PHOTOCHEMISTRY AND STABILITY OF THE ATMOSPHERE OF MARS

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ABSTRACT

An understanding of the composition, structure, transport and photochemical processes of the present atmosphere of Mars is essential for addressing such fundamental questions as the stability, evolution and the origin of the Martian atmosphere. This paper discusses our current knowledge of the photochemistry and stability of the Martian atmosphere, with special emphasis on new models and work in progress. The atmosphere of Mars is composed mainly of CO_2 (95.3% by volume), N_2 (2.7%), and ^{40}Ar (1.6%). Trace constituents, especially H_2O vapor (150-200 ppm, average), CO (0.07%), O_2 (0.13%), and ozone (0.03 ppm average) make up the rest. Vertical mixing, characterized by an eddy diffusion coefficient, is of the order of $10^6 cm^2 s^{-1}$ up to 40 km /1,2/, rising to $10^8 cm^2 s^{-1}$ at the homopause (125 km). Photochemistry initiated by the solar ultraviolet dissociation of CO_2 and H_2O, results in the formation and distribution of the above-mentioned trace constituents. O_2 and CO remain well-mixed and virtually constant because of their long photochemical lifetimes. Ozone shows an anticorrelation with water vapor amounts because of the odd oxygen loss on HO_x and H. An intermediate photochemical product in the form of hydroxyl radicals, OH, plays a catalytic role in maintaining the balance between the photodissociative loss of CO_2 and its subsequent recycling through a reaction of CO with OH. The homogeneous gas phase chemical reactions, however, do not *entirely* explain the stability of CO_2, O_2, or CO, thus necessitating the inclusion of heterogeneous adsorption as a loss mechanism for certain species, such as H_2O, OH, H_2O_2, O or O_2 on aerosols of dust or ice suspended in the Martian air /3/. Chlorine catalyzed reactions may be important in maintaining the stability of the Venus atmosphere. Recent detection of formaldehyde (CH_2O) at the 0.5 ppm level in the atmosphere of Mars /4/ is puzzling, since the conventional mechanism for its formation - oxidation of methane - would require 0.5-1% CH_4 which could not have escaped detection. Even 2-D models require at least a ppm level of CH_4, which also would have been detected, if present. Reaction of H with CO to form HCO, and subsequent reaction of HCO with HO_2, also would produce CH_2O only at a ppb level. Perhaps, a heterogeneous reaction involving long wavelength ultraviolet irradiation of a $CO - H_2O - CO_2$ mixture could help; however, laboratory experiments do not yet quantify the yield of formaldehyde. Should the presence of formaldehyde be confirmed after further observations, it would hold a tantalizing possibility of the existence of more complex organics in the interior, surface and the atmosphere of Mars. The virtual lack of organics on Mars could be attributed to the presence of oxidants such as hydrogen peroxide.

COMPOSITION AND PHOTOCHEMISTRY

The composition of the atmosphere of Mars is summarized in Tables 1a, 1b and 1c. CO_2, H_2O and N_2 are responsible for producing virtually all of the observed photochemical species in the Martian atmosphere. The average surface pressure on Mars is around 6 mb; seasonal variations of the order of 30%, however, result from seasonal evaporation and condensation of CO_2 of the polar ice caps. This phase change is caused by seasonal change in the solar flux (which at perihelion (sol angle $L_S = 350°$) exceeds that at aphelion by 45%) and the eccentricity of the orbit of Mars ($L_S = 0°$ corresponds to vernal equinox, 90° to summer solstice, 180° to autumnal equinox, and 270° to winter solstice). The relatively large surface pressure of CO_2 implies that photoabsorption by this species would occur from the surface

well into the ionosphere, that lies mostly above 100 km. Thus, it is important to include the ionospheric contribution, even if one is concerned with just the lower atmosphere. Water vapor amounts vary from a low of less than 1 pr μm in the equatorial winter-spring ($L_S \cong 0°$) of the northern hemisphere to a high of as much as 90 pr μm (at $L_S \cong 120°$) in the summer above the northern residual polar ice cap of water ice (1 precipitable micron or 1 pr μm $= 10^{-4}$ g cm^{-2}H$_2$O $= 3.35 \times 10^{18}$ cm^{-2}H$_2$O molecules, or about 15 ppm

TABLE 1A   The Composition of the Martian Lower Atmosphere

Constituent	Abundance	Ref.
CO_2	95.32%	/5/
N_2	2.7%	/5/
^{40}Ar	1.6%	/5/
O_2	0.13%	/5/
CO	0.07%	/5/
H_2O	0.02%[a]	/6/, /7/
$^{36+38}$Ar	5.3 ppm	/5/
Ne	2.5 ppm	
He	1.1±0.4 ppm[b]	
Kr	0.3 ppm	/5/
Xe	0.08 ppm	/5/
O_3	0.01 - 0.8 ppm[a]	/8/, /9/
CH_2O	0.5 ppm	/4/

[a]Seasonally and locally variable; [b]EUVE detection (V. Krasnopolsky, personal comm., 1993).

