contiguity limit, over 3333 km$^3$ of underplated basalt would be required to yield 500 km$^3$ of extractable magma.

The apparently significant volumes of basalt required to mobilize large quantities of extractable magma.

The calculations also suggest that magma generation following underplating requires elevated geotherms or greater melting will be enhanced, as will magma mixing and mingling. This process could produce a complex where assimilation and mingling.

The resulting free chlorine participates in the gas-phase recombination of chlorine monoxide (ClO) has been investigated under the conditions of pressure and temperature that prevail in the Antarctic stratosphere during the period of maximum ozone ($O_3$) depletion.

The relative importance of these and other catalytic cycles in polar $O_3$ destruction is uncertain. Because the first reaction in each of the above cycles is the rate-limiting step, the rate coefficients and product distributions for these processes must be determined under polar stratospheric conditions.

The kinetic analysis of reaction 1 has been done using both homogeneous and heterogeneous reaction rates. The heterogeneous rate is determined from the observed rate of $BrO + ClO$ reaction (cycle II) in the presence of Cl$^-$ and Cl$^+$ and the observed rate of $BrO + ClO$ reaction (cycle II) in the absence of Cl$^-$ and Cl$^+$.

The relative importance of these and other catalytic cycles in polar $O_3$ destruction is uncertain. Because the first reaction in each of the above cycles is the rate-limiting step, the rate coefficients and product distributions for these processes must be determined under polar stratospheric conditions.
The observed kinetic behavior strongly suggests that CIO reacted with itself irreversibly to form a stable dimer under these conditions. The strong dependence of $k_1$ on pressure and the inverse dependence on temperature is expected for radical addition reactions (9). In addition, rate constants in the low-pressure limiting region at 209 K increased in the ratio 1.0:1.9:2.0 for Ar, O$_3$, and N$_2$ as the diluent gases, respectively, which was consistent with the relative efficiencies of these molecules as vibrational quenchers from previous studies of termolecular reactions (9). Finally, departures from second-order kinetics were observed above 247 K. At these higher temperatures, thermal decomposition of the dimer is expected to compete with dimer formation (7). The CIO decay profiles could be separated into three components corresponding to the initial dimer formation, the dimer decomposition, and the termination of CIO from reactions 1b and 1c (10). Extrapolation of the experimental fall-off curve to $[M] = 0$ at 194 K does not reveal a measurable bimolecular component. The upper limit for this component, $2 \times 10^{-14}$ cm$^2$ molecule$^{-1}$ s$^{-1}$, is consistent with the upper limits for $k_{1a}$ and $k_{1b}$ at this temperature, given the endothermicities of 3.1 ± 2 and 2.6 ± 1 kcal mol$^{-1}$ of these pathways (7). A significant contribution from reactions 1a, 1b, and 1c in this temperature and pressure range is therefore ruled out.

Troe and co-workers have shown that the rate constant fall-off curves for addition reactions can be described by the expression (11)

$$k([M], T) = \frac{k_0 [M]}{1 + k_0 [M]/k_n} F(T)$$

where $T$ is the absolute temperature; $k_0(T) = k_0^{300}(T/300)^{-m}$, the low-pressure limiting rate constant; $k_0(T) = k_0^{300}(T/300)^{-n}$, the high-pressure limiting rate constant; $k_0^{300}$ is the low-pressure limiting rate constant at 300 K; and $k_0^{300}$ is the high-pressure limiting rate constant at 300 K. We fitted the data in Fig. 1 to this expression, using a value of 0.6 for $F_c$, the broadening factor at the center of the fall-off curve (7). The resulting parameters ($\pm 2\sigma$) were $k_0^{300} = (1.8 \pm 0.5) \times 10^{-32}$ cm$^6$ molecule$^{-2}$ s$^{-1}$, $n = 3.6 \pm 1.0$, $k_0^{300} = (6.2 \pm 2) \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, $m = 1 \pm 1$.

