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PHOTOCHEMISTRY OF PLANETARY ATMOSPHERES*

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PHOTOCHEMISTRY OF PLANETARY ATMOSPHERES

Photodissociation is the primary loss process for the major components of the atmospheres of planets. A fundamental problem is the explanation for the apparent stability of, for example, the CO_2 atmosphere on Mars. It now appears that the ultimate solution to this problem is more likely to depend on new knowledge concerning the dynamics of atomic and free radical reactions occurring subsequent to photodissociation rather than on additional details concerning the primary photochemical process. In the following sections, the atmospheric composition of Mars is presented and the applicability of laboratory data on CO_2 absorption cross sections and quantum yields of dissociation is discussed. This is followed by a summary and critical evaluation of the various mechanisms proposed for converting the photodissociation products CO and O_2 back to CO_2.

INTRODUCTION

The scope of the subject the photochemistry of planetary atmospheres is obviously too broad to be adequately described in a limited presentation. I had initially intended to discuss two examples of photochemical problems relating to the atmospheres of planets, viz. the stability of the CO_2 atmosphere on Mars and the stability of the NH_3 and CH_4 in the atmosphere of Jupiter. However, the latter problem will not be discussed because the astronomical "facts" are not yet sufficiently firm and a choice between the two theories relating to this problem depends on these "facts" as well as laboratory data not presently available. The interested reader is referred to papers by McNesby[1] and Strobel[2] for details regarding the Jupiter problem. The present discussion will therefore be limited to the question of the stability of the Martian CO_2 atmosphere.

The composition of the lower atmosphere of Mars is shown in Table 1. The densities given are those at or near the surface where the temperature is about 150°K. There are some time variations observed as well as differences between the results of different observers, but the results for CO and O_2 are certainly good to within a factor of 2 and the CO_2 density is now known to an accuracy of ±15%. The O_3 observations were made with the ultraviolet spectrometer aboard Mariner 7 and 9. No ozone is present in the equatorial region, but in the polar regions ozone appears in the fall, reaches a maximum in winter and decreases in the spring[3]. The inverse correlation of ozone with water vapor suggests that the presence of water suppresses the ozone formation.

The contents of Table 1 should be very disturbing to any laboratory photochemist who has used CO_2 as a chemical actinometer. It is well known that CO_2 is

Table 1

Mars: Atmospheric Composition

Molecule	Concentration (cm^{-3})
CO_2	1.5×10^{17}
O_2	2.0×10^{14}
CO	1.2×10^{14}
H_2O	$\sim 10^{14}$
O_3	$< 10^{10}$ [a]

a. Estimated limit for planet outside the polar regions; ozone only observed over polar regions and reaches maximum in winter of $\sim 10^{11}$ cm^{-3}.

photodissociated in the laboratory and that CO is formed with a quantum yield Φ equal to or close to unity. It may be readily calculated from the known flux of solar radiation, the absorption cross section for CO_2 as a function of wavelength and assuming $\Phi = 1$ that the amount of CO now present in the atmosphere of Mars would be produced in only two years. Even if $\Phi = 0.5$, the essential problem remains since the observed CO would then be produced in four years. One is thus forced to conclude that either the absorption cross sections or quantum yields of dissociation are many orders of magnitude smaller than inferred from laboratory data or that there is an efficient process for converting CO and O_2 back to CO_2. Julienne, Neuman and Krauss[4] have drawn attention to the possible errors involved in using room temperature laboratory cross sections in modeling studies for CO_2 kinetics. Their theoretical calculations suggest that halving the temperature from 300° to 150°K produces only about a 10% decrease in CO_2 absorption for the region 1200-1750 Å. In addition, DeMore and Patapoff[5] have shown that cross sections for the region 1700-2000 Å measured at 200°K are about one-half the room temperature values. Thus, while this effect should be considered for accurate modeling, it appears that there are no order of magnitude effects on absorption cross sections. The situation is similar for the primary quantum yield. While there may be evidence for Φ as low as 0.5 (see for example the work of Inn[6]), order of magnitude effects appear to be definitely excluded. The task thus reduces to identifying the mechanism or mechanisms by which the photodissociation products CO and O_2 are converted back to CO_2.

