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9. Stepped combustion of diamonds separated with the use of the ammonia technique of (1) give identical C release profiles, over the appropriate temperature range, to residues for which the separation was not performed; these data demonstrate the efficacy of our method.
10. Isotopic compositions are reported according to the δ convention, where

$$\delta^{13}\text{C} = \frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}} - (^{13}\text{C}/^{12}\text{C})_{\text{std}}}{(^{13}\text{C}/^{12}\text{C})_{\text{std}}} \times 1000$$

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Reduced Antarctic Ozone Depletions in a Model with Hydrocarbon Injections

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Motivated by increased losses of Antarctic stratospheric ozone and by improved understanding of the mechanism, a concept is suggested for action to arrest this ozone loss: injecting the alkanes ethane or propane (E or P) into the Antarctic stratosphere. A numerical model of chemical processes was used to explore the concept. The model results suggest that annual injections of about 50,000 tons of E or P could suppress ozone loss, but there are some scenarios where smaller E or P injections could increase ozone depletion. Further, key uncertainties must be resolved, including initial concentrations of nitrogen-oxide species in austral spring, and several poorly defined physical and chemical processes must be quantified. There would also be major difficulties in delivering and distributing the needed alkanes.

LARGE LOSSES OF ATMOSPHERIC ozone are occurring over Antarctica each austral spring (1, 2). Ozone losses have also been observed (3) at middle and higher latitudes in both hemispheres for the period 1979 to 1990. South of 60°S the ozone loss rate was more than 0.5% per year; a reasonable interpretation is that mixing of ozone-poor air from the Antarctic stratosphere is causing this wider impact (3).

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Episodes of reduced ozone have also been observed over Australia and New Zealand (4). There are also indications that the size and severity of the Antarctic ozone hole could increase (5) and that the hole will form each year for the next 100 years even if CFC releases are controlled (6).

The threat of expanded future impacts of the Antarctic ozone hole leads one to search for measures that could prevent them. Here we explore a concept for mitigating ozone-hole formation. It is based on recent gains in scientific understanding of the processes responsible for ozone loss in the polar winter stratosphere, including increased knowledge

of polar stratospheric clouds [PSCs (7)].

We explore whether injections of certain hydrocarbons into the lower stratosphere during an optimal time period each year could prevent ozone-destroying reactions in the austral spring. The annual sequence of physical and chemical events that occur during the formation of the ozone hole includes a several week period during which stratospheric Cl atoms are activated for ozone attack. Our idea is to immobilize this active chlorine through the rapid reaction of Cl atoms with simple alkanes like propane, as in



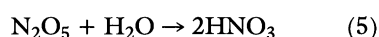
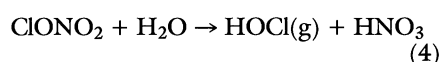
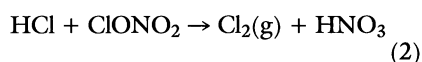
Because the concentrations of active chlorine are as large as 2 parts per billion (ppb by volume) of the local atmosphere during the period of ozone destruction, we expect that it would be necessary to raise the concentration of propane (or ethane) artificially to at least 2 ppb. In this report we test this idea with a model of Antarctic ozone-layer chemistry. Before presenting results of the model calculations we must describe the processes that we are simulating.

The formation of PSCs is now known to be essential to the formation of the ozone hole over Antarctica (7). PSCs cause dehydration and denitrification of polar air and activate inert chlorine species (HCl and ClONO₂) into photolytically unstable chlorine species (Cl₂, ClNO₂, and HOCl) that are transformed by sunlight into ozone-reactive species (Cl and ClO). The morphological properties of polar stratospheric clouds are well-defined by satellite observations (8) and by optical and physical evidence; there are two broad categories. Type I PSCs consist of an aerosol haze of micrometer-sized nitric acid ice particles composed of HNO₃ and H₂O in roughly a molar ratio of 1:3, respectively (9). Type II PSCs are composed of larger (>10 μm) water-ice crystals.

