



Rate of Formation of the ClO Dimer in the Polar Stratosphere: Implications for Ozone Loss

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contiguity limit, over 3333 km³ of underplated basalt would be required to yield 500 km³ of extractable magma.

The apparently significant volumes of basalt required to mobilize large quantities of crustal melt suggest that underplating is not a one-stage process; repeated intrusion is required for underplating to be effective; a similar conclusion was reached by Younker and Vogel (7). The calculations also suggest that magma generation following underplating requires elevated geotherms or greater depths (2, 7). If successive parcels of basalt can intrude and breach the solidified portion of the early underplated material, further melting will be enhanced, as will magma mixing and mingling. This process could produce a complex where assimilation and magma mixing would give rise to homogenization at a variety of length scales, as proposed by Hildreth and Moorbath (2) and observed in the southern Sierra Nevada batholith (30).

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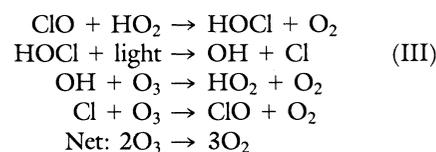
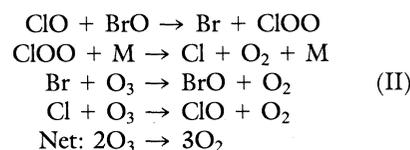
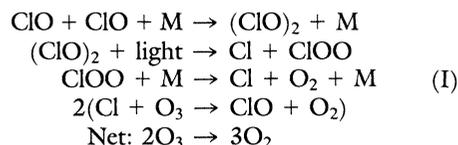
Rate of Formation of the ClO Dimer in the Polar Stratosphere: Implications for Ozone Loss

STANLEY P. SANDER, RANDALL R. FRIEDL, YUK L. YUNG

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 (O₃) disappearance. Measured rate constants are less than one-half as great as the previously accepted values. One-dimensional model calculations based on the new rate data indicate that currently accepted chemical mechanisms can quantitatively account for the observed O₃ losses in late spring (17 September to 7 October). A qualitative assessment indicates that the existing mechanisms can only account for at most one-half of the measured O₃ depletion in the early spring (28 August to 17 September), indicating that there may be additional catalytic cycles, besides those currently recognized, that destroy O₃.

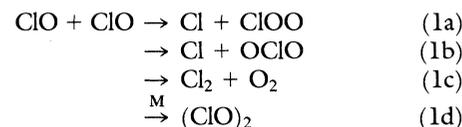
THE LARGE DECREASES IN O₃ concentrations in the Antarctic stratosphere during early spring (1) are accompanied by unusually high concentrations of ClO, OClO, and HOCl and low concentrations of HCl and of species containing odd nitrogen (NO, NO₂, and HNO₃) relative to their observed values at lower latitudes (2). Current thinking regarding the chemical mechanisms of O₃ destruction suggests that the perturbation of polar stratospheric chemistry occurs in two phases (3).

In the first phase, which occurs primarily during the polar night, the inactive chlorine reservoir species HCl and ClONO₂ are converted to photochemically labile Cl₂ and HOCl by heterogeneous reactions on ice crystals and on nitric acid trihydrate aerosols. Denitrification of the stratosphere occurs as a result of particle sedimentation. In the second phase, atomic chlorine is released by photolysis of Cl₂ and HOCl after sunrise. The resulting free chlorine participates in efficient catalytic O₃ destruction cycles, of which the following cycles are believed to be important (3, 4) (M is a third-body molecule):



The relative importance of these and other catalytic cycles in polar O₃ 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. To date, only the BrO + ClO reaction (cycle II) has been adequately described at low temperatures (5, 6). Both the ClO + HO₂ (cycle III) and the ClO + ClO (cycle I) reactions are poorly characterized under these conditions, the latter despite almost 40 years of laboratory study (7).