The processes occurring in the upper and lower atmosphere leading to the formation of O_2 and CO may be summarized as follows:

Upper Atmosphere

$$CO_2 + h\nu \rightarrow CO + O(^1D)$$

$$O(^1D) + CO_2 \rightarrow O(^3P) + CO_2$$

Lower Atmosphere

$$CO_2 + h\nu\ (\lambda > 1650\ \text{Å}) \rightarrow CO + O(^3P)$$

$$O(^3P) + O(^3P) + CO_2 \rightarrow O_2 + CO_2$$

Three body recombination of O and CO may be neglected based on the results of Slanger, Wood and Black[7].

THE HO_2 MECHANISMS

There are a number of mechanisms which may be considered jointly since they all involve reaction and formation of the HO_2 free radical. The source of H is considered to be the photolysis of H_2O, known to be present in the atmosphere ($\sim 0.1\%$ of CO_2). It is well to recall here the CO_2 photochemical equilibrium studies of Harteck et al.[8] using the 1633 Å bromine line. It was found that with as little as 0.1% water vapor present (the same level as for Mars), complete recombination to CO_2 occurred ($O_2/CO_2 < 0.005$). While these experiments do not point to a specific mechanism, they clearly show that the presence of water is important and that under conditions comparable to that of the Martian atmosphere, there is little net CO_2 dissociation.

The HO_2 mechanism may be summarized by the following cycle of reactions:

$$H + O_2 + CO_2 \rightarrow HO_2 + CO_2 \qquad (1)$$

$$HO_2 + X \rightarrow OH + XO \qquad (2)$$

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$$OH + CO \rightarrow CO_2 + H \tag{3}$$

It is clear that the net effect of X is to convert less reactive HO_2 to OH which leads to recombination of CO and O_2 to CO_2 and regeneration of the chain carriers H and OH. We will briefly consider here mechanism for X = CO, NO, O_3, H, O and HO_2. Table 2 lists the rate constant for each HO_2 + X reaction, the approximate steady state concentration required at or near the surface to compensate for the O_2 production rate. In the full model, many factors are included and concentrations are calculated as a function of altitude.

Table 2

Steady State Concentration Required by the Various HO_2 Mechanisms

X	k (cm^{-3} s^{-1})	$(X)_{ss}$ (cm^{-3})	
		Req.	Obs.
CO	$< 10^{-20}$	10^{18}	10^{14}
NO	3×10^{-13}	10^{10}	—
O_3	3×10^{-15}	10^{12}	$< 10^{10}$
H	$(\sim 10^{-11})$	10^{9}	10^{4}[a]
O	7×10^{-11}	10^{8}	10^{8}[a]
HO_2	3×10^{-12}	10^{9}	—

a. Calculated from Mariner observations at 250 km for H and 135 km for O. See ref. 9.

Despite early suggestions that reaction (4) should be fast[8,10] and the very indirect determination by Westenberg and de Haas[11] that $k_4 \cong 10^{-12}$ cm^3 $molec^{-1}$ s^{-1}, it is now relatively certain that the reaction

$$HO_2 + CO \rightarrow CO_2 + H \tag{4}$$

is negligibly slow near 300°K. This was first suggested by the high temperature work of Baldwin[12] and subsequently verified by attempts to measure k_4 at 300°K.[13-16] The best estimate comes from the isotopic labelling-product analysis experiment[14] and this result of $k_4 < 10^{-20}$ cm^3 $molec^{-1}$ sec^{-1} would require a CO density that exceeds the observed value by 10^4. Using the same isotopic labelling technique, an estimate has been made[17] of the rate constant for the reaction[18]

$$HO_2 + NO \rightarrow OH + NO_2 \qquad (5)$$

As seen from Table 2, a concentration NO equal to 10^{10} molec cm^{-3} would be required. While photolysis of NO_2 would return NO to the atmosphere, it should be emphasized that such levels of NO and NO_2 should be capable of detection by ultraviolet spectroscopy.

The $HO_2 + O_3$ reaction has been included since a good limit exists for O_3 concentration and both De More[19] and Simonaitis and Heicklen[20] have recently measured the rate constant at 300°K. The results in Table 2 show that the required O_3 concentration exceeds the observed upper limit by a factor of 10^2. Reaction with H should also be considered since atomic hydrogen is a known constituent of the atmosphere. Although the rate constant for the reaction

$$H + HO_2 \rightarrow 2\ OH \qquad (6)$$

has not been measured, the estimated[11,21] value of $k_6 = 10^{-11} cm^3\ molec^{-1}\ sec^{-1}$ leads to concentration of H many orders of magnitude too high.

