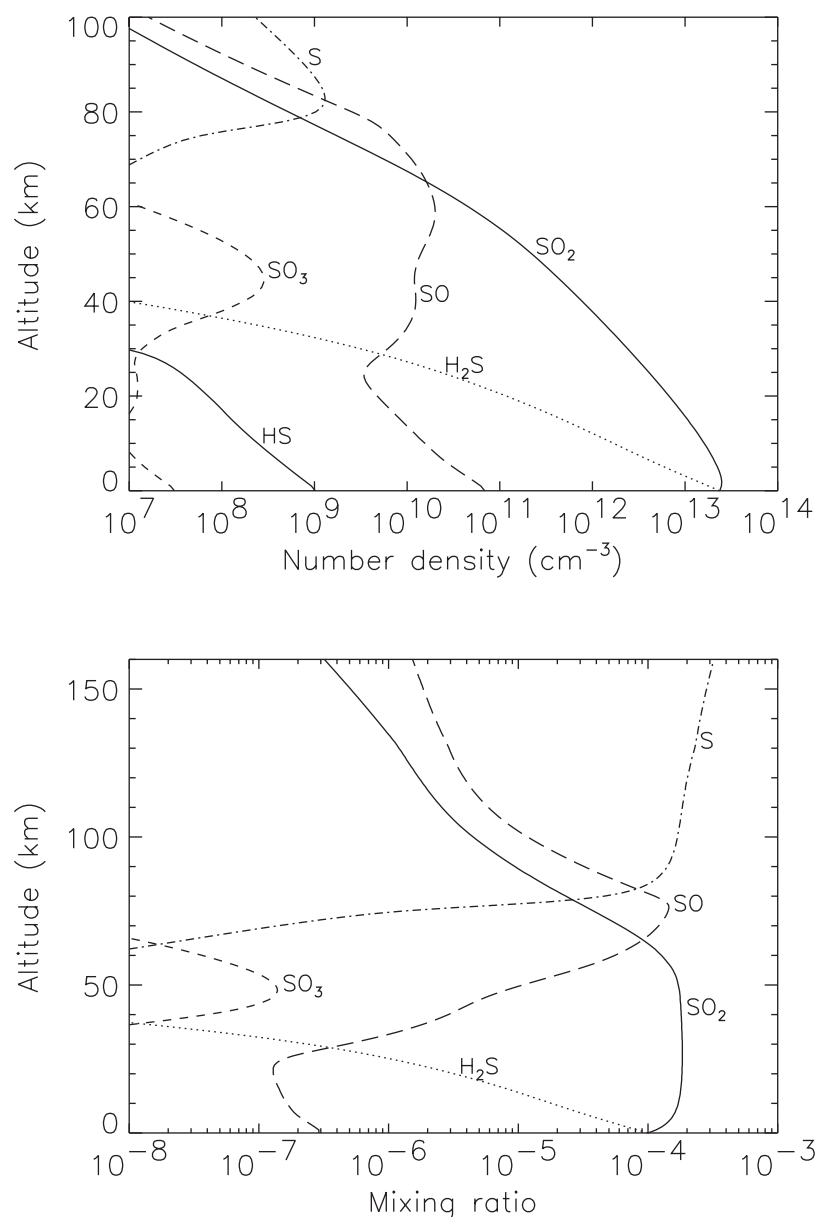


Figure 2. Number densities and mixing ratios versus altitude for important species calculated with 100 ppm each of H₂S and SO₂ at the surface of Mars (Model G).

Table 4. Photochemical Reactions of Hydrocarbon Species Along With Their Rate Coefficients and References Studied in the Model

