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PHOTOCHEMICAL REGULATION OF CO ON MARS

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Abstract. The balance between the production and loss rates of CO in the Martian atmosphere is examined in the photochemical frame defined by Parkinson and Hunten (1972). A first important point is that, for any given value of the CO abundance, the balance of CO is roughly reached in a short lapse of time through balances of short lived O, O₃ and OH. From this basic fact, we suggest a quite interesting characteristic of the photochemistry of carbon compounds on Mars, implicit in earlier models, but not yet discussed in detail. Because the production of OH is the rate-limiting step in oxidation of CO, there is in first approximation no feedback process regulating CO at any particular level. A more refined analysis shows that feedbacks exist, although there are weak. Damping processes are identified and their efficiency estimated in a rather general frame. A corollary is the intrinsic instability of the equilibrium abundance of CO, which is very sensitive to fluctuations of its production and loss rates. Nevertheless, because of the long life time of CO, temporal variations (seasonal, solar cycles) are expected to be weak ($\approx \pm 10\%$). Large latitudinal gradients predicted in static conditions are likely smoothed by dynamical mixing. The contribution of the present ideas to the understanding of the recent Earth-based and space observations of the Martian CO is finally evaluated. Some new directions of research are proposed.

Introduction

Attention has been recently called again to problems related to the photochemical stability of the Martian CO₂ atmosphere [Shimazaki, 1989; Atreya and Blamont, 1990]. Photolysis of CO₂ by solar light entering deeply the thin atmosphere might have converted it to a predominantly CO/O₂ atmosphere in some thousand years. Indeed, the three body recombination of CO and O has a very slow rate. Formally, this problem has been solved by Parkinson and Hunten (1972): CO₂ is reformed by action of OH radicals produced by photolysis of HO₂ and H₂O₂ on CO. Direct conversion of O into OH [McElroy and Donahue, 1972] through action of HO₂ requires a high eddy mixing coefficient in order to transport O produced by CO₂ photolysis above ≈ 30 km down to lower regions (where HO₂ is present) fast enough to avoid recombination of O with itself in presence of CO₂. In the scheme proposed by Parkinson and Hunten, the O atom contained in the OH molecule originates in O₂ which forms HO₂ in presence of H and CO₂, with subsequent formation of H₂O₂ (releasing OH by photolysis) through action of HO₂ on itself. Since O₂ has a long life time (≈ 30 yr), there is no need of a high eddy mixing coefficient.

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Two recent measurements suggest a possible variability of the CO abundance in the Martian atmosphere on a global scale [Lellouch et al., 1990], and above the high volcanoes [Rosenqvist et al., 1990]: 1-Millimeter-wave observations of Mars in some rotational lines of ¹²CO and ¹³CO have been performed from Earth. Line profiles, mapped as a function of the position on the disk, are consistent with a spatially uniform CO, with a CO mixing ratio of $8 \pm 2 \cdot 10^{-4}$. An increase of the CO mixing ratio from $6 \cdot 10^{-4}$ near the north pole to 10^{-3} at south middle latitudes is marginally observed together with a small longitudinal variation. 2- Observations of CO at 2.35 μm made on board the Phobos spacecraft using an imaging spectrometer suggest a local definite depletion by at least a factor of 2 of CO above high regions.

The study by Atreya and Blamont (1990) leads to the conclusion that the classical scheme is not adequate for recycling CO₂. In the light of recent measurements from the Phobos spacecraft, these authors propose a new mechanism involving oxidation of CO through heterogeneous chemistry in the presence of aerosols (ice and/or dust). Results obtained by Shimazaki (1989; paper called S in the following) studying CO₂ stability yield a quite different conclusion: using one dimensional model, this author shows that the balance between the production and loss rates of CO is realized for a water vapor amount of about 1 pr. μm , much smaller than the observed global average (10 pr. μm). As mentioned in S, Martian water vapor is highly variable and the problem of the stability of CO₂ must be considered on a global scale.