In the only previous temperature dependence study of reaction 1, Hayman et al. (12) used the molecular modulation technique from 268 to 338 K. The rate constant for dimer formation was given by

$$k_{1d} = (6.0 \pm 0.4) \times 10^{-32} (T/300)^{-2.1} \pm 0.7 \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

The extrapolation of this expression to the conditions of pressure and temperature relevant to the springtime Antarctic stratosphere ($T = 194$ K, $[M] = 1 \times 10^{16}$ to $2 \times 10^{18}$ molecule cm$^{-3}$, Fig. 1) leads to rate constants that are greater by a factor of 2 than we obtained.

Previous modeling studies (13, 14) have found that the catalytic cycle involving the CIO + CIO reaction is the dominant mechanism for the removal of O$_3$ in the polar stratosphere, based on the rate constants for reaction 1 obtained by Hayman et al. (12). Because the rate constants we obtained are significantly less, we reassessed the relative importance of the CIO + CIO catalytic cycle and the ability of current models to account for the observed O$_3$ disappearance.

The California Institute of Technology–Jet Propulsion Laboratory (Caltech-JPL) one-dimensional photochemical model (15) (without transport) was used to compute the rate of O$_3$ destruction during the austral spring. The model atmosphere and the concentrations of long-lived species (such as H$_2$O and CH$_4$) were taken from the Caltech-JPL two-dimensional model. The photochemistry and chemical kinetics were based on DeMore et al. (7) with the following updates: (i) rate constant for CIO + CIO as reported here, (ii) rate constant for CIO + BrO (6), (iii) cross sections for (CIO)$_2$ photolysis (16), and (iv) cross sections for HOCl photolysis (17). The chemical scheme was expanded to evaluate the importance of the reaction CH$_3$O$_2$ + CIO → CH$_3$O + ClOO (18). The model properly accounts for the number of hours of sunshine at different altitudes and incorporates the effect of multiple scattering. The model simulated the conditions of the U.S. National Ozone Expedition I and II at McMurdo Station, Antarctica (78°S) in 1987 in which vertically resolved ground-based measurements of the CIO radical, based on millimeter-wave radiometry and in situ O$_3$ measurements by balloon, were carried out by Barrett et al. (19) and Hofmann et al. (20), respectively.
The O₃ measurements from this data set provide adequate coverage from 28 August (day 240) to 7 October (day 280), whereas the ClO measurements refer only to the period 20 to 24 September (days 263 to 267). In interpreting their data, Barrett et al. assumed that ClO concentrations remained constant throughout the spring. Although this assumption may be reasonable, we propose that ClO may be temporarily sequestered by the formation of higher chlorine oxides (Cl₂O₅, Cl₂O₆, and possibly Cl₂O₇) by the following mechanism:

\[
\begin{align*}
\text{BrO} + \text{ClO} & \rightarrow \text{OCIO} + \text{Br} \\
\text{ClO} + \text{OCIO} + \text{M} & \rightarrow \text{Cl}_2\text{O}_5 + \text{M} \\
\text{Cl}_2\text{O}_5 + h\nu & \rightarrow \text{ClO} + \text{Cl} \\
\text{ClO}_3 + \text{ClO} + \text{M} & \rightarrow \text{Cl}_2\text{O}_6 + \text{M} \\
\text{Cl}_2\text{O}_6 + \text{O} & \rightarrow \text{Cl}_2\text{O}_7 + \text{O}_2
\end{align*}
\]

Because these oxides, which are known, stable compounds, are produced by termolecular addition reactions, their formation would be enhanced under conditions that prevail in the polar stratosphere, that is, high pressure, low temperature, and high ClO concentrations. The stabilities of Cl₂O₅ and Cl₂O₆ are further enhanced by their long photolytic lifetimes. Preliminary modeling indicates that Cl₂O₅, Cl₂O₆, and Cl₂O₇ are important reservoirs of active chlorine in the early spring but are less important in the late spring (21). We therefore conclude that the ClO profile of Barrett et al. (19) probably cannot be extrapolated back to the initial measurement period in late August.

The strategy adopted for modeling O₃ losses is as follows. We used the observed ClO and O₃ to initialize the model on 17 September (day 260). The BrO mixing ratio was set equal to 5.0 parts per trillion (ppt) in the lower stratosphere (22). For simplicity, the effects of odd-nitrogen chemistry, higher chlorine oxides, and downwelling were not included (23). The model was run from 17 September (day 260) to 7 October (day 280) with a 1-hour time step.