Type I PSCs begin to form at temperatures near 195 K, generally late in the austral fall, when the southern polar vortex has formed and cooling within the vortex has occurred in the absence of strong solar or longwave heating. These PSCs continue to form well into the austral spring. Type II PSCs condense at lower temperatures (≤187 K), at the frost point of water vapor in the polar stratosphere. Type II clouds therefore appear later in the winter season and dissipate earlier in the spring than type I clouds. Type I haze dominates during the early part of the Antarctic winter season, but the proportion of type II clouds increases as cooling progresses. Type II particles cause dehydration, and both type I and type II clouds appear to cause denitrification of the polar vortex. Chlorine activation seems to

occur primarily on type I PSCs. The systematic dehydration and denitrification of the polar winter stratosphere can affect the persistence of PSCs in the late winter and early spring, and ozone depletion can affect the stability and breakup of the vortex at that time (10). The complex sequence of events that prepares the Antarctic atmosphere for ozone depletion at first spring light is depicted schematically in Fig. 1.

The key heterogeneous chemical reactions that are catalyzed by PSCs are:



In these equations, all species are assumed to be on the surfaces of PSC particles where the reactions occur; species that readily desorb into the gas phase are indicated by "g."

We performed our calculations with a tested model (11) of stratospheric gas-phase photochemistry including about 130 reactions, to which we added a detailed C_2H_6 photooxidation sequence (12) that includes peroxyacetyl nitrate and its reactions. We also added the four important heterogeneous reactions (reactions 2 to 5 above). Gas-phase reaction rates were taken from Demore *et al.* (13) and reaction efficiencies on ice surfaces were taken from recent laboratory measurements (14, 15). Ethane (E) was chosen as a representative hydrocarbon because its chemistry is relatively simple and its degradation channels are well-defined. We have also simulated injections of propane (P), which is even more efficient at scavenging chlorine, using the C_2H_6 sequence with rate constants for C_3H_8 hydrogen abstraction. Model data

were selected to represent conditions at 80°S latitude and an altitude of 15 km, where large springtime ozone depletions are observed (16).

Initialization of photochemical calculations in mid-winter [Tables 1 and 2 (17, 18)] requires certain assumptions concerning autumn concentrations and heterogeneous processing. We used results from two-dimensional models to estimate autumnal levels of nitrogen- and chlorine-containing species (19, 21, 22) because high-latitude measurements are scarce during polar fall (19, 20). Calculations generally have not included heterogeneous decomposition of stratospheric N_2O_5 as it moves poleward; therefore, our adopted fall NO_x values may represent upper limits.

Two methods were used to quantify the effect of processing that might occur on particles before sunrise. First, reactions 2 through 5 were included in a one-dimensional microphysical simulation of PSC formation (15) along with laboratory determinations of heterogeneous efficiencies on types I and II particles (14, 23), and the processing of N_2O_5 , HCl, and ClONO_2 were calculated explicitly. Reactions 2 and 3 reached completion, yielding our baseline scenario B. We also considered simple titrations of nitrogen and inorganic chlorine species from initial levels (19, 21), leading to a number of possible alternative solutions. We focus here on models B and H in Table 2. Model B is most consistent with the detailed microphysical calculations, whereas model H maximizes the ratio of active chlorine to nitrogen. Neither model B nor H is inconsistent with data from Antarctic measurement campaigns (19, 21, 24). Indeed both models reflect conditions at the time of the 1987 ozone hole, including mole fractions of total inorganic chlorine (1.8 ppb at 15 km).

The model's heterogeneous processes

were assumed to terminate on 1 September, a rough average date for final PSC evaporation (25); HNO_3 amounts were set to equal or exceed the HNO_3 vapor pressure over NAT (26). Control simulations with both models B and H produced large ozone depletions during days 230 to 275 (Fig. 2), although not as large as the 95% depletions that have been observed on occasion (16). We eventually explored eight scenarios spanning a range of permutations of ClO_x and NO_x , not all of which yielded simulated ozone holes (27).

Model responses to additions of E and P varied (Fig. 2). In model H the addition of 1.8 ppb E or P prevented a considerable amount of ozone loss; further increases to 3.6 ppb were even more effective. This desirable response is due to the absence of NO_x at the beginning of sunlight (column 2 of Table 2). The results of model B show a

Table 1. Model parameters. The heterogeneous reactions 2 through 5 were represented as gas-phase reaction equivalents with bimolecular rate constants (17, 18). See also Table 2.