	Reaction	Rate Coefficient ^a	Reference
(R52)	CH ₄ + hν → CH ₃ + H → ³ CH ₂ + 2H → ¹ CH ₂ + H ₂ → ¹ CH ₂ + 2H → CH + H + H ₂	$J(\text{CH}_4) = 0, 1.7 \times 10^{-6}$	Gladstone et al. [1996], Mordaunt et al. [1993], Heck et al. [1996]
(R53)	HCO + hν → CO + H	$J(\text{HCO}) = 6.9 \times 10^{-10},$ 6.0×10^{-8}	König et al. [1984], Hochanadel et al. [1980], Okabe [1978]
(R54)	CH ₂ O + hν → HCO + H → CO + H ₂ → CO + 2H	$J(\text{CH}_2\text{O}) = 2.5 \times 10^{-5},$ 4.6×10^{-5}	DeMore et al. [1992, 1990, 1987, 1985], Suto et al. [1986], Okabe [1978], Glicker and Stief [1971], Mentall et al. [1971], Gentieu and Mentall [1970]
(R55)	CH ₃ OH + hν → CH ₃ + OH → CH ₂ O + H ₂ → CH ₃ O + H	$J(\text{CH}_3\text{OH}) = 4.7 \times 10^{-8},$ 1.8×10^{-6}	Satyapal and Bersohn [1989], Nee et al. [1985], Person and Nicole [1971], Hagège et al. [1968]
(R56)	C ₂ H ₄ + hν → C ₂ H ₂ + H ₂ → C ₂ H ₂ + 2H	$J(\text{C}_2\text{H}_4) = 3.3 \times 10^{-9},$ 6.9×10^{-6}	Gladstone et al. [1996], Balko et al. [1992]
(R57)	C ₂ H ₆ + hν → C ₂ H ₂ + 2H ₂ → C ₂ H ₄ + H ₂ → C ₂ H ₄ + 2H → CH ₄ + ¹ CH ₂ → CH ₃ + CH ₃	$J(\text{C}_2\text{H}_6) = 0, 1.4 \times 10^{-6}$	Gladstone et al. [1996]
(R58)	H + CO + M → HCO + M	$5.30 \times 10^{-34} e^{-370/T}$	Baulch et al. [1994]
(R59)	CH + O ₂ → CO + OH → HCO + O	2.75×10^{-11} 2.75×10^{-11}	Baulch et al. [1992] Baulch et al. [1992]
(R60)	CH + H ₂ → CH ₃	$8.55 \times 10^{-11} T^{0.15}$	Fulle and Hippler [1997]
(R61)	CH + H ₂ O → CH ₂ OH	$9.49 \times 10^{-12} e^{380/T}$	Zabarnick et al. [1988]
(R62)	¹ CH ₂ + H → CH + H ₂	2.0×10^{-10}	Moses et al. [2000]
(R63)	¹ CH ₂ + H ₂ → ³ CH ₂ + H ₂ → CH ₃ + H	1.26×10^{-11} 9.24×10^{-11}	Braun et al. [1970], Langford et al. [1983]
(R64)	¹ CH ₂ + N ₂ → ³ CH ₂ + N ₂	$5.1 \times 10^{-13} T^{0.5}$	Ashfold et al. [1981]
(R65)	³ CH ₂ + CO ₂ → CH ₂ O + CO	1.40×10^{-14}	Darwin and Moore [1995]
(R66)	³ CH ₂ + O ₂ → CO + H ₂ O	4.00×10^{-13}	Tsang and Hampson [1986]
(R67)	³ CH ₂ + H → CH + H ₂	$5.18 \times 10^{-11} e^{675/T}$	Devriendt et al. [1995]
(R68)	CH ₃ + O → CH ₂ O + H	1.40×10^{-10}	Baulch et al. [1992]
(R69)	CH ₃ + O ₃ → products	$5.40 \times 10^{-12} e^{-220/T}$	DeMore et al. [1997]
(R70)	CH ₃ + H + M → CH ₄ + M	$1.71 \times 10^{-24} T^{-1.80}$	Baulch et al. [1994]
(R71)	CH ₃ + OH → CH ₂ OH + H → CH ₃ O + H	1.31×10^{-11} 1.60×10^{-10}	Fagerstrom et al. [1994] Fagerstrom et al. [1994]
(R72)	CH ₃ + OH + M → CH ₃ OH + M	$6.26 \times 10^{-18} T^{-3.8}$	Fagerstrom et al. [1994]
(R73)	CH ₃ + HO ₂ → CH ₄ + O ₂ → CH ₃ O + OH	5.99×10^{-12} 3.30×10^{-11}	Tsang and Hampson [1986] Tsong and Hampson [1986]
(R74)	CH ₃ + H ₂ O ₂ → CH ₄ + HO ₂	$2.00 \times 10^{-14} e^{-300/T}$	Tsang and Hampson [1986]
(R75)	CH ₃ + CH ₃ → C ₂ H ₆	$3.51 \times 10^{-7} T^{-7} e^{-1390/T}$	Baulch et al. [1994]
(R76)	CH ₄ + O → CH ₃ + OH	$1.15 \times 10^{-15} T^{1.56} e^{-4270/T}$	Baulch et al. [1992]
(R77)	CH ₄ + O(¹ D) → CH ₃ + OH → CH ₂ O + H ₂	1.13×10^{-10} 7.51×10^{-12}	DeMore et al. [1997] DeMore et al. [1997]
(R78)	CH ₄ + OH → CH ₃ + H ₂ O	$9.64 \times 10^{-13} e^{-1418/T}$	Sharkey and Smith [1993]
(R79)	CH ₄ + CH → C ₂ H ₄ + H	2.49×10^{-12}	Braun et al. [1967]
(R80)	HCO + O → OH + CO → CO ₂ + H	5×10^{-11} 5×10^{-11}	Baulch et al. [1992] Baulch et al. [1992]
(R81)	HCO + O ₂ → CO + HO ₂	$2.19 \times 10^{-12} e^{170/T}$	Nesbitt et al. [1999]
(R82)	HCO + H → CO + H ₂	1.5×10^{-10}	Baulch et al. [1992]
(R83)	HCO + HO ₂ → CH ₂ O + O ₂	5.0×10^{-11}	Tsang and Hampson [1986]
(R84)	CH ₂ O + O → HCO + OH	$6.85 \times 10^{-13} T^{0.57} e^{-1390/T}$	Baulch et al. [1992]
(R85)	CH ₂ O + H → HCO + H ₂	$2.1 \times 10^{-16} T^{1.62} e^{-1090/T}$	Baulch et al. [1994]
(R86)	CH ₂ O + OH → HCO + H ₂ O	1.00×10^{-11}	DeMore et al. [1997]
(R87)	CH ₂ OH + O → CH ₂ O + OH	1.50×10^{-10}	Grotheer et al. [1989]
(R87)	CH ₂ OH + O ₂ → CH ₂ O + HO ₂	9.1×10^{-12}	DeMore et al. [1997]
(R89)	CH ₂ OH + H → CH ₃ + OH → CH ₂ O + H ₂	1.60×10^{-10} 1.00×10^{-11}	Tsang [1987] Tsong [1987]
(R90)	CH ₃ O + O → CH ₂ O + OH → CH ₃ + O ₂	1.00×10^{-11} 2.51×10^{-11}	Tsang and Hampson [1986] Zellner [1987]
(R91)	CH ₃ O + O ₂ → CH ₂ O + HO ₂	$3.90 \times 10^{-14} e^{-900/T}$	DeMore et al. [1997]
(R92)	CH ₃ O + H → CH ₂ O + H ₂	3.01×10^{-11}	Baulch et al. [1992]
(R93)	CH ₃ O + HO ₂ → CH ₂ O + H ₂ O ₂	5.0×10^{-13}	Tsang [1987]
(R94)	CH ₃ OH + OH → CH ₂ OH + H ₂ O → CH ₃ O + H ₂ O	$2.39 \times 10^{-18} T^2 e^{423/T}$ $1.66 \times 10^{-11} e^{-854/T}$	Li and Williams [1996] Warnatz [1984]
(R95)	C ₂ H ₂ + O → products	$3.01 \times 10^{-11} e^{-1600/T}$	DeMore et al. [1997]

