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Catalytic Processes in the Atmospheres of Earth and Venus

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Summary. Photochemical processes in planetary atmospheres are strongly influenced by catalytic effects of minor constituents. Catalytic cycles in the atmospheres of Earth and Venus are closely related. For example, chlorine oxides (ClO_x) act as catalysts in the two atmospheres. On Earth, they serve to convert odd oxygen (atomic oxygen and ozone) to molecular oxygen. On Venus they have a similar effect, but in addition they accelerate the reactions of atomic and molecular oxygen with carbon monoxide. The latter process occurs by a unique combination of ClO_x catalysis and sulfur dioxide photosensitization. The mechanism provides an explanation for the very low extent of carbon dioxide decomposition by sunlight in the Venus atmosphere.

Planetary atmospheres are profoundly influenced by the photochemical action of solar radiation. On Earth, a major effect of solar ultraviolet absorption is the creation of the ozone layer in the upper stratosphere. This broad band of ozone in the region from 15 to 40 kilometers protects the surface of Earth from harmful ultraviolet radiation, which would otherwise be incompatible with the existence of the biosphere in its present form. In recent years much attention has been directed to the subject of stratospheric photochemistry, with special attention to the possibility of man-made perturbation of the ozone layer. The first large-scale study of stratospheric photochemistry was a national and worldwide program (*1*) to evaluate possible reduction of the ozone layer by exhaust emissions (especially oxides of nitrogen) from high-flying aircraft, such as the supersonic transport. This program was followed by an investigation of related effects on stratospheric ozone which might arise from release of chlorofluoromethanes (CFM's) into the atmosphere (*2*). The postulated effect of CFM's is now well known as the Molina-Rowland hypothesis (*3*). Although the quantitative conclusions of these studies remain to be settled with certainty, there is no doubt that man's activities can alter the ozone layer.

Venus presents a novel and challenging problem to the atmospheric scientist because its atmospheric composition is very different from that of Earth. Although it might be assumed that the photochemical mechanisms of the two planets are very different, we will show that many of the important properties of the two upper atmospheres are controlled by related processes. Where differences arise, they are primarily the result of varying emphasis rather than fundamentally different chemistry at the conceptual level.

The upper atmosphere of Venus has been actively studied through Earth-based and space probe observations during the past decade (*4, 5*). In this connection it is of interest to note that HCl was discovered on Venus in 1967 (*6*), prior to the recognition of the significance of chlorine compounds in the earth's stratosphere. The possible role of chlorine in the Venus atmosphere was first explored by Prinn in 1971 (*7*), and other studies (*8–14*) have increased our understanding of Venus photochemistry.

Table 1 compares some of the major properties of the stratospheres of Earth and Venus. With regard to temperature and pressure the two regimes are quite similar, despite the much greater differences in these properties at low altitudes. Although the composition of the Venus atmosphere is not known as precisely as that of Earth's atmosphere, the basic features are well established. The major components are carbon dioxide (96 percent) and nitrogen (3 to 4 percent). Notably absent as a major constituent is oxygen; an upper limit of 1 part per million has been established (*15*). Why the O_2 level is so low is an intriguing question, because photochemical models have predicted that dissociation of CO_2 by sunlight should have produced greater concentrations of O_2 (and CO). As a consequence of the low O_2 concentration, Venus has essentially no ozone layer. A prominent feature is the sulfuric acid cloud layer (*16*), produced by the oxidation of the trace constituent SO_2 (*12, 17, 18*). The constituents SO_2 and HCl are much more abundant in the Venus atmosphere than they are in Earth's atmosphere. Methane and nitrous oxide (N_2O), of biological origin, are important minor constituents of Earth's atmosphere but are absent in the Venus atmosphere.

In both cases the minor constituents are present at concentrations of parts per million. However, their influence is out of proportion to their abundance. The reason is that minor constituents (or, more often, the radical species derived from them) provide the catalytic agents that can undergo repeated reactions before eventual removal from the system. Thus small concentrations can bring about large chemical changes. Although it is well known that catalysis does not alter the final equilibrium state in thermal systems, photochemical systems such as the stratosphere are strongly influenced. This is because photochemistry tends to drive the system away from thermal equilibrium, whereas catalytic effects work to restore the system to thermal equilibrium.

