The Oxidizing Environment

Possible Oxidant Sources in the Atmosphere and Surface of Mars*

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Summary. Photolysis of H_2O in the atmosphere near the surface is a copious source of OH, HO_2, and probably superoxides, some of which are likely to condense on the surface and migrate through the pores. The processes have been modeled in detail for their atmospheric interest. The models successfully account for the rarity of CO and O_2, the notable variability of ozone, and the escape flux of hydrogen. Though only qualitative estimates can be made of surface deposition rates and lifetimes, the suggested amounts are in the range inferred by Viking. The OH rapidly destroys any organic molecules that are present as vapors.

Analogous reactions involving adsorbed water have been studied by Huguenin. These processes can be driven by the much larger photon fluxes at longer ultraviolet wavelengths. The suggested explanations, and many of the experiments, make it likely that peroxides, superoxides, and adsorbed OH are all present. Both kinds of process, and their combinations, seem in principle able to explain the absence of all organic molecules and the variety of observed oxidants. Since they operate planetwide, there is a strong suggestion that the observed conditions are typical. Oases of higher than average humidity may in fact be even more hostile than the average region, because water under Martian surface conditions is anything but benign.

Laboratory simulation of the atmospheric processes must pay careful attention to scaling.

Curiously, similar OH densities occur at the Earth's surface, The notable differences are food for thought, and ideas about the origin of life may be particularly affected.

Key words: Mars — Aeronomy — Oxidants

Introduction

Perhaps the most striking result from the Viking landers was the total absence of detectable organic molecules in the soil. (Limits were 10^{-9} for most, rising to 10^{-6} for a few volatile compounds: Biemann et al., 1977). Thus, even though the metabolic experiments showed plenty of activity, great suspicion was thrown on the idea that metabolism was responsible. In fact, plausible inorganic explanations have been proposed for most of the results, and the case for life remains exceedingly weak (Horowitz, 1977). Generallly speaking, both the activity of the soil and the absence of organic molecules are attributed to the presence of oxidants; Klein (1978) suggests that three kinds are needed.

Even before Viking, studies of oxidant sources had been undertaken. They were directed toward answering two very basic questions about Mars: (1) Why is CO_2 stable on Mars? (2) Why is Mars red? The relationship to the Viking experiments was regrettably considered only after the landing. Direct destruction of molecules by solar ultraviolet had been discussed, but it is well known that organisms can shield themselves either by developing suitable skins or by staying out of the light. Oxidants (of which H_2O_2 is typical) are much more difficult to avoid.

Why is CO_2 Stable?

When a bottle of CO_2 is irradiated with ultraviolet of wavelengths less than 200 nm, it is converted to CO and O_2 with a quantum efficiency not far from unity. Yet the abundances of these gases on Mars is only about 0.1%. CO and O_2 do not react at Martian temperatures, and even CO and O react very slowly. It is now thought that the actual oxidant for CO is the radical OH, formed from the trace of water vapor in the lower atmosphere, but this identification came by a tortuous path. An important series of laboratory experiments was reported by Reeves et al. (1966); they showed that addition of H_2O or H_2 to the bottle of CO_2 would greatly reduce the buildup of CO and O_2. Their suggestion of HO_2 as the oxidant was taken up by Hunten and McElroy (1970) in a Mars model that seemed to give a satisfactory account of the situation. Concurrent laboratory work by Baldwin et al. (1970) showed however that the reaction of CO and HO_2 is too slow by many orders of magnitude. The following year a conference devoted to this and related issues was held in Tucson. Many of the papers were published in the September 1971 issue of the *Journal of the Atmospheric Sciences*. Clark (1971) concluded "There does not appear to be any known gas phase process capable of explaining the low mixing rations of CO and O_2 in the Martian atmosphere". He therefore suggested that the recombination took place on surfaces.