TABLE 1B   Upper Limits to Possible Minor Constituents[a]

Constituent	Band (cm^{-1})		Upper Limits (cm-am)	(ppm)[b]
C_2H_2	v_5	729	2×10^{-5}	0.002
C_2H_4	v_{12}	1443	4×10^{-3}	0.5
C_2H_6	v_9	821	3×10^{-3}	0.4
CH_4	v_4	1306	2×10^{-4}	0.02
N_2O	v_1	1285	1×10^{-3}	0.1
NO_2	v_3	1621	1×10^{-4}	0.01
NH_3	v_2	968	4×10^{-5}	0.005
PH_3	v_4	1122	1×10^{-3}	0.1
SO_2	v_3	1362	7×10^{-4}	0.1
OCS	v_1	859	1×10^{-4}	0.01
HCl	v_0	2890	1×10^{-3}	0.1
H_2S	Rydberg (UV)		1×10^{-3}	0.1
H_2O_2	Model		1×10^{-3}	0.1
H_2	Model		5×10^{-1}	50

[a]Table adapted from Maguire (1977), /10/, and Owen (1992), /11/; HCl from Beer et al (1971), /12/; H_2O_2 and H_2 are from photochemical model of Atreya and Gu (1994), /3/; see Table 1A for CH_2O; [b]Mixing ratio (ppm) is calculated with $CO_2 = 84$ meter-amag at (1 m-am $= 2.69 \times 10^{21}$ cm^{-2}; 84 m-am is approximately 5 mb surface pressure).

<u>TABLE 1C</u> Isotope Ratios[a]

Ratio	Earth	Mars	Ref.
D/H	1.56×10^{-4}	$9 \pm 4 \times 10^{-4}$	/13/
		$7.8 \pm 0.3 \times 10^{-4}$	/14/
$^{12}C/^{13}C$	89	90 ± 5	/15/
$^{14}N/^{15}N$	272	170 ± 15	/15/
$^{16}O/^{18}O$	489	490 ± 25	/15/
		545 ± 20	/14/
$^{16}O/^{17}O$	2520	2655 ± 25	/14/
$^{36}Ar/^{38}Ar$	5.3	5.5 ± 1.5	/16/
$^{40}Ar/^{36}Ar$	296	3000 ± 500	/5/
$^{129}Xe/^{132}Xe$	0.97	$2.5 \pm_1^2$	/5/

[a]Table compiled by Owen (1992), /11/.

H_2O for uniformly mixed water vapor). The water vapor column abundance is generally correlated with the surface temperature. The globally and seasonally-averaged value of water vapor is around 10-12 pr μm, or 150-200 ppm. Models involving water vapor amounts should, however, take into consideration the fact that uniform mixing ratio assumptions are rarely correct beyond approximately 20 km altitude because of condensation.

The attenuation of solar flux in the atmosphere of Mars is caused by both gaseous species as well as dust. The average dust opacity in the red-infrared range is around 0.8; the corresponding value in the ultraviolet would be about 0.4, /1/, and it can exceed 2 during times of the Great Dust Storms. The dust is well-mixed with the gas and is therefore distributed with the gas scale height up to about 40 km altitude. The chemical pathways for the production and loss of various neutral constituents in the Martian atmosphere are given in Table 2, and the principal pathways are illustrated in Figure 1. Absorption of the solar photons below 220 nm is caused primarily by CO_2, leading to the formation of CO and O (R2, Table 2). The reverse reaction (R3) is spin forbidden, so its rate is exceedingly slow. The main loss mechanism of CO is a reaction with the hydroxyl radicals, OH, to regenerate CO_2 (R9). Although the OH abundance is ultimately related to H_2O vapor, its main source lies in the reaction of HO_2 with O atoms (R6), producing nearly two-thirds of the OH column abundance; most of the remaining one-third is produced from photolysis of hydrogen peroxide, H_2O_2 (R7). H_2O_2 is produced in the self-reaction of HO_2 (R5), whereas HO_2 itself results from the reaction of H with O_2 (R4). H atoms are generated in the photolysis of H_2O (R1) below 190 nm. Note that the direct production of OH from H_2O photolysis or in reaction of $O(^1D)$ with H_2 (R22) or H_2O (R24) is negligible. The only other significant OH production occurs in the reaction of ozone with H atoms (R13). A schematic showing the relative contribution to OH column production rate is shown in Figure 2. The total height-integrated production rate of OH for a nominal model is $1.2 \times 10^{12} cm^{-2}s^{-1}$ /3/. This model assumes globally, seasonally and diurnally-averaged parameters for the solar flux (also taken for medium solar activity) and water vapor (10 pr μm or 150 ppm at the surface), surface temperature of 210K, dust optical depth of 0.4 (in the UV), and the eddy diffusion coefficient of $10^6 cm^2s^{-1}$ up to 40 km and rising to $10^8 cm^2s^{-1}$ at the homopause (125 km) according to an inverse square root of atmospheric number density variation. The height integrated photolysis rate for CO_2 in this model is $0.77 \times 10^{12} cm^{-2}s^{-1}$ /3/. The production and loss of oxygen species that participate in the above-mentioned reactions is discussed below.

