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Authors

Elliott, Scott
Cicerone, Ralph J
Turco, Richard P
[et al.](#)

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Influence of the heterogeneous reaction HCl + HOCl on an ozone hole model with hydrocarbon additions

Scott Elliott

Institute of Geophysics and Planetary Physics, Los Alamos National Laboratory, Los Alamos, New Mexico

Ralph J. Cicerone

Department of Geosciences, University of California, Irvine

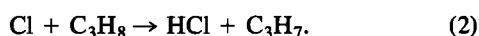
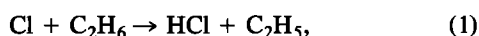
Richard P. Turco, Katja Drdla, and Azadeh Tabazadeh

Department of Atmospheric Sciences, University of California, Los Angeles

Abstract. Injection of ethane or propane has been suggested as a means for reducing ozone loss within the Antarctic vortex because alkanes can convert active chlorine radicals into hydrochloric acid. In kinetic models of vortex chemistry including as heterogeneous processes only the hydrolysis and HCl reactions of ClONO₂ and N₂O₅, parts per billion by volume levels of the light alkanes counteract ozone depletion by sequestering chlorine atoms. Introduction of the surface reaction of HCl with HOCl causes ethane to deepen baseline ozone holes and generally works to impede any mitigation by hydrocarbons. The increased depletion occurs because HCl + HOCl can be driven by HO_x radicals released during organic oxidation. Following initial hydrogen abstraction by chlorine, alkane breakdown leads to a net hydrochloric acid activation as the remaining hydrogen atoms enter the photochemical system. Lowering the rate constant for reactions of organic peroxy radicals with ClO to 10⁻¹³ cm³ molecule⁻¹ s⁻¹ does not alter results, and the major conclusions are insensitive to the timing of the ethane additions. Ignoring the organic peroxy radical plus ClO reactions entirely restores remediation capabilities by allowing HO_x removal independent of HCl. Remediation also returns if early evaporation of polar stratospheric clouds leaves hydrogen atoms trapped in aldehyde intermediates, but real ozone losses are small in such cases.

Introduction

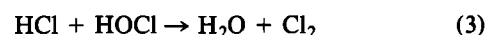
Propositions for solving pollution problems through large-scale engineering of the environment are being debated with increasing frequency in the scientific literature. Global level intervention has been discussed for both the greenhouse effect and the stratospheric ozone depletion [Stix, 1989; Martin *et al.*, 1990; Broecker, 1990; Peng and Broecker, 1991; Sarmiento, 1991; Hansen, 1991, p. 60]. Our group has studied a concept specific to the Antarctic ozone hole [Cicerone *et al.*, 1991, 1992]. We noted that injection of the light alkanes ethane and propane into the south polar vortex during winter could lead to scavenging of chlorine atoms out to the hydrochloric acid reservoir:



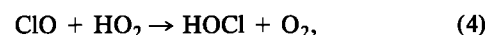
Taken alone, (1) and (2) reduce concentrations of the ClO_x radical family and so also ozone losses. In a fixed photochemical box model of Antarctic air parcels, ethane and propane suppressed springtime depletions significantly at

organic concentrations as low as 1 part per billion by volume (ppbv) [Cicerone *et al.*, 1991].

High efficiencies have recently been reported for the reaction



on the surface of polar stratospheric cloud (PSC) materials [Hanson and Ravishankara, 1992; Abbatt and Molina, 1992]. This HCl sink had been mentioned as early as 1987 [Rowland, 1987; Crutzen *et al.*, 1988; Molina, 1989] but was subsequently neglected in most Antarctic chemistry models, presumably for lack of measurement information [e.g., Jones *et al.*, 1989; Rodriguez *et al.*, 1989]. Several calculations now demonstrate that (3) is an important chlorine activation pathway during winter and spring at southern high latitudes [Prather, 1992; Crutzen *et al.*, 1992]. It is preceded by HOCl formation in



and so can be driven or limited by HO_x production. Methane oxidation is the primary source of hydrogen radicals in the existing ozone hole [Prather, 1992; Crutzen *et al.*, 1992]. By analogy with NO_x rich tropospheric environments, oxidation of larger organics would be expected to give HO_x as well [Thompson and Cicerone, 1986; Crutzen, 1988]. Under low NO_x conditions in the Antarctic vortex [Fahey *et al.*,

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1989a, b), ClO could maintain the yield of hydrogen oxides from hydrocarbons by functioning as an NO surrogate in organic peroxy radical reactions [Crutzen *et al.*, 1992]. The HCl destabilization implied by (3) and (4) may thus undermine the chlorine sequestering capabilities of ethane or propane. The present work examines the effects of the new heterogeneous process on our alkane injection concept for ozone hole remediation.