In view of the rather small sensitivity of the production rate of CO₂ (loss rate of CO) to the water vapor amount exhibited in Fig. 8 of S, and considering difficulties associated with the non uniform and unpredictable water vapor distributions on the global scale, we think that a complete 3-dimensional model is imperatively required to prove definitively the adequation of the Parkinson-Hunten scheme to mechanisms of the CO₂ stability. Therefore, we decided to treat in the present paper another aspect of this problem, implicit in earlier models, but not yet discussed in detail. The point is the intrinsic instability of the equilibrium abundance of CO. In first approximation, no feedback process regulates CO at any particular level. The lack of feedbacks of odd hydrogen catalysis was already mentioned by Hunten (1974, p. 534) but not developed.

Photochemical regulation of CO

Analysis of the CO balance:

First, we shall examine photochemical reactions involving odd oxygen O* (O, O₃) and the OH radical. The following analysis is based on the standard set of reactions between products derived from CO₂ and H₂O through action of solar photons. Ideas presented in this paper are quite general and do not depend on a particular choice of parameters. The reader

may, for example, refer to Kong and Mc Elroy (1977, Fig. 4, 5; denoted by KM in the following) or S (1989, Fig. 7). Adopting new rate constants used in S does not affect the hierarchy of reactions controlling O* and OH equilibria, as shown by Chassefière and Atreya (1990). Reactions are taken from Krasnopolski (1985) (table 1). Photolysis and chemical reactions are denoted respectively P_i (photolysis rate J_i) and C_j (reaction rate k_j). Equations expressing the balance between the production and loss rates of the constituents are averaged over the whole height of the atmosphere. The integration sign is systematically omitted.

Table 1: Useful chemical reactions.

	Production	Loss
O	CO ₂ +hν → CO+O (J ₁)	O+HO ₂ → OH+O ₂ (k ₂)
	O ₂ +hν → O+O (J ₂)	O+OH → H+O ₂ (k ₃)
	HO ₂ +hν → OH+O (J ₃)	O+O+CO ₂ → O ₂ +CO ₂ (k ₄)
	O(¹ D)+CO ₂ → O+CO ₂ (k ₇)	O+O ₂ +CO ₂ → O ₃ +CO ₂ (k ₅)
	H+HO ₂ → H ₂ O+O (k ₁)	
O ₃	O+O ₂ +CO ₂ → O ₃ +CO ₂ (k ₅)	O ₃ +hν → O ₂ +O(¹ D) (J ₄)
		O ₃ +H → OH+O ₂ (k ₆)
O(¹ D)	O ₃ +hν → O ₂ +O(¹ D) (J ₄)	O(¹ D)+CO ₂ → O+CO ₂ (k ₇)
OH		O(¹ D)+H ₂ O → OH+OH (k ₈)
	HO ₂ +O → OH+O ₂ (k ₂)	O(¹ D)+H ₂ → OH+H (k ₉)
	H ₂ O ₂ +hν → OH+OH (J ₅)	CO+OH → CO ₂ +H (k ₁₀)
	HO ₂ +hν → OH+O (J ₃)	O+OH → H+O ₂ (k ₃)
	H+HO ₂ → 2OH (k ₁₂)	HO ₂ +OH → H ₂ O+O ₂ (k ₁₁)
	O ₃ +H → OH+O ₂ (k ₆)	
	H ₂ O+hν → OH+H (J ₆)	
O(¹ D)+H ₂ O → OH+OH (k ₈)		
O(¹ D)+H ₂ → OH+H (k ₉)		
H ₂ O ₂	HO ₂ +HO ₂ → H ₂ O ₂ +O ₂ (k ₁₃)	H ₂ O ₂ +hν → OH+OH (J ₅)