Our present understanding of the photochemistry of hydrogen in the Martian atmosphere is illustrated in Fig. 1. It is convenient to classify the compounds into even (e.g. H_2O, H_2) and odd (H, OH, HO_2). Hydrogen peroxide, H_2O_2, is in the odd category by its behavior, although it has two hydrogen atoms. The various forms of odd H interconvert rapidly; thus Fig. 1 is organized to bring out as entities the production, loss, interchange, and precipation of odd H. The reaction (between OH and CO) that stabilizes the atmosphere is part of the odd-H cycle. The inner loop (which is much faster) generates OH from O atoms; the outer one uses O_2 molecules.
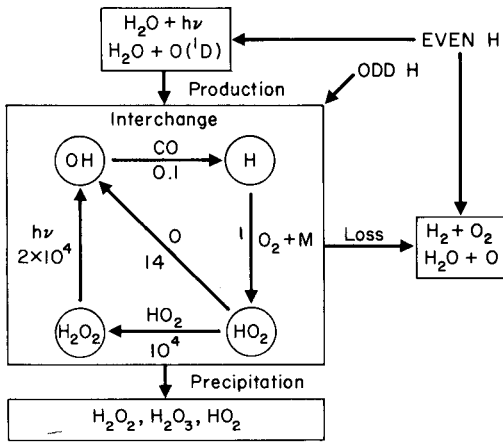
Fig. 1. An illustration of the chemistry of ood hydrogen on Mars. Only the most important reactions are shown. The numbers are mean lifetimes (sec) for typical daytime conditions near the surface.

Generation of odd H is by photolysis of H_2O and reaction of O (^1D) with H_2, itself a byproduct of the processes under discussion. (The metastable O atoms are produced from ozone.) Loss of odd H requires reaction of two radicals; those of H or OH with HO_2 make comparable contributions. The photolysis rates for H_2O have been computed by Hunten and McElroy (1970) and Kong and McElroy (1977a); the pre-Viking data on H_2O abundances were already adequate for a reasonably good estimate. In turn, the production rates for odd H give an upper bound to the rates of precipitation to the cold surface. This number is about 2×10^9 cm^{-2}s^{-1}, expressed as a global average for odd-H radicals. In terms of nanomoles of H_2O_2 per Martian year, the result is around 100. The production estimate is conservative, reflecting 3 μm precipitable H_2O illuminated half the time. However, since there is considerable loss within the atmosphere, only an unknown fraction reaches the surface. Precipitation is probably aided by the diurnal cycle, since in the dark most of the odd H is converted to H_2O_2.

The pre-Viking work on atmospheric stability has been reviewed by Hunten (1974) and McConnell (1975). It is necessary to cope with a limited supply of O atoms to run the inner cycle of Fig. 1. Two limiting solutions were published almost simultaneously. McElroy and Donahue (1972) suggested a rapid downward transport of O atoms from the upper atmosphere, such as to preserve them and make them available near the surface. Parkinson and Hunten (1972) chose conditions that made H_2O_2 fairly abundant; its photolysis then gave a sufficient supply of OH. The more detailed study by Kong and McElroy (1977a, b) lies somewhere between.

These models successfully accounted for the rarity of CO and O_2 in the atmosphere. They are also testable by their predictions of other observed phenomena. Lyman-alpha spectroscopy by Mariners 6, 7, and 9 gave the density and escape rate of H atoms in the outer atmosphere. Without any special adjustment, the models give values in this same range. (For a review, see Hunten and Donahue, 1976.) A much more striking result was the great variability of the ozone abundance, small in warm areas and much larger in cold regions, observed by the same instruments

mentioned above (reviewed by Hunten, 1974). An atmospheric model lacking odd hydrogen predicts the large abundance; a damper one predicts the small abundance, traceable to the rapid consumption of O atoms in the odd-hydrogen cycle. (O and O_3, or odd oxygen, are linked by a rapid cycle of their own.)

An obvious reason for lack of odd H in cold regions is a lack of water vapor. But this can be only part of the story: odd H is also generated from H_2, which does not freeze on Mars, and ozone, the source of $O(^1D)$, is abundant in exactly the same places. There must be another mechanism acting on the odd H itself, and precipitation of H_2O_2 is the obvious one, since its vapor-pressure curve is nearly identical to that of H_2O. A detailed model along these lines is described by Kong and McElroy (1977b). At the very low temperatures of nighttime and winter, precipitation of HO_2 and formation of polyoxides seems plausible. Such processes have received considerable study, both for their own interest and as a possible source of high-energy fuels (Venugopalan and Jones, 1968).