We begin by describing the detailed kinetic model of Antarctic stratospheric chemistry which has been used to analyze alkane additions. In common with several other efforts to simulate polar vortex ozone depletions, it is fixed in location and contains parameterized heterogeneous reactions for ClONO₂ and N₂O₅ [Rodriguez *et al.*, 1989; Prather, 1992; Crutzen *et al.*, 1992]. Complete and explicit organic oxidation schemes are included [e.g., Atkinson and Lloyd, 1981]. Within this framework we define a baseline model for the actual ozone hole incorporating heterogeneous reaction (3) and computing concentrations for key trace species which are broadly consistent with measurements [e.g., Murcray *et al.*, 1989; Deshler and Hofmann, 1991]. Over a number of injection scenarios, alkanes lead to net hydrochloric acid activation in the baseline and to slightly greater ozone depletions. When (3) is deleted to clarify the relationship with our previous work, plugging of the hole is restored. We also show that the influence of the new heterogeneous reaction is insensitive to variation in several crucial physical parameters. Among the quantities tested are the duration of PSCs and gas phase rate constants along organic decay sequences.

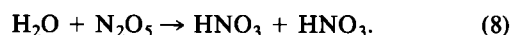
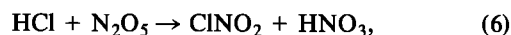
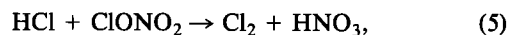
We interpret our results in terms of hydrogen radical cycling during the organic oxidations. Alkane degradation channels in the Antarctic model are similar to those responsible for photochemical production and removal of HO_x in the troposphere [Crutzen, 1988; Crutzen *et al.*, 1992]. Attack by the chlorine atom on ethane or propane does generate hydrochloric acid, but breakdown continues and releases several HO_x radicals into the photochemical system, at least one immediately, others after a short time delay. With reaction (3) operative in the baseline scenario, the HO_x activates enough chlorine to cancel the initial hydrogen abstraction, and then to increase ClO_x levels relative to real vortex chemistry. The outcome is not appreciably different under other conditions unless (3) is removed.

In a final discussion section we list some uncertainties in the model and touch briefly on the relevance of our collected ozone remediation research for environmental engineering proposals as a class; it is clear from our experience that the response of terrestrial atmospheric photochemistry to large-scale intervention may be difficult to predict.

Model Description

The high-latitude kinetics adopted here derive from an existing set of one-dimensional stratospheric programs [Turco and Whitten, 1974, 1977; Turco, 1985]. The core chemistry, consisting of 45 species and 130 reactions, was collapsed into a box model and tested at midlatitudes over the altitude range 10–50 km by comparison with other one-dimensional calculations [e.g., Ogawa and Shimazaki, 1975; Crutzen *et al.*, 1978; Brasseur *et al.*, 1983]. Gas phase processes specific to disturbed Antarctic conditions were added, including ClO dimerization, Cl₂O₂ photolysis and

thermolysis, and formation and destruction of OCIO and ClNO₂ [e.g., Solomon, 1988; Jones *et al.*, 1989; Rodriguez *et al.*, 1989; Anderson *et al.*, 1991]. The nitrate heterogeneous reactions were also put into the model [Hanson and Ravishankara, 1991a].



The purpose of the present paper is to investigate the role of yet another surface process, HCl + HOCl [Abbatt and Molina, 1992, reaction (3)]. Since we are simulating hypothetical alkane introductions, organic oxidation schemes were also required. Table 1 lists a mechanism based on several different models of atmospheric ethane chemistry [Aikin *et al.*, 1982, 1983; Thompson and Cicerone, 1986; Kasting and Singh, 1986; Trainer *et al.*, 1987; Chatfield and Delany, 1990; Kanakidou *et al.*, 1991].