Once produced in the photolysis of CO_2 (R2), oxygen atoms recombine with themselves to produce O_2 molecules (R15), i.e.
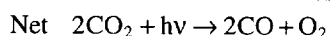
$$2CO_2 + h\nu \rightarrow 2CO + 2O \tag{R2}$$

$$2O + CO_2 \rightarrow O_2 + CO_2 \tag{R15}$$

Net $2CO_2 + h\nu \rightarrow 2CO + O_2$

TABLE 2 Chemical Reactions in the Neutral Atmosphere Important for the
Atmospheric Stability Problem[a]

	Reactions	Rate Constants[b]
R1	$H_2O + h\nu \rightarrow OH + H$	
R2	$CO_2 + h\nu \rightarrow CO + O$	
R3	$CO + O + M \rightarrow CO_2 + M$	$9.8 \times 10^{-33} \exp(-2180/T)$
R4	$H + O_2 + M \rightarrow HO_2 + M$	$5.7 \times 10^{-32}(T/300)^{-1.6}$
R5	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$2.3 \times 10^{-13} \exp(600/T)$
R6	$O + HO_2 \rightarrow OH + O_2$	$2.9 \times 10^{-11} \exp(200/T)$
R7	$H_2O_2 + h\nu \rightarrow OH$	
R8	$HO_2 + h\nu \rightarrow OH + O$	
R9	$CO + OH \rightarrow CO_2 + H$	$4.35 \times 10^{-14}(T/298)^{1.35} \times \exp(365/T)$
R10	$H + HO_2 \rightarrow 2OH$	7.2×10^{-11}
R11	$H + HO_2 \rightarrow H_2 + O_2$	5.6×10^{-12}
R12	$H + HO_2 \rightarrow H_2O + O$	2.4×10^{-12}
R13	$H + O_3 \rightarrow OH + O_2$	$1.4 \times 10^{-10} \exp(-470/T)$
R14	$O + OH \rightarrow O_2 + H$	$2.2 \times 10^{-11} \exp(120/T)$
R15	$O + O + M \rightarrow O_2 + M$	$5.21 \times 10^{-35} \exp(900/T)$
R16	$O + O_2 + M \rightarrow O_3 + M$	$6.0 \times 10^{-34}(T/300)^{-2.3}$
R17	$OH + HO_2 \rightarrow H_2O + O_2$	$4.8 \times 10^{-11} \exp(250/T)$
R18	$H_2O_2 + OH \rightarrow HO_2 + H_2O$	$2.9 \times 10^{-12} \exp(-160/T)$
R19	$O_3 + h\nu \rightarrow O_2 + O(^1D)$	
R20	$O_3 + h\nu \rightarrow O_2 + O(^3P)$	
R21	$O_2 + h\nu \rightarrow 2O$	
R22	$O(^1D) + H_2O \rightarrow 2OH$	2.2×10^{-10}
R23	$O(^1D) + CO_2 \rightarrow O + CO_2$	$7.4 \times 10^{-11} \exp(120/T)$
R24	$O(^1D) + H_2 \rightarrow OH + H$	10^{-10}

[a]From Atreya and Gu (1994), /3/; [b]The units for rate constants are $cm^3 s^{-1}$ for two body reactions and $cm^6 s^{-1}$ for three body reactions. NIST Chemical Kinetics Database (version 5.0) was also consulted in choosing the rate constants. M represents the background gas, CO_2. References for rate constants are given in /3/.
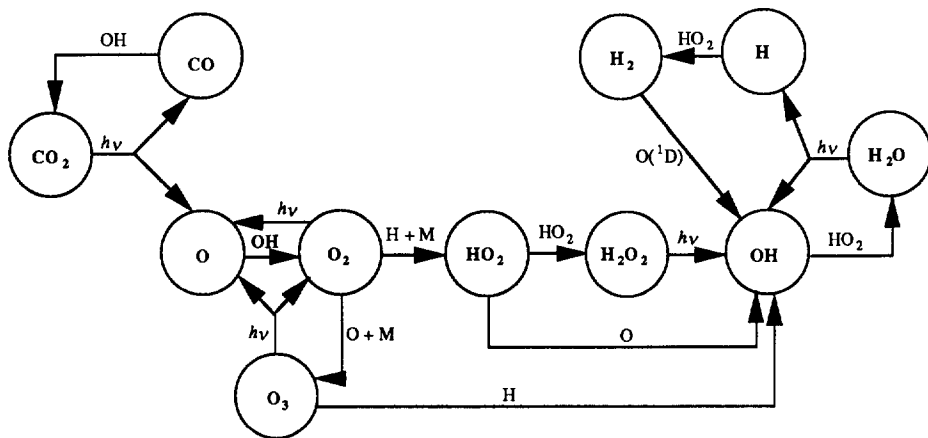