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It is necessary in connection with catalytic processes to distinguish between thermal catalysis and photosensitization. Thermal catalytic processes accelerate thermal reactions which otherwise are relatively slow. Photosensitization occurs when the minor constituent absorbs light to which the bulk medium is transparent and ultimately utilizes the photon energy to bring about a chemical change in the medium. Both types of processes are important. The constituents SO_2 and NO_2, being strong absorbers of sunlight, play major roles as photosensitizers in the atmospheres of Earth and Venus. In later sections we will discuss several examples of catalytic and photosensitization effects, and show how they influence the stratospheric composition of both planets.

The minor species do not, for the most part, enter directly into catalytic reactions. Instead they serve as sources or parent molecules of free radicals, which are the active catalytic agents. As examples, the free radicals in the HO_x family (H, OH, and HO_2), the NO_x family (NO and NO_2), and the ClO_x family (Cl and ClO) are derived, respectively, from parent molecules such as H_2O, N_2O, and chlorofluoromethanes.

Photochemistry

For both Earth and Venus the atmospheric component with which we are concerned is oxygen, with particular emphasis on the question of how it is distributed among the various forms such as O_2, O, O_3, and CO_2. The species O and O_3 are often referred to as odd oxygen, and O_2 is even oxygen.

The concentration of a particular species depends on the balance between its rates of formation and destruction, reactions which are largely photochemical in nature. In order to understand the chemically delicate nature of this balance on both Earth and Venus, it is useful to examine four categories of reactions:

1) Reactions that make the O_2 bond.
2) Reactions that inhibit O_2 formation.
3) Reactions that break the O_2 bond.
4) Reactions that suppress catalytic processes.

Some of the most important reactions in categories 1 and 2 are catalytic in nature. A given catalytic agent (HO_x, for example) may act in more than one capacity, with the relative importance of its different roles depending on the particular conditions (mainly atmospheric composition) under which it is functioning.

Table 1. Comparison of some important features of the stratospheres of Earth and Venus.

Feature	Earth	Venus
Altitude (km)	20–40	60–80
Pressure (mbar)	100–5	300–5
Temperature (K)	200–250	270–200
Mixing ratios of major constituents		
N_2	78.1 percent	3–4 percent
O_2	21.0 percent	$< 1 \times 10^{-6}$
Ar	0.93 percent	0.01 percent
CO_2	0.03 percent	96 percent
Mixing ratios of minor constituents		
Total chlorine	2.3×10^{-9}	4×10^{-7}
Total sulfur	$\sim 1 \times 10^{-9}$	$\sim 2 \times 10^{-6}$
Total NO_x	2×10^{-8}	$\leq 3 \times 10^{-8}$
Water	$\sim 5 \times 10^{-6}$	$1\text{–}30 \times 10^{-6}$
Methane	$\sim 1 \times 10^{-6}$	~ 0
Hydrogen	0.5×10^{-6}	Unknown*
N_2O	0.25×10^{-6}	~ 0

*See text.

Table 2. Some catalytic cycles that make the O_2 bond.

I (HO_x)		II (HO_x)	
$H + O_2 + M$	$\rightarrow HO_2 + M$	$OH + O_3$	$\rightarrow HO_2 + O_2$
$O + HO_2$	$\rightarrow OH + O_2$	$HO_2 + O_3$	$\rightarrow OH + 2O_2$
$O + OH$	$\rightarrow O_2 + H$		
Net: $O + O$	$\rightarrow O_2$	Net: $2O_3$	$\rightarrow 3O_2$
III (ClO_x)		IV (NO_x)	
$Cl + O_3$	$\rightarrow ClO + O_2$	$O + NO_2$	$\rightarrow NO + O_2$
$O + ClO$	$\rightarrow Cl + O_2$	$NO + O_3$	$\rightarrow NO_2 + O_2$
Net: $O + O_3$	$\rightarrow O_2 + O_2$	Net: $O + O_3$	$\rightarrow O_2 + O_2$

Reactions of type 3 often involve photosensitization, with the sensitizing agent absorbing photon energy at wavelengths not absorbed directly by O_2 itself. In some important cases the photon energy alone is insufficient to break the strong O_2 bond, and a combination of photon energy and chemical energy is necessary to effect bond breakage. Reactions in category 4 tend to suppress the other three types of reactions, usually by converting the catalytic or photosensitizing agent to an inert form.

