The Oxidizing Environment

Possible Oxidant Sources in the Atmosphere and Surface of Mars*

Donald M. Hunten

Lunar and Planetary Laboratory Department of Planetary Sciences, University of Arizona
Tucson, Arizona 85721, USA

Summary. Photolysis of H₂O in the atmosphere near the surface is a copious source of OH, HO₂, 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 O₂, 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

* Based on an invited paper at the Second International Colloquium on Mars, Pasadena, January 15–18, 1979

0022–2844/79/0014/0071/$ 01.60
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). Generally 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$_2$O$_2$ 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$_2$O 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$_2$O, H$_2$) and odd (H, OH, HO$_2$). Hydrogen peroxide, H$_2$O$_2$, 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 precipitation 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.