The kinetic analysis of reaction 1 has been greatly complicated by the existence of at least four product channels:

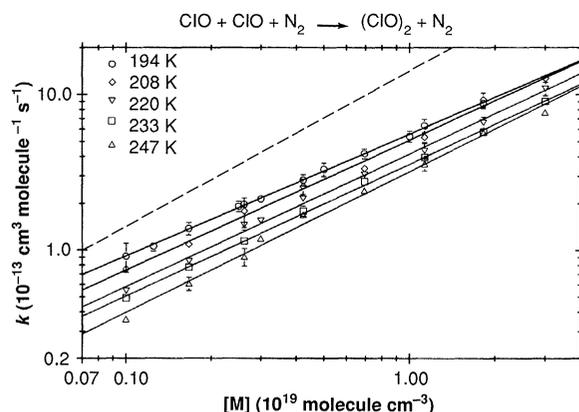


We studied the ClO + ClO reaction under conditions relevant to the polar stratosphere and have concluded both that the reaction proceeds at rates significantly lower than previously believed and that the only reac-

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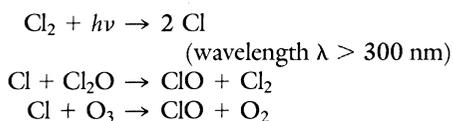
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Fig. 1. Plot of $\log k_1$ versus $\log [N_2]$ for the reaction $\text{ClO} + \text{ClO} + \text{N}_2 \rightarrow (\text{ClO})_2 + \text{N}_2$ over the temperature range 194 to 247 K. Solid lines are least-squares fits to the data. The dashed line is from the temperature dependence expression given by Hayman *et al.* (12) extrapolated to 194 K. Error bars represent the $\pm 2\sigma$ uncertainty limits.



tion channel of importance is reaction 1d, the pathway that forms the ClO dimer. We use these results in a one-dimensional chemical model to calculate the relative contributions of the known catalytic cycles to polar O₃ depletion.

We generated ClO radicals by flash photolysis of Cl₂-Cl₂O or Cl₂-O₃ mixtures,



and monitored their decay by long-path ultraviolet absorption detection (8). With either source, Cl atoms were converted rapidly and stoichiometrically into ClO. Removal of ClO occurred on time scales two to three orders of magnitude longer than formation, effectively decoupling formation and removal kinetics. We determined the rate constants from the observed second-order decay profiles of ClO, using our previous measurements of ClO absorption cross sections (6) to convert ClO absorbances to absolute concentrations. A small downward correction ($\approx 10\%$) was applied to account for residual probe beam absorption by the ClO dimer.

Experiments were carried out over the temperature range 194 to 247 K and with diluent gas densities N₂, Ar, or O₂ in the range 1×10^{18} to 30×10^{18} molecule cm⁻³. The decay curves were always second-order in [ClO], indicating that the mechanism of ClO loss was by self-reaction. Plots of $\log k_1$, the observed rate constant for reaction 1, versus $\log [M]$, the bath gas density, were linear and had slopes that ranged from 0.78 at 194 K to 0.91 at 247 K (Fig. 1), indicating that the reaction was in the fall-off regime between second- and third-order kinetics in this pressure range. The rate constant varied inversely with temperature, decreasing by a factor of 3 as the temperature increased from 194 to 247 K at the lowest bath gas density.

The observed kinetic behavior strongly suggests that ClO 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 are 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, O₂, and N₂ 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 ClO decay profiles could be separated into three components corresponding to the initial dimer formation, the dimer decomposition, and the termination of ClO 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, 2×10^{-14} cm³ 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)

$$k([M], T) = \frac{k_0 [M]}{1 + k_0 [M]/k_\infty} F_c \{1 + [\log_{10}(k_0 [M]/k_\infty)]^2\}^{-1}$$

where T is the absolute temperature; $k_0(T) = k_0^{300}(T/300)^{-n}$, the low-pressure limiting rate constant; $k_\infty(T) = k_\infty^{300}(T/300)^{-m}$, the high-pressure limiting rate constant; k_0^{300} is the low-pressure limiting rate constant at 300 K; and k_∞^{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 $k_0^{300} = (1.8 \pm 0.5) \times 10^{-32}$ cm⁶ molecule⁻² s⁻¹, $n = 3.6 \pm 1.0$, $k_\infty^{300} = (6 \pm 2) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹, $m = 0 \pm 1$.