In the following sections these reaction types are discussed individually in terms of their application to Earth and Venus.

Reactions That Make the Oxygen Bond

Reactions in this category are the essential element in the destruction of odd oxygen in an atmosphere, by both catalytic and noncatalytic processes. For that reason they have received attention in connection with the question of ozone destruction. On Venus, in addition to destroying ozone, these processes determine the extent to which atomic oxygen formed by solar photolysis of CO_2 is converted to O_2. Thus they are influential in setting the equilibrium O_2 concentration in the Venusian atmosphere.

For a pure O_2 atmosphere (no minor constituents), the noncatalytic reactions (Chapman chemistry) are:

$$O + O_3 \rightarrow O_2 + O_2 \quad (1)$$

$$O + O + M \rightarrow O_2 + M \quad (2)$$

where M represents a third body. It is well known that in the terrestrial atmosphere the Chapman reactions are dominated by much faster catalytic cycles involving free radicals derived from the minor constituents. The most common cycles are listed in Table 2. Based on a recent model (*19*), the relative contributions of the different mechanisms to odd-oxygen destruction in the earth's entire atmosphere (not only the stratosphere) are approximately as follows: Chapman scheme, 12 percent; HO_x, 40 percent; NO_x, 31 percent; and ClO_x, 15 percent.

The major O_2-forming reactions that have been considered for the Venus atmosphere in recent models (*12, 14, 17, 18*) are the following.

$$O + O + M \rightarrow O_2 + M \quad (2)$$

$$O + OH \rightarrow O_2 + H \quad (3)$$

$$O + ClO \rightarrow Cl + O_2 \quad (4)$$

$$O + NO_2 \rightarrow NO + O_2 \quad (5)$$

Table 3. Some important net-nothing cycles.

V ($ClO_x - NO_x$)	VI (HO_x)
$NO_2 + h\nu \rightarrow NO + O$	$CO_2 + h\nu \rightarrow CO + O$
$O + O_2 + M \rightarrow O_3 + M$	$O + HO_2 \rightarrow OH + O_2$
$Cl + O_3 \rightarrow ClO + O_2$	$OH + CO \rightarrow H + CO_2$
$ClO + NO \rightarrow Cl + NO_2$	$H + O_2 + M \rightarrow HO_2 + M$
Net: nothing	Net: nothing
VII (ClO_x)	VIII (ClO_x)
$CO_2 + h\nu \rightarrow CO + O$	$CO_2 + h\nu \rightarrow CO + O$
$Cl + CO + M \rightarrow ClCO + M$	$Cl + CO + M \rightarrow ClCO + M$
$ClCO + O_2 + M \rightarrow ClCO_3 + M$	$ClCO + O_2 + M \rightarrow ClCO_3 + M$
$ClCO_3 + O \rightarrow Cl + CO_2 + O_2$	$ClCO_3 + Cl \rightarrow Cl + CO_2 + ClO$
	$O + ClO \rightarrow Cl + O_2$
Net: nothing	Net: nothing

These reactions are thus exactly analogous to those which convert odd oxygen to O_2 in the earth's atmosphere, as can be seen by reference to Table 2. The model of Winick and Stewart (*12*) for the Venus atmosphere predicts levels of O_2 about two orders of magnitude higher than the known upper limits. The $O + ClO$ reaction was largely responsible for the O_2 production.