Table 4. (continued)

	Reaction	Rate Coefficient ^a	Reference
(R96)	$C_2H_2 + OH \rightarrow \text{products}$	$1.91 \times 10^{-12} e^{-233/T}$	Atkinson [1986]
(R97)	$C_2H_4 + O \rightarrow CH_2O + {}^3CH_2$	$8.30 \times 10^{-12} e^{-754/T}$	Westenberg and DeHaas [1969]
(R98)	$C_2H_4 + OH \rightarrow \text{products}$	$2.14 \times 10^{-12} e^{411/T}$	Atkinson [1986]
(R99)	$C_2H_6 + OH \rightarrow \text{products}$	$8.60 \times 10^{-12} e^{-1070/T}$	DeMore et al. [1997]

^aUnits are s^{-1} for photolysis reactions, $cm^3 s^{-1}$ for two-body reactions, and $cm^6 s^{-1}$ for three-body reactions. Photolysis rate coefficients are given at 10 km and 200 km.

process is very efficient and occurs all the way down to the surface. Mercapto radical quickly reacts with O_3 to form HSO (R43), which upon reaction with O_2 forms SO_2 (R50). The subsequent chemistry then follows that of SO_2 . Because there is no fast reaction that recycles sulfur atoms back to H_2S , the H_2S concentration decreases rapidly with altitude, and the sulfur atoms eventually combine with O_2 to form SO_2 . Therefore the mixing ratio of SO_2 increases slightly with altitude just above the surface (see Figure 2).