A spherical radiation package was substituted into the program to calculate photolysis rates for polar zenith angles. The direct incoming beam is attenuated through both absorption and Rayleigh scattering in full spherical geometry. Wavelength-dependent multiple-scattering adjustment factors are taken from Anderson [1983] and Anderson and Lloyd [1990].

All our box models have been positioned at 15 km altitude, or around 100 mbar. Vertical ozone profiles have shown large losses in this region [Hofmann *et al.*, 1987; Hofmann, 1988; Deshler and Hofmann, 1991]. Most of the runs considered in the current work were conducted at 70°S latitude. The location optimizes the ability of our fixed calculations to reproduce major ozone hole chemical processes. At 70° the model sees daily sunlight over most of the winter. Typical air parcels circulating around the vortex move in and out of sunlit areas [Jones *et al.*, 1989]. The latitude lies near the edge of the chemically perturbed region [Fahey *et al.*, 1989a] and so is representative of the bulk of the total ozone hole volume. Concentrations of NO_y remain relatively large at lower latitudes, permitting a return of NO_x as nitric acid photolyzes in the spring [Fahey *et al.*, 1989a; Solomon *et al.*, 1989]. In keeping with our earlier computations [Cicerone *et al.*, 1991], many runs were also performed at 80°S. They were treated as sensitivity tests here.

SAM extinction measurements suggest that polar stratospheric clouds first condense over Antarctica at about the solstice [McCormick *et al.*, 1982, 1989; McCormick and Trepte, 1986; Watterson and Tuck, 1989]. We begin our calculations on July 1, with PSCs present from the outset. Measurement constraints on the partitioning of chlorine and nitrogen-containing species are sparse for the polar autumn. Accordingly, we have constructed two initial concentration data sets representing a range of possibilities. Until recently, ozone hole simulations were often initialized from two-dimensional models which did not take heterogeneous reactions on background sulfate aerosols into account [Ko *et al.*, 1984, 1985; Rodriguez *et al.*, 1989; Fahey *et al.*, 1989a]. In the absence of (7) and (8) on sulfate, NO_x tended to be preserved as chlorine nitrate and as N₂O₅. The initial concentration set labeled NO_x in Table 2 is not atypical

Table 1. Sources for Ethane Oxidation Rate and Photolysis Constants

Reaction	Rate Constant	References	Note
$C_2H_6 + OH(+O_2) \rightarrow C_2H_5O_2 + H_2O$	$1.1 \times 10^{-11} e^{-1100/T}$	D	
$C_2H_6 + Cl(+O_2) \rightarrow C_2H_5O_2 + HCl$	$7.7 \times 10^{-11} e^{-90/T}$	D	
$C_2H_5O_2 + C_2H_5O_2 \rightarrow C_2H_5O + C_2H_5O + O_2$	$1.6 \times 10^{-13} e^{-300/T}$	D	1
$C_2H_5O_2 + HO_2 \rightarrow C_2H_5O_2H + O_2$	$6.5 \times 10^{-13} e^{650/T}$	D, TC, KS	1
$C_2H_5O_2H + OH \rightarrow C_2H_5O_2 + H_2O$	1.0×10^{-11}	D', T, KS	
$C_2H_5O_2 + NO \rightarrow C_2H_5O + NO_2$	8.9×10^{-12}	D, P	
$C_2H_5O_2 + ClO \rightarrow C_2H_5O + ClO_2$	1.0×10^{-12}	D	2
$C_2H_5O + O_2 \rightarrow C_2H_4O + HO_2$	$2.9 \times 10^{-14} e^{-380/T}$	Gu, KS, TC	
$C_2H_4O + OH(+O_2) \rightarrow CH_3CO_3 + H_2O$	$6.9 \times 10^{-12} e^{260/T}$	T, AP, B	
$C_2H_4O + Cl(+O_2) \rightarrow CH_3CO_3 + HCl$	$8.1 \times 10^{-11} e^{-30/T}$	D, SH	2
$CH_3CO_3 + NO(+O_2) \rightarrow CH_3O_2 + NO_2 + CO_2$	$4.2 \times 10^{-12} e^{180/T}$	T, TC, KS, B, AL	
$CH_3CO_3 + ClO(+O_2) \rightarrow CH_3O_2 + ClO_2 + CO_2$	1.0×10^{-12}	D	2
$CH_3CO_3 + Cl \rightarrow HCl + CH_2O + CO_2$	$3.8 \times 10^{-11} e^{-90/T}$	D, SH	3
$CH_3CO_3 + NO_2(+M) \rightarrow CH_3CO_3NO_2(+M)$	3.0×10^{-12}	T, TC, KS, B, AL	
$CH_3CO_3NO_2 + Cl \rightarrow HCl + CH_2O + CO_2 + NO_2$	$3.8 \times 10^{-11} e^{-90/T}$	D, SH, KS	3
$C_2H_5O_2H + h\nu \rightarrow C_2H_4O + OH + H$		D, VR, T, TC	2
$C_2H_4O + h\nu(+O_2) \rightarrow CH_3O_2 + CO + H$		W, HC, T, KS, Ga	1