Parameter	Baseline	Alternatives
Altitude	15 km	
Latitude	80°S	
Calculations begun	8 August	
Sunrise	15 August	
PSC evaporation	1 September	1 October
Rate constant 2	$3 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$	$3 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$

Table 2. Initial (8 August) concentrations at 15 km. Concentrations of key species used to initialize the photochemistry were obtained from two dark processing scenarios. In one scenario (model H), chlorine and nitrogen species were simply titrated by reactions 2 to 5, and relative efficiencies were assumed to be defined by sticking coefficients. In the second scenario (model B), a detailed one-dimensional microphysics-heterogeneous chemistry model was used to estimate presunrise concentrations (15); also see text. Total inorganic chlorine was taken to be 1.8 ppb in autumn, partitioned as 1.5 ppb HCl and 0.3 ppb ClONO_2 (19-21). Autumn concentrations of N_2O_5 were 1.8 ppb (that is, 3.6 ppb of NO_x) for models B and H. Sunrise concentrations for N_2O_5 , ClONO_2 , and HCl are all zero, that is, these species were assumed to react to completion during austral winter.

Species	Concentrations (ppb)	
	Model B	Model H
HNO_3	0.9	2.1
ClNO_2	1.2	0.0
Cl_2	0.3	0.9
NO_x	1.2	0.0
NO_y	2.1	2.1
Cl active	1.8	1.8
Cl_y	1.8	1.8

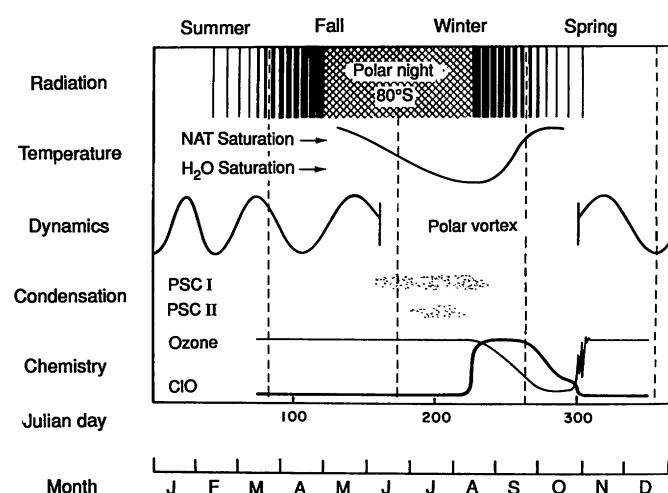


Fig. 1. A schematic calendar of major physical and chemical factors leading to massive Antarctic ozone depletions. Dates correspond roughly to the location for which modeling was conducted; NAT signifies nitric acid trihydrate.

mixed response, however. The initial 1.8 ppb of added hydrocarbon increased the ozone depletion, but increasing the hydrocarbon mole fraction to 3.6 ppb greatly reduced the depletion. This behavior arose mostly from reactions 1 and 2 followed by photolysis of Cl_2 . In model B there was 1.2 ppb of NO_x at first sunlight, allowing ClONO_2 to form. Reaction 1 created HCl, which then produces active chlorine (Cl_2) through reaction 2. Photolysis of Cl_2 released Cl atoms. By contrast, in model H there was no NO_x remaining at the end of winter darkness, so the additional HCl from reaction 1 could not encounter any ClONO_2 .

Thus, the ability of injected hydrocarbons to prevent formation of the ozone hole depends on the amount of NO_x that survives the heterogeneous processing of winter darkness (mainly in the form of ClONO_2) and on the relative amounts of active chlorine and NO_x . Will this hold in the stratosphere of the future as chlorine increases? Early next century the concentration of chlorine in the atmosphere will be about 5 ppb

(6), leading to about 2.64 ppb inorganic chlorine at 15 km over Antarctica. With 1.8 ppb NO_x available in autumn (Fig. 3A), the response upon the addition of hydrocarbons is similar to that of model B, but with 1.2 ppb NO_x available (Fig. 3B), the response is a decreased ozone loss, as for model H. In models without added hydrocarbons, the ozone loss is larger than was calculated for 1987 conditions (Fig. 2) when there was less chlorine.