The production and loss rates of O*, obtained summing rates for O, O₃ and O(¹D) are denoted respectively L_O and P_O in the following. Omitting terms accounting for exchange reactions between the three members of the family (present in both production and loss rates), P_O and L_O may be written:

$$P_O = J_1[CO_2] + 2J_2[O_2] + J_3[HO_2] + k_1[H][HO_2] \quad (1)$$

(84,86) (10,9) (6,5) (0.01,0.01)

$$L_O = k_2[O][HO_2] + k_6[O_3][H] + k_3[O][OH] + 2k_4[O]^2[CO_2] \quad (2)$$

(63,80) (4,7) (8,10) (25,3)

Dominant sink and source terms are indicated by bold-faced types. Numbers between parentheses below reaction rates are their relative contributions in percents to the total rate as deduced from a simple photochemical modelling for K=4 10⁶ cm²s⁻¹ (left) and K=4 10⁷ cm²s⁻¹ (right) [Chassefière and Atreya, 1990]. These values, obtained adopting a water vapor mixing ratio of ≈10⁻⁴ between 20 and 50 km and using observed mixing ratios of long live species, are only indicative. They are well supported by profiles presented in KM or S. Production and loss rates of OH may be written:

$$P_{OH} = k_2[O][HO_2] + 2J_5[H_2O_2] + J_3[HO_2] + 2k_{12}[H][HO_2]$$

(65,77) (22,10) (7,5) (1,1)

$$+ k_6[O_3][H] + J_6[H_2O] \quad (3)$$

(5,7) (0.1,0.1)

$$L_{OH} = k_{10}[CO][OH] + k_3[O][OH] + k_{11}[HO_2][OH] \quad (4)$$

(92,90) (8,10) (0.1,0.1)

It results from Eq. 2 and 3 that L_O ≈ P_{OH}. Assuming O* and OH balances, this yields P_O (=P_{CO}) = L_{OH} (=L_{CO}), i.e. CO balance. More precisely, neglecting terms with weights smaller than 5 %, Eq. 1 to 4 may be combined to give the following value of the loss to production ratio LPR of CO:

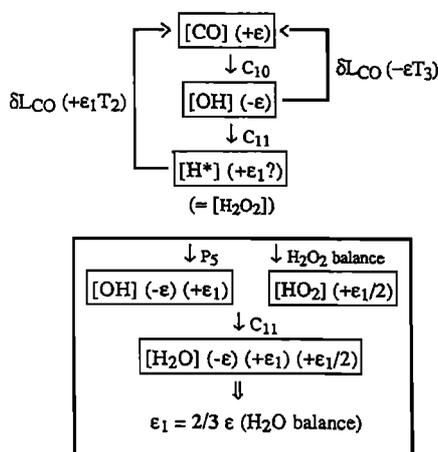
$$LPR \approx 1 + T_1 + T_2 + T_3 + T_4 \quad (5)$$

where T₁=-2k₄[O]²[CO₂]/P_{CO}, T₂=2(J₅[H₂O₂]+J₃[HO₂])/P_{CO}, T₃=-2k₃[O][OH]/P_{CO} and T₄=2J₂[O₂]/P_{CO}. The positive (T₂+T₄) and negative (T₁+T₃) terms in the right hand side of Eq. 5 are both in the range from ≈0 to 50%, as deduced from values of relative contributions indicated below Eq. 1 to 4. In usual conditions, the two opposite terms are of the same order of magnitude, implying that the balance between the production and loss rates of CO is roughly realized. This fact is indirectly confirmed by recent calculations of S (Fig. 8): the production rate of CO₂ (=L_{CO}) varies very slowly with the water vapor column abundance, LPR increasing from ≈0.95 for 0.2 pr. μm to ≈1.35 for 10 pr. μm. This increase of about 40 % is weak relative to the factor 50 applied to the water vapor abundance. It may be attributed to the terms accounting for photolysis of HO₂ and H₂O₂ in Eq. 5. Since the lifetimes of OH and O* are short (resp. ≈1 s and ≈1 day), the balance of CO within some tens percent is rather fast established through balances of short lived O, O₃ and OH for any value of the CO abundance.