[11] It is also noted that the mixing ratio of atomic sulfur at high altitudes increases due to its smaller molecular weight relative to CO_2 . Unlike on Venus, carbonyl sulfide (OCS) does not get formed with SO_2 and H_2S outgassing, because the major reaction pathway that leads to the OCS production, $HS + CO \rightarrow OCS + H$, is found to be extremely slow under the martian atmospheric conditions of low temperature, and also the abundance of HS is quite small.

[12] The photochemical lifetime of SO_2 is about 1.4×10^7 s (180 days); for H_2S it is 7.9×10^5 s (9 days), and for SO it is 1.7×10^4 s (4.6 hours). In a relatively short time of an hour, ordinary convective processes alone can reduce the mixing ratios of outgassed species by factors of 10^4 – 10^5 approximately 50 km from the source, and the time for spreading the source material more or less uniformly over the planet (with corresponding dilution factor of $\sim 10^8$) would be approximately one year (N. Renno, personal communication, 2003). In view of these time scales and the above photochemical lifetimes of the species, detection of any sulfur species would indicate presence of currently active hot spot(s) in close proximity of the observation.

Unless the source flux is extremely large, detection far from a transient source would be unlikely due to dilution.

4. Hydrocarbon Chemistry

[13] Methane has not been detected on Mars. Since the observations represent an average over large areas, methane, like the sulfur species (section 3), could go undetected even if there was copious outgassing from a localized source, especially a transient one. We use the photochemical model to calculate the abundances of new species that are formed upon the introduction of CH_4 into the Martian atmosphere by outgassing. The new species included in the calculations are: CH, singlet methylene (1CH_2), triplet methylene (3CH_2), methyl radical (CH_3), CH_4 , HCO, formaldehyde (CH_2O), CH_2OH , CH_3O , methyl alcohol (CH_3OH), C_2H_2 , C_2H_4 , and ethane (C_2H_6). The list of important reactions is given in Table 4. The principal reaction pathways are illustrated in Figure 3 and will be discussed later in this section.

[14] The global average upper limit of methane is 0.02 ppm [Maguire, 1997]. Starting with 0.02 ppm of methane at the surface, we increase the concentration gradually in subsequent model runs up to 100 ppm above any possible hot spots. Larger or smaller enhancement factors may apply over hot spots, as discussed in the context of the sulfur species (section 3). Table 5 tabulates a sample of the model results. For the purpose of illustration, the result of a “nominal” case, Model L, is summarized here. In this case, the surface concentration of methane is assumed to be

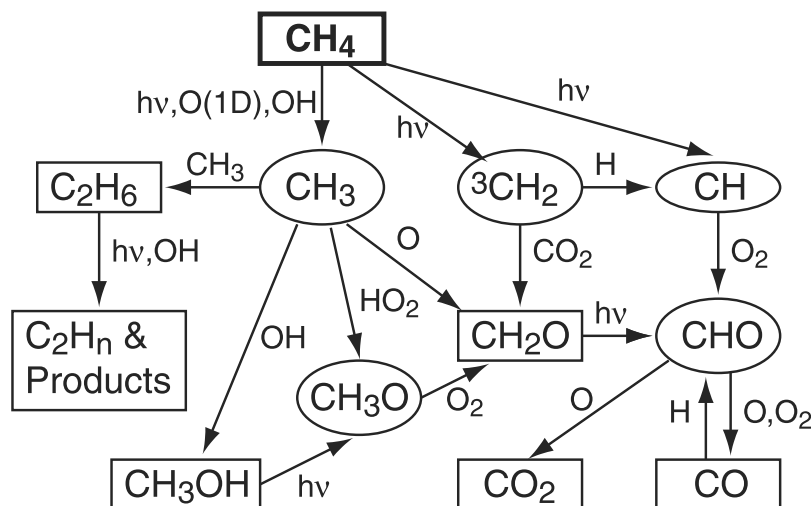


Figure 3. Schematic diagram illustrating the important reaction pathways of hydrocarbon chemistry in Martian atmosphere. Stable species are in rectangles, radicals are in ovals, and outgassing species are in bold.