The results of Figs. 2 and 3 are potentially sensitive to many assumptions; we have tested some of these. When we maintained PSCs and heterogeneous processing until 1 October in the model with no added E or P, the ozone holes were deeper and lasted longer. Responses to E or P injections remained sensitive to NO_y amounts but were more encouraging than those of Fig. 2. Reducing the equivalent bimolecular rate constant for reaction 2 from $3 \times 10^{-14} \text{ cm}^3/\text{s}$ by a factor of 10 did not affect the results substantially. Note also that, if the sequestering of Cl atoms by reaction 1 prevents formation of ClO, the effects of bromine could also be diminished even though the addition of alkanes will not convert Br atoms to HBr [the reaction of Br atoms with E and P to produce HBr is endothermic (13)]. The effects of bromine are diminished because the attack of bromine on ozone proceeds through the reaction of BrO with ClO (28).

Other serious uncertainties remain. The present model calculations rest on current understanding of the mechanism of ozone-hole formation; many specific processes and their rates must be clarified. Processes that control the Antarctic vortex, its temperature, and PSC formation are not well understood nor are the mechanisms that determine the extent of denitrification and NO_x and NO_y distributions (29). Atmospheric concentrations of N_2O_5 and other NO_x compounds must be measured more completely, and the absence of background E and P should be verified. Significant questions remain about the mechanisms and rates of heterogeneous chemical reactions that activate chlorine and denitrify the stratosphere. If, for example, HCl and HOCl react quickly on PSC surfaces to form Cl_2 and H_2O (30), there may be a pathway to continue to produce Cl atoms in the absence of ClONO_2 . This pathway could reduce the effectiveness of alkane additions. Furthermore, because concentrations of NO_x and Cl_y species should increase with altitude above 15 km (19, 21, 22), the potential effectiveness of E or P should be examined at other altitudes. Also, the sensitivity of the results to the date of PSC evaporation should be tested further and the

response of air parcels that experience intermittent sunlight during winter should be modeled.

Although these initial calculations are encouraging, it is not clear whether such an intervention would be feasible. In our calculations, it was assumed that hydrocarbons could be delivered in the required quantities uniformly throughout a $2 \times 10^7 \text{ km}^2$ region of about 5 km depth (15 to 20 km altitude). It may be possible to deliver the gross quantity, say 50,000 tons of E, to an altitude of 15 km with a fleet of several hundred large airplanes, for example, but it would be very difficult to assure that the E would mix adequately with air in the Antarctic polar stratosphere. Inside the winter vortex of the Antarctic stratosphere, vertical mixing would likely require significantly more than one month, although horizontal mixing might be accomplished within a month (31). If the hydrocarbons were to be injected into the confines of the vortex, then either the

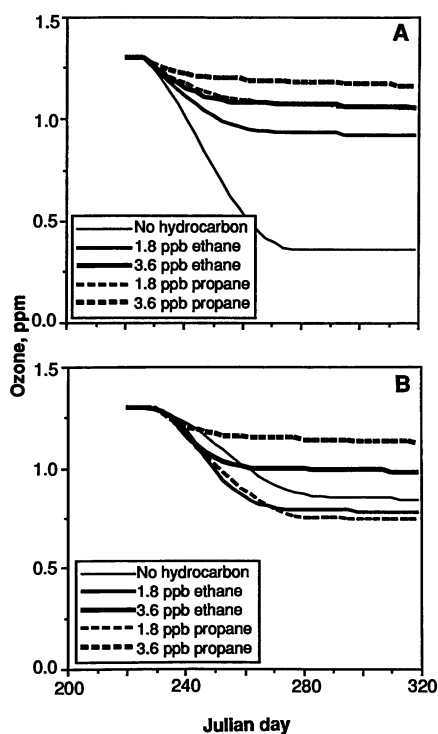


Fig. 2. Time development of ozone concentrations at 15 km in several models of Antarctic stratospheric chemistry with inorganic chlorine set approximately at 1987 levels. (A) Scenario H (Table 2) in which the ratio of active chlorine to active nitrogen is a maximum. (B) Scenario B in which the potential for storage of NO_x as ClONO_2 is defined by the amount of HCl available after reaction 2 proceeds to completion before sunrise. Hydrocarbon additions are made in increments of one and two inorganic chlorine atom equivalents. Final evaporation of PSCs is set for 1 September.