Figure 1.   Schematic of significant chemical reactions in the neutral atmosphere of Mars (after /3/).
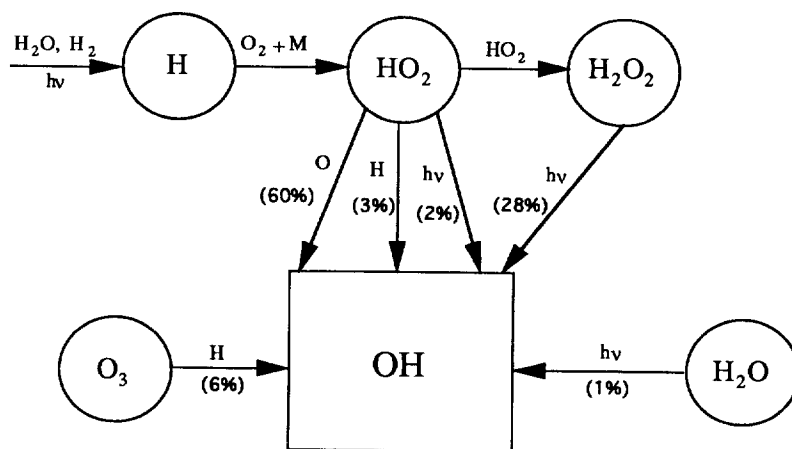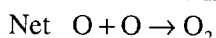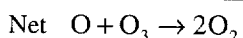
Figure 2. Sources of OH production along with their relative contributions in the atmosphere of Mars (based on nominal model (see text), /3/).

These reactions therefore imply that CO and O_2 should be in a 2 to 1 ratio, not 0.54 to 1 obtained from Table 1 on composition. The mixing ratios of CO and O_2 are nearly constant in the atmosphere of Mars, as their photochemical lifetimes ($\sim$ 8 years for each) are long, so the above discrepancy is significant. As seen above, the abundances of CO and O_2 are controlled by odd hydrogen, particularly OH, and therefore by H_2O. McElroy (1972), /17/, and Liu and Donahue (1976), /18/, have shown that the CO/O_2 ratio should adjust itself such that the escape fluxes of hydrogen and oxygen are in a 2:1 ratio, which is their stoichiometric ratio in H_2O. This could explain why the observed CO/O_2 ratio is not 2:1.

More than four-fifths of the oxygen atom production occurs in the CO_2 photolysis, the remaining results from the photolysis of the newly-formed O_2 (R21) and of HO_2 (R8). The loss of oxygen atoms is by the recombination reaction (R15) and the reaction with HO_2 which forms OH (R6). Molecular oxygen is formed either directly in the recombination of oxygen atoms (R15), or through odd hydrogen catalysis as follows:

$$H + O_2 + M \rightarrow HO_2 + M \qquad (R4)$$

$$O + HO_2 \rightarrow O_2 + OH \qquad (R6)$$

$$O + OH \rightarrow O_2 + H \qquad (R14)$$

$$\overline{\text{Net} \quad O + O \rightarrow O_2}$$

Also,

$$O_3 + H \rightarrow OH + O_2 \qquad (R13)$$

$$O + OH \rightarrow H + O_2 \qquad (R14)$$

$$\overline{\text{Net} \quad O + O_3 \rightarrow 2O_2}$$

The above "indirect" recombination of odd oxygen accounts for virtually all of the O_2 production rate below about 60 km; in other words, odd hydrogen catalysis plays a crucial role in the formation of O_2. The column production rate of O_2 for the nominal model is $2 \times 10^{11} \text{cm}^{-2}\text{s}^{-1}$. The loss of O_2 is via ultraviolet photolysis (R21), and the loss of even oxygen species, HO_2 and H_2O_2, is also by photolysis. This latter (indirect) photolysis accounts for nearly 70% of the O_2 loss rate in the nominal model. The

photochemical lifetime of O_2 in the atmosphere of Mars is 8 years, which is much longer than the average mixing time of ~ 10^6 sec or ~10 days in the lower atmosphere. O_2 is therefore expected to remain well-mixed throughout the atmosphere.

The reaction of O_2 with O produces O_3 (R16), as in the earth's atmosphere. The main mechanisms for the loss of ozone are ultraviolet photolysis in the daytime (R19, R20) and the reaction with atomic hydrogen (R13). The latter is the dominant loss mechanism for O_3 at night. The odd oxygen abundance distribution can be written as

$$[O_3]/[O] = k_{16}[O_2][CO_2]/(J_{O_3} + k_{13}[H])$$

where rate constants k_{16} and k_{13} are for reactions R16 and R13 (for production and loss of ozone), and J_{O_3} is the O_3 photolysis rate. The second term in the denominator is negligible in the nominal model.