Vacillation of CO in Martian atmosphere:

A natural outcome of the previous reasoning is that the equilibrium abundance [CO]_{eq} of CO could be rather unstable. Indeed, there is no direct loop stabilizing [CO], as it should occur if the loss rate of CO were proportional to [CO]: L_{CO}=k[CO], k being a fixed constant. In this case ("perfect regulation"), any variation of [CO] involves an equal variation of L_{CO}, with a subsequent damping of the initial fluctuation. The situation is quite different in Martian conditions: the production of OH is the rate-limiting step in oxidation of CO (P_{OH}≈L_{CO}, see Eq. 3 and 4). The reader may refer also to the Parkinson-Hunten flow-diagram (Chamberlain and Hunten, 1987, p. 309). Assuming in first approximation that the only reaction destroying OH is C₁₀ and that initially P_{CO}=L_{CO}, any variation of [CO] involves at each altitude an inversely proportional variation of [OH], since [OH] is everywhere the ratio of P_{OH} (Eq. 3) to k₁₀[CO]. Thus L_{CO} and L_{OH}, which are both equal to the product k₁₀[CO][OH], do not change, as well as balance equations of CO₂, H₂O and their by-products. In other words, all couples of CO and OH vertical distributions of the form k[CO], k⁻¹[OH] are solutions of the continuity equations. [CO] is not fixed at a particular level and may evolve without any lack of balance ("pure vacillation").

The actual situation is more complex due to the fact that OH reacts also with O, mainly above 30 km where O is abundant. The loss rate of OH by action of O is about one tenth of the total OH loss rate (see Eq. 4). Although the rate of C₁₁ is very weak relative to those of other processes destroying OH (about 0.1 %; see Eq. 4), C₁₁ is a key reaction for the Martian



Flow diagram 1: Feedback mechanisms. δL_{CO} is the relative variation of L_{CO} induced by feedbacks. The frame at the bottom shows the principle of the calculation of the relative variation ϵ_1 of H^* in response to ϵ .

photochemistry. It is the main process converting odd hydrogen into water vapor. Any variation of $[OH]$ modifies the balance between the production and loss rates of odd hydrogen H^* (H , OH , HO_2 , H_2O_2), thus abundances of HO_2 and H_2O_2 which are the main source of OH through photolysis. An increase of $[OH]$ accelerates the loss of H^* and thus reduces $[H_2O_2]$, yielding a slowing down of the OH production and a progressive damping of the fluctuation.

In order to study the reaction of the ambient atmosphere to a variation of $[CO]$, P_{CO} and L_{CO} being fixed, we assume an initial perturbation of $[CO]$ and estimate its effect on each term of Eq. 5 (diagram 1). T_1 is insensitive to variations of $[CO]$ because C_4 works mainly above ≈ 40 km, where the atomic oxygen abundance depends mostly on the value of the eddy diffusion coefficient, not on photochemical processes. T_2 is a damping term because any relative variation ϵ of $[CO]$ involves an opposite variation $-\epsilon$ of $[OH]$ below ≈ 30 km. Through C_{11} , which is the major sink for H^* , OH reacts with HO_2 to form H_2O . Therefore, $[H^*]$ varies in the same sense as $[CO]$, with a reduced amplitude $\epsilon_1 (\approx 2\epsilon/3)$ due to the tempering effect of the $[HO_2]$ variation. T_3 is a damping term since C_3 acts mainly above ≈ 30 km and $[O]$ may be supposed nearly invariable, mostly depending on K . Due to the great lifetime of O_2 (≈ 30 yr) relative to the one of CO (≈ 3 yr), T_4 may be considered as fixed in the present study.