Units are $cm^3 \text{ molecule}^{-1} s^{-1}$. AL, Atkinson and Lloyd [1981]; AP, Atkinson and Pitts [1978]; B, Baulch et al. [1984]; D, Demore et al. [1990]; D', Demore et al. [1983]; Ga, Gardner et al. [1984]; Gu, Gutman et al. [1982]; HC, Horowitz and Calvert [1982]; KS, Kasting and Singh [1986]; P, Plumb et al. [1982]; SH, Singh and Hanst [1981]; T, Trainer et al. [1987]; TC, Thompson and Cicerone [1986]; VR, Vaghjani and Ravishankara [1989]; W, Weaver et al. [1976]. 1, Minor product sets excluded in most runs; 2, estimated based on value for analogous C-1 hydrocarbon; 3, estimated following Atkinson and Lloyd [1981] and Singh and Hanst [1981] to be one-half the rate of hydrogen abstraction by chlorine atom from ethane.

[Rodriguez et al., 1989]. Over the last few years an awareness has arisen that sulfate aerosol reactions may alter stratospheric chlorine and nitrogen distributions dramatically [Rodriguez et al., 1991]. This is particularly true after volcanic eruptions [Hofmann and Solomon, 1989] and at high latitude, as temperatures drop [Keys and Johnston, 1986; Wolff and Mulvaney, 1991; Turco and Hamill, 1992;

Granier and Brasseur, 1992; Prather, 1992]. In one ozone hole preprocessing calculation, N_2O_5 was removed almost completely, and there was a large net shift of inorganic chlorine from the $ClONO_2$ reservoir toward HOCl [Prather, 1992]. The concentration set labeled Sulfate in Table 2 is close to the Prather [1992] autumn estimates, but for simplicity we have converted chlorine nitrate entirely to HOCl. Our results prove to be rather insensitive to initializations over the wide range in the table. Absolute concentrations were set at levels consistent with the extensive 1987 field campaigns.

Table 2. Initial Concentrations for Key Species, Taken Largely From 1987 Field Data

	NO_x	Sulfate	Reference
NO_y	8.0	8.0	P, F
NO_x	2.66	0	
N_2O_5	1.0	0	P, R
$ClONO_2$	0.66	0	P, R
HNO_3	5.33	8.0	P, F
Cl^i	2.0	2.0	He, R
ClO_x	0	0	
HOCl	0	0.66	P, C
$ClONO_2$	0.66	0	P
HCl	1.33	1.33	P, R
H_2O	3.0	3.0	F
O_3	1.5	1.5	Ho, D
CH_4	1.3	1.3	He

C, Crutzen et al. [1992]; D, Deshler and Hofmann [1991]; F, Fahey et al. [1989a, b]; He, Heidt et al. [1989]; Ho, Hofmann [1988]; P, Prather [1992]; R, Rodriguez et al. [1989]. Chlorine nitrate is listed twice, as an NO_x and Cl reservoir, Cl^i signifies inorganic chlorine. NO_y is defined here to be $NO + NO_2 + NO_3 + 2 \times N_2O_5 + ClONO_2 + ClNO_2 + HNO_3$ and NO_x as $NO_y - HNO_3$. ClO_x is defined to be $Cl + ClO + Cl_2 + ClO + 2 \times Cl_2O_2$. Units are parts per billion by volume for chlorine and nitrogen species, parts per million by volume (ppmv) for water, ozone, and methane.