The above relationship reveals that the dominant form of odd oxygen is O_3 below about 25-30 km, and O above it. The peak in odd oxygen sets in at around 50 km altitude in the nominal model. The distribution of odd hydrogen, hydrogen peroxide and the odd oxygen (O and O_3) calculated for the nominal model is shown in Figure 3.
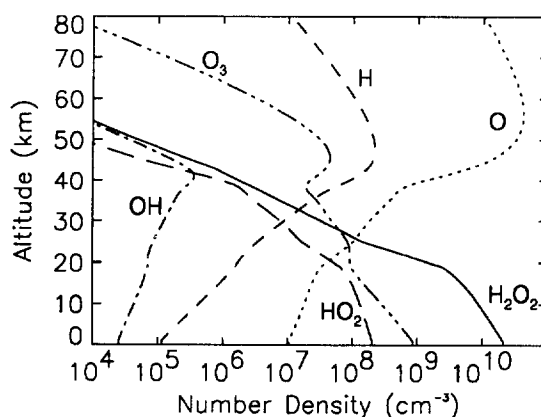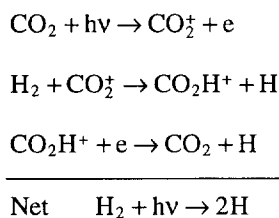

Figure 3.   The distribution of photochemical constituents in the atmosphere of Mars (based on nominal model (see text), /3/).

The ozone abundance in the atmosphere of Mars shows considerable seasonal variation as was revealed from observations in the Hartley absorption continuum (220-330 nm) on Mariner 9, /8/. A maximum of 57 μm-atm was measured at mid-latitudes in the northern hemisphere winter (1 μm-atm = 2.687×10^{15} molecules cm^{-2}), whereas the value dropped to less than 3 μm-atm over the northern polar cap region. The lowest ozone amounts were seen in the summer. The *Phobos* solar occultation experiments done at the northern spring equinox near the equator revealed ozone amounts equal to or less than 2μm-atm when extrapolated to the surface /9/, and even smaller amounts (10^{-2}μm – atm) have been reported from HST observations over the northern polar caps during spring equinox /19/. Specifically, the *Phobos* measurements, done in the 275-285 nm region, gave a maximum in the ozone density of 10^8cm^{-3} (within a factor of 2) at an altitude of 42-45 km. On the other hand, a large ozone density of 10^{10}cm^{-3} was measured at ~40 km on Mars 5, /20/. These observations reveal an anticorrelation between the ozone amounts and the water vapor abundance. The largest ozone values are seen in the winter when water vapor abundance drops to its lowest value, and the smallest ozone values are recorded in the summer period when the water abundance reaches its peak. As for the ozone maximum at 42-45 km, the *Phobos* measurements of $[O_3] = 10^8$cm^{-3} (within a factor of 2) are well in agreement with the peak values calculated in the diurnally-averaged photochemical model of Atreya and Gu /3/, (Figure 3) which assumes

an abundance of H_2O of 10 pr μm, which is close to the value measured by *Phobos* IR spectrometers. Even better agreement of ozone peak concentration with the measurements is obtained once the model simulates the terminator-observing geometry of the above *Phobos* solar occultation. The large value of 10^{10} cm^{-3} seen by Mars 5 occurs in a region where water ice haze layer was also seen, thus depressing severely the water vapor abundance. The above anticorrelation between O_3 and H_2O vapor is expected since the odd oxygen (O and O_3) reactions with H and HO_x (R6, R13, R14) are the dominant loss mechanisms for ozone as O and O_3 are interchangeable during the day. This assertion of $O_3 - H_2O$ anticorrelation is further strengthened by another aspect of the *Phobos* observations that the detectable levels of ozone (10^8 cm^{-3}) were seen only in one of the six occultations, implying that large local relative humidity may be responsible for lower ozone amounts in the other cases. The atmospheric thermal structure, hence the humidity levels, can be driven by the regional dynamical as well as regular seasonal changes.

The production and loss of hydrogen is controlled by both photochemistry and escape. Molecular hydrogen is produced in the lower atmosphere on reaction between hydrogen atoms and HO_2 (R11) at a rate of 3×10^9 cm^{-2}s^{-1} in the nominal model. The upward flux of H_2 is 5×10^8 cm^{-2}s^{-1} from the lower atmosphere to the ionosphere. Once in the ionosphere, H_2 undergoes dissociation both by the ultraviolet photons and the following set of reactions:

$$CO_2 + h\nu \rightarrow CO_2^+ + e$$

$$H_2 + CO_2^+ \rightarrow CO_2H^+ + H$$

$$CO_2H^+ + e \rightarrow CO_2 + H$$

$$\text{Net} \quad H_2 + h\nu \rightarrow 2H$$

In the middle atmosphere, the removal of H_2 occurs on its reaction with $O(^1D)$, producing a small amount of OH and H (R24). The net mixing ratio of H_2 for the nominal model turns out to be 5×10^{-5}. The lifetime of H_2 against photochemical loss in the lower atmosphere (> 30 years), is long, whereas the vertical mixing time is on the order of 10 days (for $K = 10^6$ cm^{2}s^{-1}). This allows this species to remain relatively well-mixed in the Martian atmosphere. The loss from the upper atmosphere occurs at the critical level in the form of atomic hydrogen escape, whereas direct escape of H_2 is small. The H_2 mixing ratio and the H atom escape rate can be affected somewhat by the following nitrogen reaction,

$$NO + HO_2 \rightarrow NO_2 + OH \qquad k = 3.7 \times 10^{-12} \exp (240 / T) \text{ cm}^3\text{s}^{-1}$$
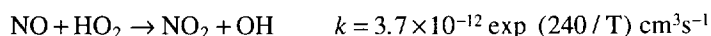
The above reaction effectively results in loss of HO_2 and thus smaller OH, which in turn produces somewhat smaller H_2 mixing ratio ($H + HO_2 \rightarrow H_2 + O_2$, R11), and therefore a somewhat smaller atomic hydrogen escape flux.