Denoting by β the quantity $-T_3 + 2/3 T_2$, Eq. 5 yields the following relationship in first approximation:

$$L_{CO} \propto [CO]^\beta \quad (6)$$

where β is in the range from 0.1 to 0.5. Processes involved in Eq. 6 act with time delays from some seconds (T_3) to some weeks (T_2). These times are very short relative to the photochemical lifetime τ_1 of CO (3 yr). Eq. 6 means that any variation $\Delta[CO]$ of $[CO]$ (where $\Delta[CO] = \epsilon[CO]$, $\epsilon \ll 1$) yields a variation $\Delta L_{CO} = \beta \epsilon L_{CO}$ of L_{CO} . The damping time τ_d of CO is obtained by dividing $\Delta[CO]$ by ΔL_{CO} , namely, $\tau_d \approx \beta^{-1} \tau_1 \approx 6-30$ yr. τ_d is increased by a factor β^{-1} (2-10)

relative to the case of perfect regulation ($\beta=1$, $\tau_d=\tau_1$). Pure vacillation corresponds to $\beta=0$, $\tau_1=\infty$. In the dry and cold winter atmosphere, small water vapor abundances and eventual massive condensation of H_2O_2 make the damping very inefficient (large β^{-1}). The wet and hot summer atmosphere favours regulation (moderate β^{-1}).

Variability of CO on a global scale:

A corollary of Eq. 6 is the very high sensitivity of $[CO]_{eq}$ to fluctuations of P_{CO} and L_{CO} , given respectively by $J_1[CO_2]$ and $k_{10}[CO][OH]$. The three factors determining the balance of CO are the solar flux (J_1), the atmospheric pressure (CO_2) and the humidity of the atmosphere (OH).

The two first factors are influenced in particular by: - the high eccentricity of the Martian orbit which is responsible for both an annual variation of insolation by $\approx \pm 20\%$ and an oscillation of the atmospheric pressure between the northern mid summer (minimum) and the northern winter solstice (maximum) of $\approx \pm 15\%$. Due to the combination of these two effects, the production rate of CO varies annually (1 Martian year ≈ 1.9 terrestrial year) by $\approx \pm 35\%$; - the solar cycle fluctuation of insolation with a period of 11 yr. Using full-disk solar irradiances at solar minimum and solar maximum given by Mount and Rottman (1981), we have performed a rigorous calculation of the impact of the solar cycle on the photolysis rate of CO_2 (P_{CO}). We assume a pressure of 7 mb at the ground level and adopt the mean temperature profile proposed by Krasnopolski (1985). Species included in absorption calculations are N_2 , Ar , CO , O_2 , H_2 , H_2O and CO_2 , yielding an absolute amplitude of the P_{CO} fluctuation of $\pm 1.2 \cdot 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$. Dividing CO_2 absorption cross-sections by 2 above 170 nm because of low temperatures (see S) does not modify this result.

Let us assume a relative variation ϵ' of P_{CO} : in perfect regulation conditions, $[CO]$ evolves from its initial value $[CO]_{eq}^0$ until reaching its final equilibrium level $[CO]_{eq}^1 = (1+\epsilon') [CO]_{eq}^0$ on a typical time scale τ_1 ($\beta^{-1}=1$); at the other extreme (pure vacillation), $[CO]$ does not reach equilibrium, because of the inverse variation of $[OH]$ keeping L_{CO} at a constant level ($\beta^{-1}=\infty$), with a relative variation ϵ'/τ_1 per year. Because half periods of seasonal and solar cycle fluctuations (resp. 1 and 5.5 years) are smaller than the typical damping time (6-30 years), one may assume in first approximation that L_{CO} does not follow P_{CO} fluctuations, remaining nearly constant. The P_{CO} seasonal variation of $\pm 35\%$, occurring over about one third of the CO lifetime, involves CO fluctuations of about $\pm 10\%$. The P_{CO} solar cycle variation involves CO fluctuations of absolute amplitude $\pm 2 \cdot 10^{10} \text{ s}$ ($5.5 \text{ yr} \times 1.2 \cdot 10^{11} \text{ cm}^{-2} \text{ s}^{-1} = \pm 2.4 \cdot 10^{19} \text{ cm}^{-2}$ or $\approx \pm 10^{-4}$ in terms of mixing ratio. Amplitudes of seasonal and solar cycle fluctuations are both $\approx \pm 10\%$, thus rather weak.