Hunten (1974) pointed out that any methane released to the atmosphere would be destroyed in about 10^{10} s or 300 Earth years by reaction with OH. It is a curious fact, inexplicable but true, that nobody thought to make the connection to the Viking experiments until after they had landed on Mars. All models except the very driest ones predict an OH concentration of $(1-2) \times 10^5$ cm^{-3} in the whole daytime Martian troposphere. A suitable diurnal and global mean value is therefore 10^5 cm^{-3}. Table 1 shows a collection of simple molecules for which rate coefficients for reaction with OH were readily available. The last column gives their mean lifetimes under these typical Martian conditions. As might be expected, methane is by far the most stable; as molecules become bigger, or contain double bonds, they are more subject to attack. There can be little doubt that the degradation products have similar or shorter lifetimes. Therefore, any volatile hydrocarbon or organic molecule must

Table 1. Rate coefficients at $200^{\circ}K$ (Hampson and Garvin, 1978) and lifetimes for a mean OH concentration of 10^5 cm^{-3}

Molecule	Rate, $cm^3 s^{-1}$	Lifetime, s
CH_4	4.6 - 16	2.2 + 10
C_2H_2	5.7 - 13	1.7 + 7
C_2H_4	4.3 - 12	2.3 + 6
C_2H_6	2.6 - 13	3.8 + 7
C_3H_6	6.1 - 11	1.6 + 5
C_3H_8	2.7 - 13	3.7 + 7
C_4H_{10}	1.1 - 12	9.3 + 6
C_6H_6	1.0 - 12	1.0 + 7
$C_6H_5CH_3$	4.0 - 12	2.5 + 6
CO	1.4 - 13	7.1 + 7
CH_2O	8.6 - 12	1.2 + 6

CH_4 METHANE
$\downarrow$ OH
CH_3 METHYL
$\downarrow$ $O_2 + M$
CH_3O_2 METHYLPEROXY
$\downarrow$ NO_2
CH_2O ——┐ FORMALDEHYDE
    $h\nu$, │OH
       HCO   FORMYL
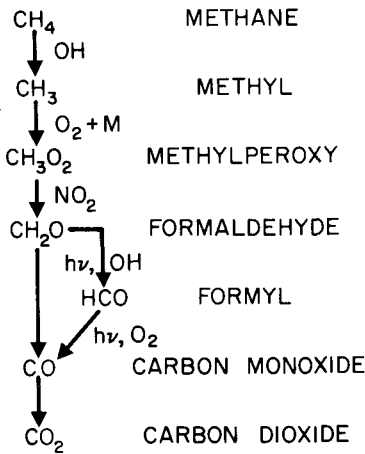 $h\nu$, O_2
CO CARBON MONOXIDE
$\downarrow$
CO_2 CARBON DIOXIDE

Fig. 2. The oxidation scheme for methane on the Earth.

quickly be converted to CO_2 and H_2O. The details of this process have been studied for CH_4 in the Earth's atmosphere (Wofsy et al., 1972), and are illustrated in Fig. 2.

It is much less clear what rate would apply to organic molecules in the soil. OH and the other oxidants must be bombarding the surface, and some of them surely are mixed downwards as the soil is stirred by the winds. That oxidation must be proceeding is inevitable, and even if the rates were slower by orders of magnitude than in the atmosphere, organic molecules must be destroyed to a considerable depth.

The other aspect of the Viking results is to explain the various responses of the biology instruments. Here the atmospheric chemist is far out of his depth. During the cold season, deposition rates could perhaps approach 100 nanomoles per Martian year, as noted above. It appears that several years' accumulation would be needed to account for the observed response. It remains to be demonstrated that such stability is possible.

Why is Mars Red?

The red color of Mars has been remarked for as long as we have possessed records, and led to the association with the god of war. In more scientific terms, the association with iron oxide is obvious and perhaps almost as ancient. But why is the iron so oxidized? The liquid water that assists oxidation on Earth is absent on Mars. About a decade ago, Bruce Hapke suggested that photo-oxidation might be the answer; this suggestion was taken up by Huguenin (1973a, b). It was found that the process is extremely effective, especially in the presence of water vapor. Clearly, there is a family resemblance to the atmospheric processes discussed above. Adsorption of H_2O molecules on the surface permits longer (and more intense) wavelengths to be effective, and the radicals produced are in the right place to go right to work. Huguenin varied the external conditions and derived empirical kinetics for the process. In his original scheme (Huguenin 1974, 1976), the H_2O acted as a catalyst, but the source of oxygen was atmospheric O_2; Fe_3O_4 was converted to Fe_2O_3. Some limitations on the availability of O_2 were discussed by McElroy and Kong (1976). An alterna-

tive scheme, in which the source is the H_2O itself, was then put forward by Huguenin et al. (1977). As a byproduct, adsorbed OH and H_2O_2 are thought to be generated.