The lack of organics on Mars may be due to the existence of oxidants. One possible candidate for such an oxidant is hydrogen peroxide, H_2O_2, whose lifetime against photochemical loss is about 1 day. Furthermore, its mole fraction (0.1 ppm) in the latest nominal models (e.g., in /3/) is a factor of 1000 greater than in the previous models. However, the recent tentative detection of formaldehyde (CH_2O) at 2710 cm^{-1} and 2730 cm^{-1} in a mixing ratio of approximately 0.5 ppm (Table 1) poses a challenge. If correct, this measurement requires a viable mechanism for the production of CH_2O. The conventional mechanism - oxidation of methane - requires nearly 0.5-1% of methane (CH_4), which could not have gone undetected. Assuming a value of 1 ppm for CH_4, D. Moreau (personal communication, 1992) arrived at 0.5 ppm of CH_2O in a 2-D model. Although the details of the model are not available, it should be remarked that methane, even at 1 ppm level, could not have escaped detection, and the current upper limit is only 0.02 ppm. Homogeneous gas phase photochemical models involving reaction of CO with H can produce only ppb levels of CH_2O /4/. Furthermore, the photochemical lifetime of CH_2O is short, about 13 hours, so that it would be necessary to have a continuous source. In a laboratory experiment, synthesis of CO and H_2O vapor in the presence of CO_2, N_2 and "surfaces" by long wavelength ultraviolet ($\lambda > 250$ nm) resulted in the production of formaldehyde; however, most of the yield was in the form of

formic acid, HCO_2H /21/. Such heterogeneous reactions are known to occur in experiments conducted by others (such as by L. Mukhin, personal communication, 1993); however, the yield of formaldehyde is not known and the irradiated mixtures do not represent the proportions of CO, CO_2 and H_2O found in the Martian atmosphere. In conclusion, although a satisfactory explanation for the formation of formaldehyde on Mars is lacking at this time, if the detection is confirmed by further observations, it holds much promise for the existence of more complex organics and even carbonates in the atmosphere, surface or the interior of Mars.

ATMOSPHERIC STABILITY

The atmosphere of Mars is stable against photochemical loss. This is particularly striking in the case of its main atmospheric constituents, CO_2, whose photolysis rate is of the order of $10^{12} cm^{-2} s^{-1}$, as mentioned earlier. This means that the entire 6 mb CO_2 atmosphere on Mars would be dissociated into its products CO and O_2 in about 6000 years, i.e. in a relatively short period of time. Moreover, the present atmospheric levels of CO and O_2 (about 0.1% each) would be attained in 3-6 years. Yet, we know that except for regular seasonal changes of 30%, the CO_2 level in the atmosphere of Mars is constant, and the CO and O_2 levels have not continued to build up beyond their present atmospheric levels. The recycling of CO_2 by the reaction of CO with O (R3) is spin forbidden. The apparent success of the early attempts at explaining the recycling (/22/, /23/) by the reaction between CO and OH, (R9), was fortuitous, as those models assumed incorrect values for either the eddy mixing coefficient in the middle atmosphere or the amount of water vapor. In addition, they assumed incorrect CO_2 absorption cross sections and the chemical kinetic data, especially for the key reaction for catalytic recycling of CO_2 by OH (R9). The values of the parameters used in the above models were the best available at that time. Note, however, the proposed hypothesis for recycling CO_2 in these models was essentially sound. These issues have been discussed in detail in a recent paper by Atreya and Gu (1994) /3/. With the data on CO_2 absorption cross section and CO + OH rate constant available in 1972, and using the correct values for the eddy mixing coefficient in the middle atmosphere ($10^6 cm^2 s^{-1}$) and the average water vapor amount (150 ppm), it is found that the ratio of the rate of reformation of CO_2 to the rate of CO_2 loss by photolysis (referred to as the stability parameter, S_a, in /3/) is about 0.15 and 0.3, respectively in the models of McElroy and Donahue (1972), /22/, and Parkinson and Hunten (1972), /23/. In other words, loss of CO_2 exceeds its recycling rate by factors of 3 to 6. However, recent improvements in the CO_2 absorption cross section data, which are found to be temperature-dependent, show that at the low temperature of the surface and lower atmosphere of Mars the CO_2 absorption cross section is a factor of 2-3 *smaller* than the room temperature value available at the time these models were calculated. This means that the loss rate would be reduced if the new CO_2 absorption cross sections were used. It is further discovered that the new rate constant for the recycling reaction, R9, $CO + OH \rightarrow CO_2 + H$ is *greater* than the value used in the 1972 models, by about a factor of 2-3. Thus, use of the new rate constant would result in a greater recycling rate for CO_2. The new data on the relevant cross section and the rate constant, therefore, both work in tandem to effectively increase the rate of CO_2 reformation so that they would tend to pull the stability parameter closer to 1. A detailed photochemical model developed by Atreya and Gu (1994), /3/, however, shows that the latest available laboratory data on reaction kinetics, cross sections and the relevant atmospheric parameters gives a 40% discrepancy between the production and the loss rates of CO_2, with the production *exceeding* the loss. Although it is a huge improvement over the earlier models in which the average discrepancy between production and loss was by factors of 3 to 6 (even 10 in some models), it is still significant and calls for a physical mechanism to reconcile the difference. It should be pointed out, however, that the current models are one-dimensional, and there may be some adjustment in the stability parameter once "actual" temporal, latitudinal and longitudinal changes in the atmospheric water vapor, eddy mixing, dust opacity and the temperatures, as well as atmospheric dynamics, are available and taken into account in the models.