Table 5. Model Results for Methane Chemistry in the Martian Atmosphere^a

Model	Outgassing		Major Photochemical Products						
	CH ₄		CH ₂ O		CH ₃ OH		C ₂ H ₆		
	Surface Mixing	Mixing	Mixing	Column	Mixing	Column	Mixing	Column	
J	2×10^{-8}	2×10^{-8}	2.0×10^{15}	6.0×10^{-15}	4.0×10^9	1.4×10^{-15}	2.1×10^8	2.1×10^{-18}	2.3×10^5
K	1×10^{-6}	1×10^{-6}	1.0×10^{17}	2.9×10^{-13}	2.0×10^{11}	4.3×10^{-14}	8.1×10^9	6.4×10^{-16}	9.7×10^7
L	1×10^{-4}	1×10^{-4}	1.0×10^{19}	2.8×10^{-11}	1.6×10^{13}	4.3×10^{-12}	8.2×10^{11}	6.4×10^{-12}	9.6×10^{11}
Photochemical lifetime		2.1×10^{10} s (670 years)		2.7×10^4 s (7.5 hours)		6.4×10^6 s (74 days)		7.9×10^8 s (25 years)	

^aMixing ratios (labeled "mixing") and the column abundances (in cm^{-2} , labeled "column") are compared at 10 km in this listing. Lifetime of a species indicates the time to destroy all of that species in the atmosphere photochemically.

100 ppm. The most abundant hydrocarbon species are CH₄, CH₂O, CH₃OH, and C₂H₆, and the calculated mixing ratios for these species at 10 km are 1×10^{-4} , 2.8×10^{-11} , 4.3×10^{-12} , and 6.4×10^{-12} , respectively (see Table 5). The number densities and mixing ratios of important species of hydrocarbon chemistry are plotted in Figure 5 for this case.

[15] At high altitudes above 80 km, methane is photo-dissociated into CH, ³CH₂, ¹CH₂, and CH₃ (R52). ³CH₂ reacts with the background gas CO₂ to form CH₂O (R65). This explains the upper peak in CH₂O concentration at high altitudes. At low altitudes, the oxidation of methane by O(¹D) and OH forms CH₃ (R76), (R77). CH₃ reacts with O to form CH₂O (R68) and with OH to form CH₃OH (R71). C₂H₆ is produced by recombination of CH₃ (R74) and its concentration is proportional to the square of that of CH₃. From C₂H₆, other hydrocarbons with two or more carbon atoms can be formed. The model also shows that the increase in the concentrations of CH₂O and other single carbon species is proportional to the increase in the CH₄ abundance, as would be expected, whereas increase in the concentrations of C₂H₆ and other double carbon species is proportional to square of the increase in the CH₄ abundance (see Table 5).

[16] We find that the abundances of hydrocarbons derived from the methane photochemistry are very low even when the concentration of methane is relatively large in the

atmosphere. The reason is that the dissociation of methane, the starting point of the hydrocarbon chemistry, is very inefficient in the Martian atmosphere. The destruction rates of methane via different channels are shown and compared in Figure 4. Photolysis of methane occurs only high in the atmosphere, at around 90 km (see Figure 4), because UV destruction of methane in the lower atmosphere is largely shielded by the much more abundant CO₂ which has an overlapping absorption cross-section spectrum with methane. In the lower atmosphere the fastest pathway to break down methane is by reaction with OH (R77), the photoproduct of water. However, increasing the amount of water does not significantly promote the destruction of methane. The reason is that once formed, OH is quickly removed by CO and O via reactions R16 and R17. Compared to R16 and R17, the reaction rate of R77 is much slower.

[17] The photochemical lifetime of methane is found to be about 670 years, which is the longest amongst the principal hydrocarbon species (see Table 5). This fact, combined with the larger abundance of methane, means that methane may be the easiest hydrocarbon to detect even far from the source region, provided that its source flux is reasonably large. On the other hand, formaldehyde has a very short lifetime of only several hours. Therefore if formaldehyde is detected, it would imply a nearly continuous supply of very large quantities of methane, whose oxidation forms CH₂O. How-