Huguenin's work has two aspects, which should be clearly distinguished. By making assumptions about the rate of exposure of fresh surface, he has come up with large numbers for the amount of material (both crustal and atmospheric) that might be processed in several billion years. Although these ideas are controversial, they are not involved at all in the specific issue of the presence of oxidants, and the absence of organic molecules, to the depths sampled by Viking. The experiments demonstrate that substantial effects take place under simulated Martian conditions.

A recent set of experiments (Huguenin et al., 1978, 1979) gives the surprising result that oxygen can be liberated in the absence of any photons. The ingredients are a fresh surface of olivine and water frost. On warming and humidification of the product, O_2 is released. In this case, iron in the rock is thought to be reduced, and adsorbed H_2O_2 generated. Operation of this kind of process on Mars is speculative, and one even wonders if it would give a red planet.

Finally, it seems possible that there could be combination processes involving the atmospheric oxidants, especially OH and HO_2, acting on surface materials. At present, this idea is pure, if plausible, speculation.

Concluding Remarks

This paper has been confined to a fairly narrow range of topics that have either been modeled in detail or studied empirically. A full explanation of all the Viking results is not yet at hand. Nevertheless, we seem to have several reasonable sources of oxidants, perhaps yielding even more than the three kinds required by Klein (1978). And the absence of organic molecules does find a reasonable explanation. If even more sinks were needed, one could turn to the catalysis by TiO_2 suggested by Chun et al. (1978). All these processes should operate planetwide, and it can be predicted that the conditions found by Viking are entirely typical.

It will be noted that the two main sections of this paper describe very different approaches. Within the atmosphere, use is made of detailed chemical models, while for the surface the ideas rest almost entirely on detailed simulation, and more than one model may be used to explain the same data. There is good reason for this difference. A realistic simulation of surface processes can be carried out in a laboratory chamber. But the experience of atmospheric chemists and their laboratory colleagues has taught them that this is not the best approach to the understanding of processes in the free atmosphere. The problem is that reactions on the walls of the chamber frequently dominate the situation and confuse or mask the processes going on in the gas. The only successful procedure has been to isolate and measure the individual reactions in the laboratory, and then apply them in a theoretical model of the atmosphere. If the results pass all available empirical tests, the model can be provisionally accepted.

We are here also concerned with a hybrid case, the supply of oxidants to the Marian surface from atmospheric processes. Simulation of this process has a better chance of success, but great care is still necessary. There must be enough free volume

for the atmospheric reactions to take place without interference. Since the true scale of the atmosphere cannot be reproduced, it may be necessary to adjust other variables to compensate. In the Martian atmosphere, the source of oxidants is a column of depth 5–10 km, containing certain amounts of H_2O, H_2, O_2, and O_3 and irradiated by sunlight filtered through CO_2. The best way to get the same flux of chemicals out of a 1-meter column is probably to raise the ultraviolet flux, but this is not fully satisfactory either: the density of odd H will be increased, and second-order processes such as generation of H_2O_2 will increase quadratically. Since a valid simulation is impossible, conditions must be varied and a considerable input of theory used for interpretation and guidance.

Since Mars has turned out to be so hostile to life, suggestions have often been made that there may be a few oases that are much more benign. Important aspects of such a region would be higher temperatures and more water. But if the ideas reviewed here have any validity, higher humidity leads to a greater production of oxidants and a still more hostile environment. The requirements for a true oasis on Mars are much more than mere warmth and humidity.

An interesting comparison can be made between Mars and Earth. The OH concentration in our troposphere is also close to 10^5 cm^{-3} (Wofsy et al., 1972); the greater abundance of H_2O is compensated by the smaller ultraviolet flux. The lifetimes shown in Table 1 are therefore applicable here as well. Presumably the supply of organic molecules is so great that the atmospheric destruction does not matter. Conversely, this destruction is an important cleansing mechanism for pollutants, both natural and artificial, and including CO (Wofsy, 1976). Survival of organic molecules on the primitive Earth can presumably be attributed to the presence of liquid water, which dilutes and helps destroy the atmospheric oxidants, aided by higher temperatures. Conversely, as Fig. 2 suggests, reaction with atmospheric oxidants can generate some interesting organic compounds from various precursors.

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