Thus we see that catalytic O_2-forming reactions are important in the Venus atmosphere and that they are the same processes which destroy odd oxygen in the earth's atmosphere. But if these processes are so efficient, why is O_2 present only at trace levels on Venus? The answer lies in the effect of reactions in categories 2 to 4. In the following sections, we will discuss current thinking on these processes, and we will show that on Venus ClO_x catalyzes both O_2 formation and destruction.

Reactions That Inhibit Oxygen Formation

In the previous section we dealt with reactions that tend to reverse O_2 photolysis—that is, they recombine odd-oxygen species to form O_2. Catalytic processes can also reverse the photolysis (that is, accelerate the recombination) of molecules other than O_2, and such reactions play important roles in the terrestrial and Venusian atmospheres. They do not produce or destroy O_2 and are often called net-nothing cycles. Some important examples are discussed below.

It is a well-known feature of the earth's atmosphere that the ClO_x-catalyzed conversion of odd oxygen to O_2 is mitigated by the presence of nitric oxide (NO). The mechanism is cycle V in Table 3, and the key reaction is

$$ClO + NO \rightarrow Cl + NO_2 \tag{6}$$

This cycle interferes with the formation of O_2, which otherwise occurs when ClO reacts with atomic oxygen, as shown in Eq. 4. Inspection of cycle V shows that the photolysis of NO_2 has also been reversed. Analogous catalytic processes play important roles in certain planetary atmospheres because they tend to reverse the photolysis of CO_2, thereby preventing O_2 formation. Some major cycles that accomplish this are cycles VI to VIII (Table 3).

Cycle VI involves HO_x catalysis of the recombination of O and CO, a reaction that is otherwise quite slow. This cycle is of particular importance in the Martian atmosphere (*20*), where the H_2O (and therefore HO_x) concentration is high. It is less important for Venus because of the relative dryness of the Venusian atmosphere.

Thus HO_x cycles may either enhance O_2 formation (cycle I, Table 2) or inhibit O_2 formation (cycle VI, Table 3), depending on conditions. A dual role for ClO_x is also possible for Venus. Whereas on Earth the only significant effect so far known for ClO_x is odd-oxygen destruction, the Venus atmosphere offers the proper conditions for an opposing effect of ClO_x. This novel role of ClO_x in the Venus atmosphere was recently put forward by Krasnopolsky and Parshev (*17*) and Yung and DeMore (*18*) and has also been explored in detail by Yung and DeMore (*14*). The basic Krasnopolsky-Parshev (KP) mechanism is based on earlier literature studies of the chlorine-catalyzed photooxidation of CO and the photooxidation of phosgene (*21*). These processes are believed to involve the ClCO radical and its reaction with O_2. A principal cycle in the KP mechanism is:

$$CO_2 + h\nu \rightarrow CO + O \tag{7}$$

$$Cl + CO + M \rightarrow ClCO + M \tag{8, -8}$$

$$ClCO + O_2 \rightarrow ClO + CO_2 \tag{9}$$

$$O + ClO \rightarrow Cl + O_2 \tag{4}$$

Net: nothing

Unfortunately, the database for the kinetics of ClCO formation and reactivity is quite poor, and Krasnopolsky and Parshev were forced to estimate values for the relevant reaction rate constants. With their assumed set of rate parameters, they concluded that conversion of CO to CO_2 via the ClCO mechanism is a dominant factor in Venusian photochemistry and is primarily responsible for the low ambient levels of O_2 in the Venus atmosphere. However, measurements in our laboratory and previous literature reports (*21*) suggest that the equilibrium constant for ClCO formation is much smaller (about two orders of magnitude) than that assumed by Krasnopolsky and Parshev. Also, recent results of Spence *et al.* (*22*) and of Ohta and Mizoguchi (*23*) show that the reaction of ClCO with O_2 is not a simple bimolecular reaction giving ClO and CO_2 as products, but rather is a three-body reaction

$$ClCO + O_2 + M \rightarrow ClCO_3 + M \tag{10}$$

Yung and DeMore (*14*) postulated the following reactions of $ClCO_3$ in their Venus model:

$$O + ClCO_3 \rightarrow Cl + CO_2 + O_2 \tag{11}$$

$$Cl + ClCO_3 \rightarrow Cl + CO_2 + ClO \tag{12}$$

With these two reactions, the overall processes are cycles VII and VIII (Table 3). The net effect is ClO_x catalysis of $O + CO$ recombination, which tends to offset the ClO_x-catalyzed enhancement of O_2 formation. However, the model shows that these cycles can account for only about 50 percent of the required rate of CO oxidation, and hence are insufficient to prevent rapid O_2 accumulation by the O_2-forming reactions of category 1. Reactions in category 3 are required to explain how this remaining O_2 is removed.