As a first step for testing the validity of the globally averaged nominal model, a calculation is done in which actual variations of the relevant atmospheric parameters over a Martian day were taken into account. This calculation reveals that the production and loss rates nearly balance each other when averaged over the 24-hour period. This illustrative calculation was done for the site of Viking 1 Lander, with actual diurnal changes in the three most important parameters - water vapor amount, atmospheric and

surface temperature, and the solar zenith angle - taken into consideration. The H_2O-vapor varies from 1 pr μm at dawn to 10 pr μm at noon with only a slight change at dusk /24/. The surface temperature varies from dawn to noon by 45°K /25/; interpolations are done where temperature information is unavailable (e.g., at 2 AM, 6 AM, 10 AM and 6 PM). The critical parameter in the CO_2 stability problem is the OH density, as it can vary dramatically from day to night. This is because its photochemical lifetime is less than 1 second; the lifetime of the other critical constituent, CO, is so long (~ 8 years) so that its density is not expected to have a diurnal change. Figure 4 shows the distribution of OH density over a 24 hour period in the Martian atmosphere. The midnight value of [OH] is depleted dramatically below 40 km because of the severely depleted atomic oxygen density in this region at night, which prevents formation of OH (R6). Further reduction in OH occurs because of the absence of H_2O_2 photolysis (R7). Although the resulting recycling rate of CO_2 (R9) would be reduced dramatically at night, so is its photolysis loss. Table 3 gives the height integrated production and loss rates of CO_2 over the course of a Martian day (these values in the model were actually calculated at each 2-hour interval).
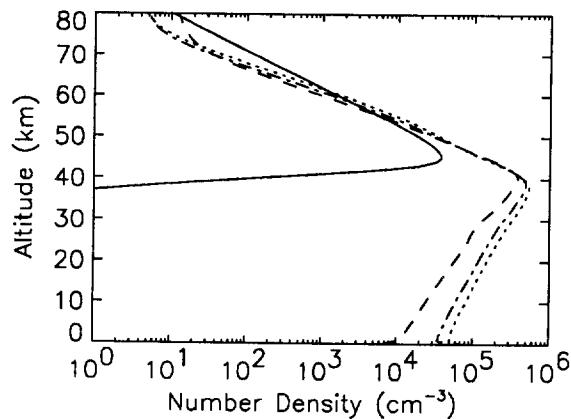

Figure 4. OH concentrations in the atmosphere of Mars for midnight (solid line), 6 AM (broken line), 8 AM (dot-dashed line) and noon (dotted line) conditions. Calculations shown are for 20°N summer season. The diurnal change of water vapor is taken from Farmer et al, /24/.

TABLE 3 Height-Integrated Production and Loss Rates (in $cm^{-2}s^{-1}$) for Different Time Zones

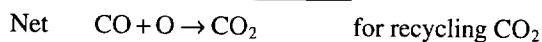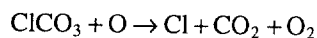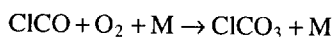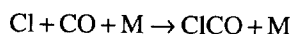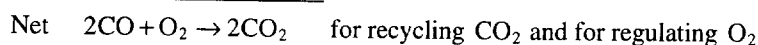|	12m	4am	6am	8am	12am	4pm	6pm	8pm
P_{CO_2}	0.45(10)	0.53(10)	0.80(12)	0.17(13)	0.23(13)	0.18(13)	0.89(12)	0.89(10)
L_{CO_2}	0.83(6)	0.71(9)	0.44(12)	0.17(13)	0.28(13)	0.18(13)	0.54(12)	0.67(10)

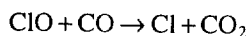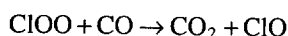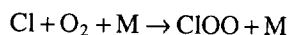0.45(10) represents 0.45×10^{10}