The third factor to determine the CO balance plays also a key role because of the large annual variation of the water vapor content. From table 7 of S, it may be seen that $[CO]_{eq}$ is increased by a factor of ≈ 5 as the water vapor amount decreases from 10.35 to 1.39 pr. μm . Fig. 8 of S shows that the corresponding variation of L_{CO} is only $\approx 30\%$. As expected from arguments presented in previous sections, L_{CO} is much less sensitive to a change of $[H_2O]$ than $[CO]_{eq}$. The

increase of L_{CO} from northern summer to northern winter by the release of H_2O from the polar cap tempers the effect of the simultaneous increase of P_{CO} , still reducing the amplitude of seasonal variations. Solar cycle fluctuations of the photolysis rate of H_2O have an amplitude of $\approx \pm 5\%$. In view of a small sensitivity of L_{CO} to $[H_2O]$, this effect may be neglected. Adding to the small seasonal and solar cycle fluctuations, some latitudinal gradients could exist for at least two reasons: - less CO is produced at low solar zenith angle ; - the latitudinal distribution of water vapor measured by Viking shows a marked global depletion in the south hemisphere. From the previous analysis, it follows that equilibrium values of CO might exhibit a large south/north and/or equator/poles contrast of nearly one order of magnitude. Although global circulation is expected to reduce this asymmetry, some gradients could be maintained.

Conclusion

The purpose of this analysis was to bring out an interesting feature of the Martian photochemistry, unquestionably related to the problem of the CO_2 stability, that is the weakness of feedback processes regulating CO at its equilibrium level. From a detailed study of feedbacks, damping times of CO fluctuations are found to be long, 2 to 10 times larger than its photochemical lifetime (≈ 3 yr). Although small variations of the production and loss rates of CO yield in principle large variations of its equilibrium abundance, significant variations are improbable. Considering temporal effects, the main limitation is the shortness of transition periods which does not allow CO to reach its equilibrium value. Small seasonal and solar cycle fluctuations ($\approx \pm 10\%$) are expected. The plausibility of latitudinal gradients is increased in view of the present work. A more extensive study, including global convection, would be required to give quantitative estimates.

Arguments presented in the present paper may certainly help to the understanding of the CO depletion detected from the Phobos 2 spacecraft above the big volcanoes. But they are far from providing a complete framework. They tell us that such a depletion, if it exists, is photochemically stable. Yet, time constants associated to stability are very large and damping must be due primarily to dynamical mixing. The origin of the depletion is quite problematic. Let X be the chemical species which converts CO into CO_2 . In order to create the depletion, an amount of X equivalent to the one of CO must be brought within a time scale smaller than some days or weeks. OH formed through water vapor (volcanism, permafrost...) is not a good candidate because of the very slow rate of H_2O photolysis ($6 \cdot 10^{-10} \text{ s}^{-1}$ at 20 km altitude): 10 mbar partial pressure of H_2O would be required to oxidize large amounts of CO in one week! X might be O reacting with CO in presence of aerosols [Atreya and Blamont, 1990] but at the present time there are no published laboratory measurements of CO sticking coefficients in martian conditions. Odd oxygen being about 10^4 less abundant than CO, this mechanism would require rapid injection of an amount of O about ten thousand times larger than the current amount. But in this case, the recycling mechanism may be easily found in the classical scheme of catalytic cycles due to HO_x : excess O atoms react within some hours with HO_2 (Eq. 2), forming OH radicals. OH reacts instantly with CO,

yielding CO_2 and H. Subsequent reaction of H and O_2 reforms HO_2 , which reacts on O to form OH and so on. Whatever may be the process recycling CO_2 , the main difficulty is to explain such a massive injection of O. A possible explanation could be the rapid downward diffusion from high altitudes of large amounts of atomic oxygen above mountains, where vertical eddy mixing must be enhanced by wave activity. This is, on a local scale, the McElroy-Donahue scheme. Renewal of available O at high altitude might be insured by zonal wind. Simultaneous observations of O_3 and CO above high regions should allow to check this hypothesis.

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