Reactions That Break the Oxygen Bond

The most important source of O_2 bond breaking on Earth is the direct photolysis of O_2 by solar ultraviolet at wavelengths below 242 nanometers:

$$O_2 + h\nu\ (\lambda < 242\ \text{nm}) \rightarrow O + O \tag{13}$$

This is not, however, the only means of breaking the O–O bond, since there are additional photochemical paths that accomplish the same result. Although these other paths are less significant in

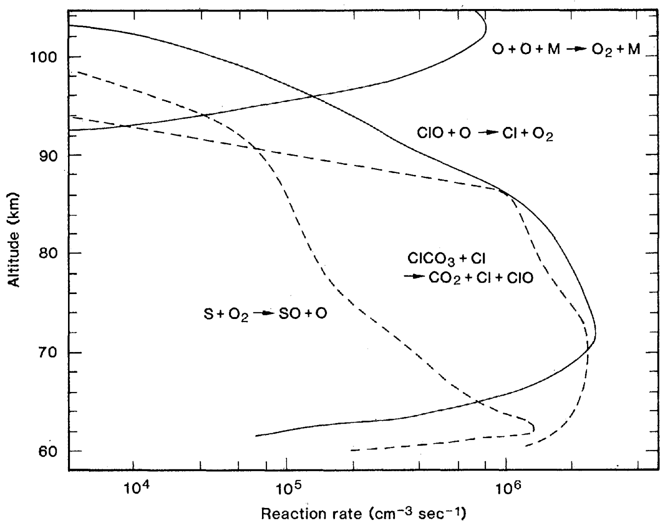

Fig. 1. Major reactions that make and break the O_2 bond in the stratosphere of Venus, based on the model of (*14*). Catalysis by ClO_x is dominant in both O_2 formation and destruction.

terms of their overall rates relative to direct O_2 photolysis, they have great practical importance because they are sources of odd oxygen in lower regions of the atmosphere not reached by solar photons with wavelengths sufficiently short to dissociate O_2. Such reactions in the lower atmosphere are the basic cause of photochemical oxidant formation, which is an essential feature of smog.

Some important O_2 bond-breaking cycles in terrestrial and planetary atmospheres are listed in Table 4. The most important bond-breaking cycle for Earth is IX. The net reaction is equivalent to oxidation of CO by O_2 to form CO_2 and atomic oxygen, a process that is otherwise negligibly slow at atmospheric temperatures. Thus CO is consumed by the process, and the energy released by CO oxidation is, in effect, used to drive the process (by breaking the O–H bond). The two important properties of NO are (i) that it reacts rapidly with HO_2 and (ii) that its oxidation product, NO_2, absorbs solar radiation in a wavelength range ($\lambda > 300$ nm) that penetrates with high intensity to the lower atmosphere. Other compounds, particularly hydrocarbons, may play the role of CO; that is, they may be consumed following attack by OH, producing a radical species that incorporates O_2 to form a peroxy compound of the general type RO_2 ($R = H$, CH_3, C_2H_5, and so on), which rapidly oxidizes NO to NO_2. Thus, through the effect of photoxidation, the introduction of a reducing species such as CO or RH to the atmosphere leads to the production of odd oxygen.