The ratio of these height integrated production and loss rates comes out to be 0.98, when a simple averaging of values over the 24-hour period is carried out. This would imply that the problem of stability of CO_2 does not exist on Mars. However, this simplified illustration is for a single day on Mars, and does not take into account actual latitudinal and seasonal changes in the relevant atmospheric parameters, but it does provide us some confidence in the globally averaged model, which gives a 40% discrepancy between the CO_2 production and loss rates. Should this small discrepancy between the CO_2 recycling and the loss rates still persist after appropriate latitudinal, longitudinal and temporal variations are available and included in the models, it would be necessary to invoke some mechanism to reduce the production of OH or allow additional loss of CO, since the recycling mechanism (R9) depends on CO and OH abundances. Heterogeneous processes on the surfaces of aerosols of dust or ice in the atmosphere of Mars have the potential for providing a sink for CO, O, O_2, OH, H_2O, H_2O_2 or other species involved in the recycling of CO_2. Heterogeneous processes were suggested previously by Atreya and Blamont (1990), /26/;

however, the photochemical model they used was incomplete. For a detailed discussion of the stability of the Martian atmosphere problem and its possible resolution, the reader is referred to the paper by Atreya and Gu (1994), /3/; other recent works on photochemistry are by Nair et al (1994), /27/, and Krasnopolsky (1993), /1/.
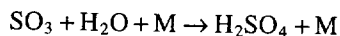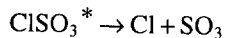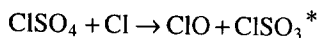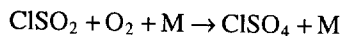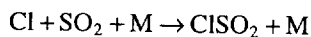
The atmospheric mole fractions of CO and O_2 are tightly coupled to the CO_2 stability. A complete balance between the loss and the recycling rates of CO_2 would also imply stable levels of CO and O_2 according to the photochemical scheme for the atmosphere of Mars given in Table 2. The above explanation for the stability of CO_2 in the Martian atmosphere, i.e. reaction between CO and OH, would not be very effective on Venus since both water vapor (1×10^{-6}) and the CO (4×10^{-5}) mixing ratios in the photolysis region (cloud tops) of the Venus atmosphere are far lower than those in the atmosphere of Mars. Moreover, the O_2 mixing ratio in the Venus atmosphere is about a factor of 1000 smaller than in the atmosphere of Mars. A possible explanation for the stability of CO_2 and the low O_2 on Venus comes from the presence of HCl and H_2SO_4, whose ultimate source lies in the active volcanoes of this planet (HCl and H_2SO_4 are absent from Mars atmosphere, presumably due to its extinct volcanism). Catalytic oxidation of CO involving Cl (photolysis product of HCl) may be responsible for the recycling of CO_2 /28/, and the loss of O_2 may be due to its participation in these reactions and in the formation of sulfuric acid on Venus. The relevant sets of reactions are as follows:

$$Cl + CO + M \rightarrow ClCO + M$$

$$ClCO + O_2 + M \rightarrow ClCO_3 + M$$

$$ClCO_3 + O \rightarrow Cl + CO_2 + O_2$$

Net $\quad CO + O \rightarrow CO_2 \qquad$ for recycling CO_2

or

$$Cl + O_2 + M \rightarrow ClOO + M$$

$$ClOO + CO \rightarrow CO_2 + ClO$$

$$ClO + CO \rightarrow Cl + CO_2$$

Net $\quad 2CO + O_2 \rightarrow 2CO_2 \qquad$ for recycling CO_2 and for regulating O_2

and

$$Cl + SO_2 + M \rightarrow ClSO_2 + M$$

$$ClSO_2 + O_2 + M \rightarrow ClSO_4 + M$$

$$ClSO_4 + Cl \rightarrow ClO + ClSO_3{}^*$$

$$ClSO_3{}^* \rightarrow Cl + SO_3$$

$$SO_3 + H_2O + M \rightarrow H_2SO_4 + M$$

Net $\quad Cl + SO_2 + H_2O + O_2 \rightarrow H_2SO_4 + ClO \qquad$ for H_2SO_4 formation and for regulating O_2.

The kinetics of the reactions forming ClCO, $ClCO_3$, ClOO, $ClSO_2$, $ClSO_3$ and $ClSO_4$ are poorly understood; therefore it would be premature to say that the question of stability of the Venus atmosphere does not pose a challenge. Perhaps heterogeneous processes involving aerosols are even more relevant and important in the atmosphere of Venus than on Mars.

In conclusion, it is important to recognize that although tremendous progress has been made in the area of modeling of the atmosphere of Mars (and Venus); there are many challenging questions that would require two-, even three-dimensional modeling and the availability of column abundances and altitude distributions of at least H_2O, CO, O_2, O, O_3, H_2O_2 and CH_2O. In addition, at least firm upper limits on trace constituents for which presently only tentative upper limits exist (Table 1B) will be desirable. Isotopic ratios of noble gases, deuterium, oxygen and nitrogen should also be revisited for answering fundamental questions of the origin and evolution of the atmosphere on Mars. Finally, interpretation of planetary observations with physico-chemical models would require availability of state-of-the-art laboratory data on relevant chemical kinetics, cross sections, as well as on the solar fluxes. In the area of planetary observations, future missions such as the Mars '96 and Mars Surveyors 1 and 2 hold much promise. Careful planning will be needed to ensure highest *science* returns from the many Mars missions currently under consideration for the years beyond 1998.

ACKNOWLEDGMENT

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