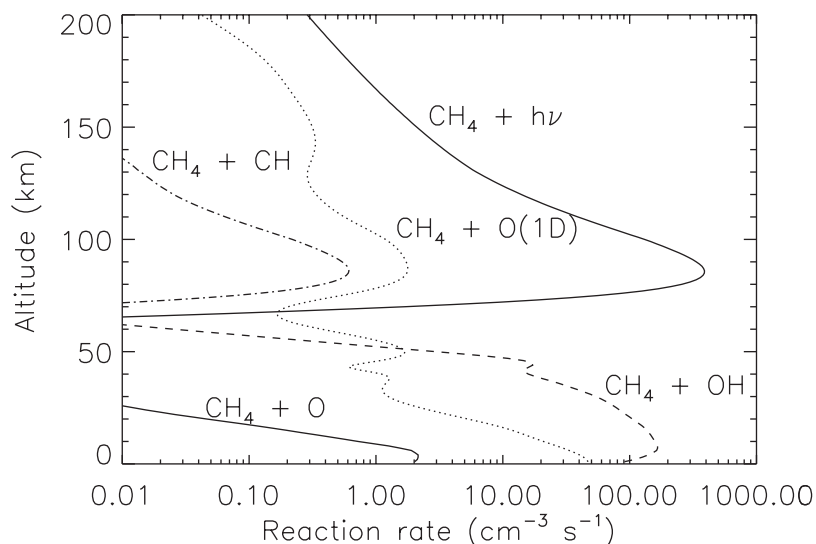


Figure 4. Destruction rates of methane versus altitude, assuming 100 ppm of methane is outgassed at the surface of Mars.

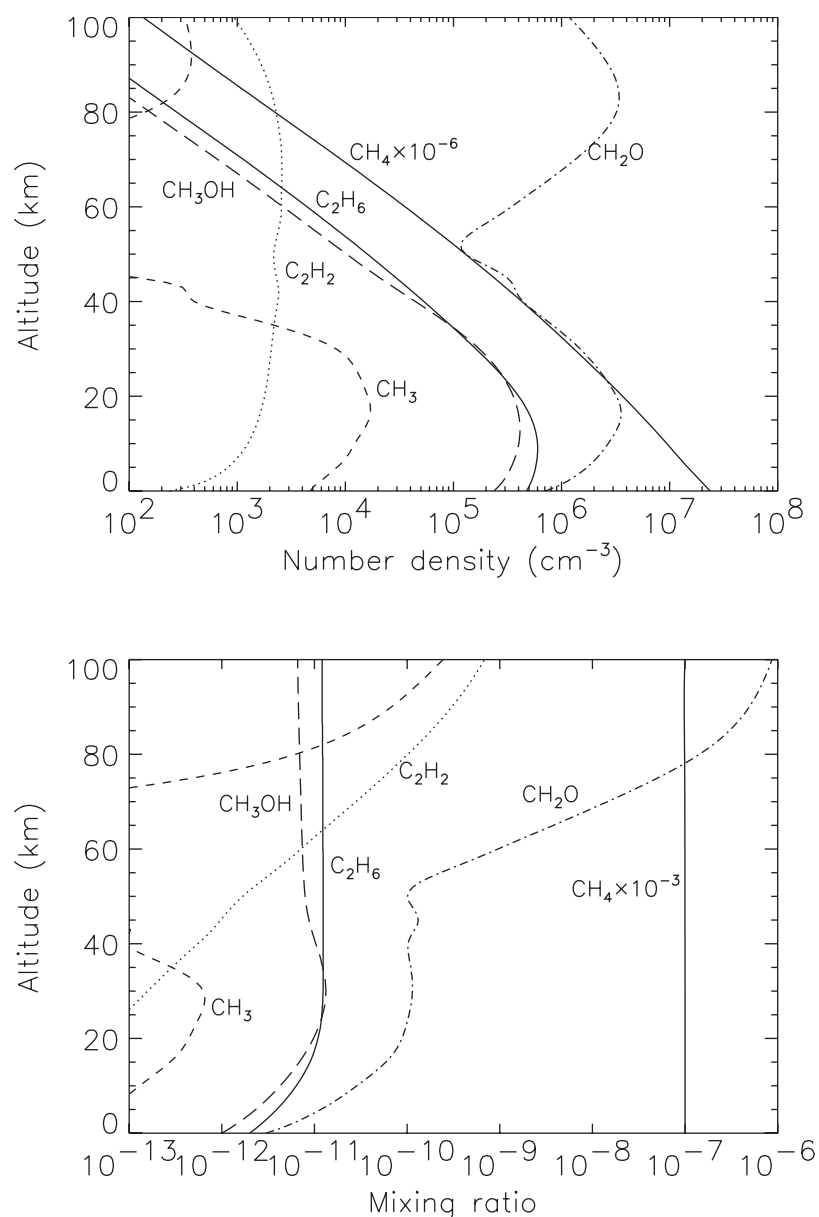


Figure 5. Number densities and mixing ratios versus altitude for important species calculated with 100 ppm of CH₄ at the surface of Mars (Model L).

ever, if formaldehyde is detected without any methane associated with it, there maybe other possibilities for its existence. For example, formaldehyde itself might have been outgassing directly, or it maybe formed in surface reactions between condensed phase H₂O and CO₂ under the action of solar ultraviolet radiation.