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

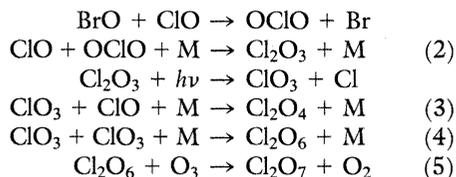
$$k_{1d} = (6.0 \pm 0.4) \times 10^{-32} (T/300)^{-2.1 \pm 0.7} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

The extrapolation of this expression to the conditions of pressure and temperature relevant to the springtime Antarctic stratosphere ($T = 194$ K, $[M] = 1 \times 10^{18}$ to 2×10^{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 ClO + ClO reaction is the dominant mechanism for the removal of O₃ 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 ClO + ClO catalytic cycle and the ability of current models to account for the observed O₃ 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 O₃ destruction during the austral spring. The model atmosphere and the concentrations of long-lived species (such as H₂O and CH₄) 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 ClO + ClO as reported here, (ii) rate constant for ClO + BrO (6), (iii) cross sections for (ClO)₂ photolysis (16), and (iv) cross sections for HOCl photolysis (17). The chemical scheme was expanded to evaluate the importance of the reaction $\text{CH}_3\text{O}_2 + \text{ClO} \rightarrow \text{CH}_3\text{O} + \text{ClOO}$ (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 II at McMurdo Station, Antarctica (78°S) in 1987 in which vertically resolved ground-based measurements of the ClO radical, based on millimeter-wave radiometry and in situ O₃ 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 (Cl₂O₃, Cl₂O₄, and possibly Cl₂O₇) by the following mechanism:



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 Cl₂O₄ and Cl₂O₇ are further enhanced by their long photolytic lifetimes. Preliminary modeling indicates that Cl₂O₄, 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 1.9×10^{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_x 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 en-

hanced concentrations of HO_x radicals. Thus our model predicts a much higher column abundance of HOCl than that of a mid-latitude model. The value predicted for day 265, 2.3×10^{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 ± 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. 2, A 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.

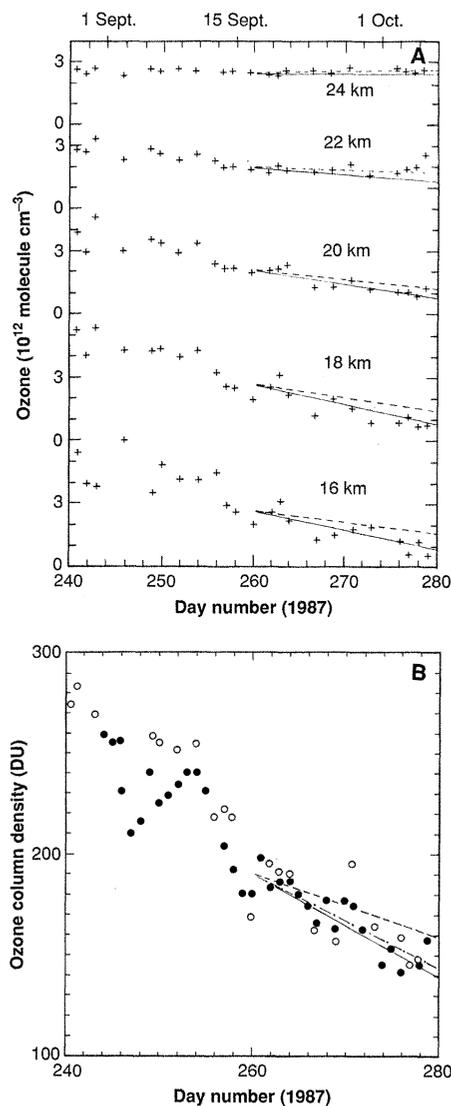


Fig. 2. (A) Concentrations of O₃ in spring over McMurdo Station (78°S). (+) Balloon ozone-sonde data from Hofmann *et al.* (20); (---) model calculations of O₃ depletion based on cycle I only; (—) model calculations of O₃ depletion based on cycles I, II, and III. (B) Column density of O₃ over McMurdo Station (1 DU = 2.69×10^{16} molecule cm⁻²). (○) Balloon ozone-sonde data from Hofmann *et al.* (20). (●) Satellite data from the Nimbus-7 Total Ozone Mapping Spectrometer (20). (---) Model calculations based on cycle I only; (----) model calculations based on cycles I and II; (—) model calculations based on cycles I, II, and III.

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Circadian System Controlling Release of Sperm in the Insect Testes

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Release of mature sperm from the testis 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 testis 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- seminal 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 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- seminal 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, *Ephesia kuehniella* (8). In the gypsy moth the release of sperm from the testes 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

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