An O_2 bond-breaking mechanism that is very important for the Mars atmosphere (*19*) is the HO_x cycle, X in Table 4. However, this process is inadequate to account for the efficient removal of O_2 in the Venus atmosphere because there are insufficient concentrations of HO_2, due largely to the much lower H_2O concentrations. Winick and Stewart (*12*) noted this problem and introduced two new mechanisms for breaking the O_2 bond, both involving SO_2 photosensitization (cycles X and XI in Table 4). These processes produce atomic sulfur, which reacts rapidly with O_2. Ultimately, formation of SO_3 occurs by the reaction

$$O + SO_2 + M \rightarrow SO_3 + M \qquad (14)$$

and SO_3 is converted to H_2SO_4 by reaction with H_2O. Thus, the SO_2 effectively photosensitizes its own conversion to H_2SO_4. However, despite the success of the Winick and Stewart model in accounting for SO_2 behavior with regard to H_2SO_4 formation, it fails to reproduce the low observed levels of O_2 and CO. In seeking a solution to this problem, Yung and DeMore introduced an additional path involving SO_2 for breaking the O_2 bond (cycle XIII). The efficiency of this process is based on the reaction of SO with HO_2, a reaction which has not been observed in the laboratory but which is believed to be fast based on its similarity to the recently studied reaction $ClO + SO \rightarrow Cl + SO_2$ (*24*). It is well known that the species HO_2 and ClO have similar patterns of reactivity in reactions in which they serve as oxidants, owing to the nearly equal values of the HO–O and Cl–O bond energies (~ 60 kcal/mole). However, the importance of this mechanism (cycle XIII) in Venus photochemistry was found to be dependent on the presence of high H_2 concentrations in the Venus atmosphere, a subject of considerable controversy at present (*4, 25, 26*). As a possible alternative to the "high H_2" model, which suffers from the lack of an obvious source of H_2, Yung and DeMore also examined a model with total NO_x present at a mixing ratio (mole fraction) of 3×10^{-8}. Such amounts are theoretically possible, as NO_x is formed by lightning and has a long residence time in the relatively anhydrous Venus atmosphere. The NO_x mechanism accounts reasonably well for the low O_2 and CO levels observed for Venus, and the photochemical cycle is identical to the smog cycle (cycle IX) previously discussed in connection with the earth's atmosphere.

Thus, while the trace species HO_x, SO_x, and NO_x can in principle account for the conversion of CO and O_2 to CO_2 in the Venus atmosphere, the models require postulation of H_2 and NO_x levels that are unconfirmed by measurement or

Table 4. Reactions that break the O_2 bond.

IX ($HO_x - NO_x$)	X (HO_x)
$OH + CO \rightarrow H + CO_2$	$H + O_2 + M \rightarrow HO_2 + M$
$H + O_2 + M \rightarrow HO_2 + M$	$\frac{1}{2}(HO_2 + HO_2 \rightarrow H_2O_2 + O_2)$
$HO_2 + NO \rightarrow NO_2 + OH$	$\frac{1}{2}(H_2O_2 + h\nu \rightarrow OH + OH)$
$NO_2 + h\nu \rightarrow NO + O$	$OH + CO \rightarrow H + CO_2$
Net: $CO + O_2 \rightarrow CO_2 + O$	Net: $CO + \frac{1}{2}O_2 \rightarrow CO_2$
XI (SO_x)	XII (SO_x)
$SO + h\nu \rightarrow S + O$	$SO_2 + h\nu \rightarrow SO + O$
$S + O_2 \rightarrow SO + O$	$SO + SO \rightarrow SO_2 + S$
	$S + O_2 \rightarrow SO + O$
Net: $O_2 \rightarrow O + O$	Net: $O_2 \rightarrow O + O$
XIII ($SO_x - HO_x$)	XIV ($SO_x - ClO_x$)
$SO_2 + h\nu \rightarrow SO + O$	$SO_2 + h\nu \rightarrow SO + O$
$H + O_2 + M \rightarrow HO_2 + M$	$Cl + CO + M \rightarrow ClCO + M$
$SO + HO_2 \rightarrow SO_2 + OH$	$ClCO + O_2 + M \rightarrow ClCO_3 + M$
	$Cl + ClCO_3 \rightarrow Cl + CO_2 + ClO$
	$ClO + SO \rightarrow Cl + SO_2$
Net: $H + O_2 \rightarrow OH + O$	Net: $CO + O_2 \rightarrow CO_2 + O$