Thus we are finally left with only two possibilities. One is the reaction[22]

$$HO_2 + O \rightarrow OH + O_2 \qquad (7)$$

which is part of the complete model proposed by McElroy and Donahue[21]. The required 0 atom concentration is at least not inconsistent with observations; the model does however require large eddy diffusion to transport atomic oxygen from the upper to the lower atmosphere. The final reaction is HO_2 disproportionation[23]

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad (8)$$

which is followed by photolysis of H_2O_2

$$H_2O_2 + h\nu \rightarrow 2OH. \qquad (9)$$

This suggestion is due to Parkinson and Hunten[22] and the large eddy diffusion requirement of the McElroy-Donahue model is avoided. These are some minor problems with both models, but it is not inconceivable that both could be important depending on the relative concentration of O and HO_2 in the lower atmosphere. These could be variable with time. At the present writing, these two models seem to offer the most hope for eventually understanding the stability of CO_2 in the atmosphere of Mars.

OZONE MECHANISM

This may be treated much more briefly. The proposed[8,18] sequence of reactions is:

$$O + O_2 + CO_2 \rightarrow O_3 + CO_2 \qquad (10)$$

$$H + O_3 \rightarrow OH + O_2 \qquad (11)$$

$$OH + CO \rightarrow CO_2 + H \qquad (3)$$

Again, the net result is to convert the less reactive O and O_2 to OH to achieve conversion of CO and O_2 back to CO_2. However, since there are laboratory measurements for k_{11}[25] and k_1[26] and observational data for concentration of O_3, O_2 and CO_2 (see Table 1), we can readily calculate the O_3 concentration required for H + O_3 (11) to be competitive with H + O_2 + CO_2 (1).

$$k_{11}(H)(O_3) = k_1(H)(O_2)(CO_2)$$

$$O_3 = \frac{5 \times 10^{-32} \times 2 \times 10^{14} \times 1.5 \times 10^{17}}{2.6 \times 10^{-11}}$$

$$O_3 = 6 \times 10^{10} \text{ molec cm}^{-3}$$

This is well above the limit of $O_3 < 10^{10}$ molec cm^{-3} from the Mariner observations for the equatorial regions and is within a factor of 2 of the maximum values observed over the polar region in winter. In addition, for the $H + O_3$ mechanism to dominate over the HO_2 mechanism, we should assume $R_{11} = 10R_1$ which leads to O_3 concentrations of 6×10^{11} molec cm^{-3}. Clearly this mechanism is not important under the known condition of the Martian atmosphere.

IONIC MECHANISM

Finally, for completeness we consider the mechanism proposed by Parks[27] which is based on the interesting observation that CO_2 shows apparent stability under radiolysis. Essentially the idea is that CO_2 is converted by ultraviolet radiation to CO and O_2 and that the photochemical products are converted back to CO_2 by means of ion-molecule reactions involving positive ions produced from CO_2. The mechanism requires positive ion concentrations of the order of 10^3 cm^{-3} and rate constants all of the order of 10^{-11} cm^{-3} $molec^{-1}$ sec^{-1}. Without going into the details of the full mechanism, we point out two serious problems. The first is that a laboratory measurement[28] of one of the key reactions of the mechanism

$$CO_4^+ + CO \rightarrow CO_3^+ + CO_2 \qquad (12)$$

shows that the rate constant is much too slow ($k_{12} \lesssim 10^{-12}$ cm^3 $molec^{-1}$ sec^{-1}). The second problem, which applies to any ionic mechanism proposed, is that a means must be found to transport the positive ions from the upper atmosphere where they are formed to the very low atmosphere near the surface where CO and O_2 concentrations are many orders of magnitude larger.

SUMMARY

The persistence of the CO_2 atmosphere on Mars appears to require some mechanism which converts the photolysis products CO and O_2 back to CO_2. At the present time, the mechanism most consistent with both astronomical observations and laboratory data involves the chain sequence: $OH + CO \rightarrow CO_2 + H$, $H + O_2 + CO_2 \rightarrow HO_2 + CO_2$ and $HO_2 + O \rightarrow OH + O_2$ and/or $HO_2 + HO_2 \rightarrow H_2O_2$ $h\nu \rightarrow 2OH$. The chain carries H and OH are supplied by photolysis of H_2O which is present to the extent of 0.1% of the CO_2.

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