The model results for the decline of O₃ concentrations from 16 to 24 km over McMurdo are shown in Fig. 2A along with the balloon measurements of Hofmann et al. (20). The model predicts significant O₃ destruction throughout this period. The observed O₃ loss between day 260 and day 280 at 18 km is \((2.0 \pm 0.5) \times 10^{12}\) molecule cm\(^{-3}\), which may be compared with the total computed loss of \(1.9 \times 10^{12}\) molecule cm\(^{-3}\). The relative contributions due to cycles I, II, and III are 70, 23, and 7% respectively, near the region of maximum O₃ loss (18 km). The computed O₃ losses due to cycle I are less than the model calculations of Barrett et al. because these investigators used the much higher ClO + ClO rate constant of Hayman et al. (12). The O₃ losses due to ClO + BrO are consistent with the results of Salawitch et al. (24) for their low-BrO model.

This model appears to be the first quantitative assessment of the loss of O₃ due to cycle III with updated rate data. The net effect of cycle III is much smaller than that of the other cycles. As pointed out by Crutzen and Arnold (25), the denitrification of the Antarctic stratosphere results in enhanced concentrations of HO₃ radicals. Thus our model predicts a much higher column abundance of HOCI than that of a mid-latitude model. The value predicted for day 265, \(2.3 \times 10^{14}\) molecule cm\(^{-2}\), is consistent with that observed by Toon and Farmer (26).

A comparison between the observed O₃ column abundances and the model predictions is presented in Fig. 2B. Within the uncertainties of the combined balloon and satellite measurements, the model accounts for 100% of the O₃ lost during this time period. We conclude that existing mechanisms can adequately account for the observed O₃ losses in late spring, subject to the assumptions stated above.

A detailed model study of the early spring period is beyond the scope of this paper. Nevertheless, we can make a qualitative assessment. If we had initialized our model on 28 August (day 240) with the O₃ concentrations measured by Hofmann et al. (20) and the ClO concentration measured in September, the model would have predicted a column O₃ loss of 43 Dobson units (DU), compared with the observed loss of about 80 \(\pm 20\) DU (see Fig. 2B). Inclusion of the mechanism for the higher chlorine oxides (21) leads to a predicted O₃ loss that is less than one-half of that observed. This result is noteworthy because all photochemical destruction mechanisms are driven by sunlight. The number of sunlit hours at 78°S at 18 km for days 240, 260, and 280 is 8.6, 13.5, and 19.8, respectively, and yet, from Fig. 2A and B, there is at least as much destruction of O₃ during the first 20 days (days 240 to 260) as during the latter 20 days (days 260 to 280). We therefore conclude that, in the early spring, there must be additional catalytic O₃ destruction cycles besides those currently recognized. Alternatively, the existing ground-based measurements, which are made at the periphery of the polar vortex, may not be fully representative of conditions at higher latitudes. Increased ClO concentrations poleward could result in higher O₃ destruction rates, the effects of which would be propagated to lower latitudes.

**REFERENCES AND NOTES**

4. L. T. Molina and M. J. Molina, J. Phys. Chem. 91,


35. Y. L. Yung, S. P. Sander, R. R. Friedli, W. B. D. Hull. The following estimates were made for the rate constants forming the higher oxides at 195 K: $k_2 = 2k_2$, $k_3 = 2k_4$. When the formation of CIO is included in the mechanism (G. D. Hayman and R. A. Cox, Chem. Phys. Lett. 185, 1 (1989)), we estimate a CIO thermal lifetime on the order of 100 s in the lower stratosphere. To the extent that the predicted concentrations of the higher oxides of chlorine are decreased by about a factor of 2. The equilibrium constant has never been measured in the gas phase below 230 K, and this is a major uncertainty in the modeling of the higher oxides.