(in the case of H_2) are difficult to explain on the basis of known chemistry. A more acceptable mechanism is a third possibility considered in (*14*), based on cycle XIV of Table 4. This cycle involves the rapid reaction

$$ClO + SO \rightarrow Cl + SO_2 \qquad (15)$$

The cycle is similar to the net-nothing cycle (VIII) previously discussed (Table 3), with the exception that in this case the O_2 bond is broken, as opposed to the simple catalytic recombination of atomic oxygen and carbon monoxide. The key step is utilization of SO_2 photosensitization to break the ClO bond:

$$\begin{array}{l} SO_2 + h\nu \rightarrow SO + O \\ ClO + SO \rightarrow Cl + SO_2 \\ \hline \text{Net: } ClO \rightarrow Cl + O \end{array}$$

The mechanism is thus based on a synergistic effect of ClO_x catalysis and SO_2 photosensitization. It requires no unproven or improbable hypotheses concerning the atmospheric composition. It may be noted that the overall process is analogous to the terrestrial smog cycle (IX), with SO_2 playing the role of NO_2 and ClO_x playing the role of HO_x. The atomic oxygen produced in cycle XIV is available for oxidation of SO_2 via reaction 11, as previously discussed in connection with the Winick and Stewart cycles XI and XII.

Figure 1, based on the model of (*14*), summarizes the relative importance of the reactions making and breaking the O_2 bond. The dominant role of the O + ClO reaction in O_2 formation is apparent, as is the fact that the resulting O_2 formation is almost exactly counterbalanced by the $ClCO_3$ cycle.

Reactions That Suppress Catalytic Processes

In previous sections we have seen that catalytic cycles play a dominant role in establishing the balance between the making and breaking of O_2 bonds in the atmospheres of Earth and Venus and also that the cycles are closely related in the two cases. Further parallels exist with regard to the processes that control the effectiveness of certain cycles. For example, the ClO_x-catalyzed destruction of odd oxygen in the earth's atmosphere is limited by the presence of CH_4, which converts atomic chlorine to the inert reservoir HCl

$$Cl + CH_4 \rightarrow HCl + CH_3 \qquad (16)$$

The CH_4 is biogenic in origin and is irreversibly consumed by the reaction. Changes in the rate of CH_4 supply to the atmosphere, either natural or due to human activity, would have important consequences for stratospheric chemistry. On Venus, H_2 could in principle play a role similar to that of CH_4 because it can suppress ClO_x chemistry by converting atomic chlorine to HCl

$$Cl + H_2 \rightarrow HCl + H \qquad (17)$$

The principal sink for HO_x is

$$OH + HCl \rightarrow H_2O + Cl \qquad (18)$$

which is important because the product H_2O is shielded from solar photons by CO_2 and therefore is not readily photodissociated. Thus, to maintain a stable HCl concentration, H_2 must be supplied to the atmosphere at a rate at least equal to that of reaction 15 [see (*14*)]. In the absence of a supply of H_2, Cl builds up to very high concentrations, as first demonstrated in the model of Krasnopolsky and Parshev (*13*). This circumstance (low H_2) favors the role of ClO_x in Venus chemistry. We consider this mechanism, when combined with SO_2 photosensitization, to represent the most successful Venus photochemical model.

Concluding Remarks

We have discussed in a general way how catalytic cycles affect the stratospheres of Earth and Venus. Similar processes operate in other planetary atmospheres. The basic principle is that catalysis tends to restore thermal equilibrium, in opposition to solar photochemical effects, which establish thermal disequilibrium. Earth's ozone layer is an example of thermal disequilibrium produced by photochemistry, and its stable existence is important to terrestrial biology. The ClO_x catalytic cycles play an important role in limiting the stratospheric ozone concentration. On Venus ClO_x has a similar effect, converting odd oxygen to O_2. However, the ClO_x goes one step further, in concert with SO_2 photosensitization, and catalyses the oxidation of CO by O_2. Thus the small extent of CO_2 decomposition on Venus is explained.

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