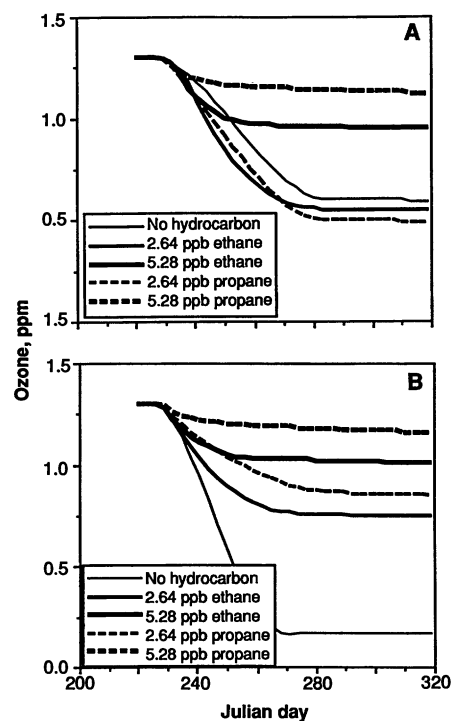


Fig. 3. Time development of ozone concentrations at 15 km in several models of Antarctic stratospheric chemistry with inorganic chlorine levels raised to 2.64 ppb, partitioned into 2.2 ppb HCl and 0.44 ppb ClONO_2 . (A) Model in which the dark-processing reaction sequence is identical to that used to construct scenario B, but with sufficient NO_x present as N_2O_5 to titrate the larger amounts of HCl remaining after reaction 2. (B) Model in which autumn N_2O_5 concentrations are restricted to 1.2 ppb; in this case the heterogeneous reactions leave an excess of HCl, which can then react with chlorine nitrate during the sunlit period to further reduce NO_x . Hydrocarbon additions are in increments of one and two inorganic chlorine atom equivalents. Final evaporation of PSCs is set for 1 September.

delivery system would have to distribute the material over the volume, or one would have to allow adequate time for slow internal mixing. The possibility that the vortex region exchanges and processes air from lower latitudes (32) could lead to some losses of the added alkanes. If instead the gases would be introduced into the stratosphere before the vortex sets up (when there is more mixing), much larger quantities would be needed, and their chemical fate would be more uncertain. Experiments can be imagined with vertically thin atmospheric layers wherein the injected hydrocarbons would be consumed (reaction 1) and the present concept could be tested. Before any actual injection experiment is undertaken there are many scientific, technical, legal, and ethical questions to be faced, not the least of which is the issue of unintended side effects (33).

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34. We acknowledge useful comments from J. D. Mahlman, S. Solomon, and M. J. Prather and support from the National Science Foundation Atmospheric Chemistry Program (ATM-8911836), National Aeronautics and Space Administration awards W-NAGW-2183 and NAS1-19155, and the University of California's INCOR Program.

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Transgenic Plants with Enhanced Resistance to the Fungal Pathogen *Rhizoctonia solani*

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The production of enzymes capable of degrading the cell walls of invading phytopathogenic fungi is an important component of the defense response of plants. The timing of this natural host defense mechanism was modified to produce fungal-resistant plants. Transgenic tobacco seedlings constitutively expressing a bean chitinase gene under control of the cauliflower mosaic virus 35S promoter showed an increased ability to survive in soil infested with the fungal pathogen *Rhizoctonia solani* and delayed development of disease symptoms.

PLANTS RESPOND TO ATTACK BY pathogenic fungi by mobilizing a complex network of active defense mechanisms (1). These include modifications designed to strengthen the plant cell wall and thereby restrict or inhibit access of the pathogen to the plant cell. More aggressive tactics involve the synthesis of toxic antimicrobial compounds (phytoalex-

ins) and the induction and accumulation of proteinase inhibitors and lytic enzymes such as chitinase and β -1,3-glucanase. The success of the plant in warding off phytopathogen invasion appears to depend on the coordination between the different defense strategies and the rapidity of the overall response (2).

Chitinase catalyzes the hydrolysis of chitin, a β -1,4-linked polymer of *N*-acetyl-D-glucosamine and a major component of the cell wall of most filamentous fungi except the Oomycetes (3). Although chitinase is generally found at low or basal levels in healthy plants, its expression is increased

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