37. These effects reduce the predicted depletion of O$_3$, NO, and the higher chlorine oxides decrease the efficiency of the catalytic cycles by sequestering CIO, and HO$_3$. Downwellings (D. L. Hartmann et al., J. Geophys. Res., in press) provides a source of O$_3$-rich air from higher altitudes. Observations of OCN (S. Solomon et al., J. Geophys. Res., in press) during spring 1987 at McMurdo suggest a slow increase in NO$_3$ near 15 to 20 km from values less than about 10 ppt in late August to values on the order of 10 to 20 ppt in mid-September and to a few hundred parts per trillion in early October. The impact of including NO$_3$ (NO + NO$_3$) on the model depletion of O$_3$ was investigated by McElroy and Salawitch (14). In our model, the inclusion of 50 ppt of NO$_3$ reduced the O$_3$ depletion by about 10%.


40. G. C. Toon and C. B. Farmer, personal communication. The “standard” model quoted in the text does not include the reaction CIO + CH$_2$O proposed by Simon et al. (18). Inclusion of this reaction in the model leads to an increase in HO$_3$ and hence of HOCI, due to a decrease in the concentration of CH$_2$O and the rate of the HO$_3$-initiated reaction OH + CH$_3$OH. If we use the room temperature rate coefficient estimated by Simon et al. (18), the model predicts a column density of HOCI equal to 4.2 x 10$^{14}$ molecule cm$^{-2}$ on day 260. The corresponding loss of O$_3$ at 18 km due to cycles I, II, and III are 68, 23, and 9%, respectively. Using a much larger rate constant does not change the results significantly because the reaction CH$_2$O + CIO is now much faster than the competing pathway, CH$_3$O$_2$ + HO$_2$.

The observations rule out the extremely high HO$_3$ model of Crutzen and Arnold (25), at least for September.

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**Circadian System Controlling Release of Sperm in the Insect Testes**


Release of mature sperm from the testes into seminal ducts of the gypsy moth exhibits a circadian rhythm. The rhythm of sperm release was shown to persist in vitro, in isolated complexes of testes and seminal ducts cultured in light-dark cycles or in constant darkness. The phase of the rhythm was also reset in vitro by exposure to shifted light-dark cycles. Therefore, the testis–semen ducts complex from the gypsy moth is photosensitive and contains a circadian pacemaker, which controls the rhythm of sperm movement. This finding extends the range of structures in multicellular organisms that are known to contain circadian oscillators and provides a new model system in which circadian mechanisms may be studied.

**Studies of the Circadian Systems in Multicellular Animals**

In multicellular animals have focused on identification of the structures and mechanisms involved in generating rhythmicity. Several pacemakers, that is centers capable of self-sustaining oscillations that control various behavioral and biochemical rhythms, have been localized in anatomically discrete sites by means of tissue transplants or by the monitoring of the rhythm in the organs cultured in vitro. Circadian oscillators have been reported primarily in parts of the nervous system. Examples include optic lobes of insects (1), eyes of mollusks (2), pineals of lizards (3) and birds (4), and suprachiasmatic nuclei of mammals (5). In addition, the insect prothoracic glands have been implicated as the site of a circadian clock (6) and insect cuticle has exhibited circadian-like growth in vitro (7). More experimental data are needed to determine whether circadian oscillators of multicellular animals are confined to nervous and endocrine tissues or whether they also exist in other tissue types. We present here direct evidence that the testis–semen ducts complex of the gypsy moth, *Lymantria dispar*, contains a light-sensitive circadian pacemaker, which controls rhythmic release of sperm from the testis.

In Lepidoptera, as in most other insects, sperm cells develop in clones, and mature spermatozoa are released from the testis in the form of elongated sperm bundles. The intriguing observation that the sperm release occurred in a daily rhythmic pattern was first made for the flour moth, *Ephestia kuehniella* (8). In the gypsy moth the release of sperm from the testis is also rhythmic and starts several days before adult eclosion when spermatogenesis is completed (9). The rhythm of sperm movement can be entrained by different photoperiods in intact animals, as well as in isolated abdomens in both flour moth (10) and gypsy moth (9). The rhythm has a circadian nature since it persists in constant darkness with the temperature-compensated period of approximately 24 hours (11). In male gypsy moths kept in light-dark cycles consisting of 16...