5. Location Consideration

[18] In the past the most active outgassing presumably occurred in the vast Tharsis volcano region. Could it be that small vents in the calderas of the volcanoes are still sending small quantities of gases into the Martian atmosphere? It would be desirable to investigate the Tharsis volcano region in future observations. Another area would be the Martian high latitudes where most of the signs of recent water seepage and ground water runoff have been seen. The

calculations presented in this paper assume that outgassing is taking place from the surface of Mars. Should there be vents in the calderas of the volcanoes, the source of outgassing would move up to higher elevations. This would have an impact on the calculated abundance of the photochemical products of outgassed species once they react with the known Martian atmosphere. This is due to a number of factors including the condensation of water vapor between 10 and 20 km and the varying distribution of oxygen bearing species with altitudes. For example, if the source of outgassing lies at 10 km above the surface of Mars, the column abundances (in cm⁻²) at 10 km of the most abundant constituents, assuming 100 ppm each of SO₂, H₂S, and CH₄ would be SO₂ = 1.6 × 10¹⁹, H₂S = 4.0 × 10¹⁸, SO = 1.4 × 10¹⁷; CH₄ = 1.0 × 10¹⁹, CH₂O = 1.6 × 10¹³, CH₃OH = 4.3 × 10¹¹, C₂H₆ = 3.2 × 10¹¹. If the source with 100 ppm each of SO₂, H₂S, and CH₄ is situated

on top of Olympus Mons (27 km above reference level), then the column abundances (in cm^{-2}) at 27 km would be $\text{SO}_2 = 2.6 \times 10^{18}$, $\text{H}_2\text{S} = 6.8 \times 10^{17}$, $\text{SO} = 1.4 \times 10^{17}$, $\text{CH}_4 = 1.3 \times 10^{18}$, $\text{CH}_2\text{O} = 1.1 \times 10^{13}$, $\text{CH}_3\text{OH} = 1.8 \times 10^{10}$, $\text{C}_2\text{H}_6 = 1.3 \times 10^9$.

6. Conclusion

[19] In this paper we have shown that if outgassing is taking place somewhere on Mars today, only a handful of new species with significant abundance would be formed as a result of photochemical processes involving the products of outgassing. In particular the outgassed H_2S and SO_2 would produce significant amounts of only SO. For example, 100 ppm each of H_2S and SO_2 at the surface would result in a column abundance of $7.8 \times 10^{16} \text{ cm}^{-2}$ of SO. The bulk of H_2SO_4 produced in the photochemistry is expected to condense out. Similarly, photochemistry of any outgassed CH_4 would produce appreciable amounts of only formaldehyde and methyl alcohol. With 100 ppm of outgassed CH_4 at the surface, for example, $1.6 \times 10^{13} \text{ cm}^{-2}$ of CH_2O and $8.2 \times 10^{11} \text{ cm}^{-2}$ of CH_3OH would result. Unlike the sulfur species, the hydrocarbon photochemical products would be far less abundant. The abundance of any halogens outgassed from the hot spots is expected to be small; therefore the photochemical products would be even less abundant. Thus the best candidates for the chemical markers of any hot spots on Mars are SO_2 , H_2S , CH_4 , possibly SO, CH_2O , and CH_3OH . The largest source of methane in the Earth's atmosphere is from fermentation of the biomass, with smaller contributions from fossilized matter. Methane and its products could serve as possible biomarkers in the Martian atmosphere as well. To conclude, we are not suggesting that hot spots exist on Mars today, but if they did, abovementioned chemical species predicted by our photochemical model would be their best indicator. Finally, it should be stressed that the aim of the present study is to identify possible hot spot related species in the Martian atmosphere. Should chemical signatures of hot spots be detected and the species abundance measured in future observations of Mars, their interpretation would warrant a more sophisticated model that combines photochemistry with full dynamics including general circulation.

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