Polar stratospheric clouds persist over Antarctica until early October [McCormick et al., 1989; Watterson and Tuck, 1989]. Extinction observations [Watterson and Tuck, 1989], temperature measurements [Hofmann et al., 1987; Hofmann, 1988; Deshler and Hofmann, 1991] and microphysical considerations [Drdla and Turco, 1991; Drdla et al., 1993] indicate that type I PSCs dominate early, that type II PSCs join them during midwinter, and that type I PSCs are again predominant later on. To simulate the effect of polar stratospheric clouds on ozone chemistry, we adopt a coarse time development which is broadly consistent with both theory and observation. We assume type I particles appear during the months of July, August, and September, and type II particles only during August [Drdla and Turco, 1991].

Air parcels tend to circulate around the polar vortex on a timescale of a few days [Jones et al., 1989], and as they do, their temperatures oscillate because of orographic forcing [Drdla and Turco, 1991]. For much of the PSC period, types I and II particles may exist only at low points of the oscillations [Watterson and Tuck, 1989; Jones et al., 1989; Drdla and Turco, 1991]. In the present work we take our PSC surface areas from microphysical calculations [Drdla and Turco, 1991; Drdla et al., 1993] checked against the few pertinent measurements [Watterson and Tuck, 1989; Toon et al., 1990]. To avoid parameterizing parcel circulation fre-

Table 3. Surface Areas and Nitric Acid Vapor Pressures

	July	August	September
Type I	2×10^{-8}	2×10^{-8}	2×10^{-8}
Type II	0	8×10^{-8}	0
HNO ₃	>8.0	0	>8.0

Surface areas are given in units of $\text{cm}^2 \text{cm}^{-3}$. Nitric acid vapor pressures are relative to nitric acid trihydrate [Hanson and Mauersberger, 1988], in units of ppbv.

quencies, we average the calculated surface areas over the entire PSC period in the type I case and from first formation to disappearance for type II. Surfaces were modulated in several sensitivity tests, but the effect on ozone and important nitrogen- and chlorine-containing trace constituents was insignificant. All runs reported here employed the time-averaged surface areas in Table 3.

Photolysis of nitric acid is a major mechanism for regeneration of NO_x lost to heterogeneous reactions (5) through (8). Before and after type II clouds form, type I particles are present only of the order of a few tens of percent of the time as an air parcel circulates [Watterson and Tuck, 1989; Drdla and Turco, 1991; Drdla et al., 1993]. Nitric acid is thus present mainly in the gas phase [Fahey et al., 1989a, b]. We allow all the HNO₃ in our model to participate in photolytic and gas phase reactions during the months of July and September. While temperatures are low enough for type II clouds to form, type I particles may exist almost continually [Watterson and Tuck, 1989; Drdla and Turco, 1991], restricting the vapor phase nitric acid content because of the low nitric acid trihydrate vapor pressure [Hanson and Mauersberger, 1988]. To simulate this restriction, we turn off HNO₃ photolysis and gas phase reactions during the month of August. The overall treatment of nitric acid chemistry is summarized in Table 3. Fahey et al. [1989a] document denitrification of about 50% in the first 5° latitude away from the boundary of their chemically perturbed region, which is generally near 65°. In the microphysical calculations of Drdla and Turco [1991] the NO_y losses were about equally distributed through the pre-type II and the type II periods. In our model we remove one quarter of NO_y in the month of July and one quarter in August. Autumn and September concentrations match the observations of Fahey et al. [1989a].

Photochemical rates for (3) and (5) through (8) on PSCs were calculated by translating the surface areas of Table 3, along with particle collision rates and laboratory reaction efficiencies, into equivalent bimolecular rate constants. The method is approximate but has been applied in previous modeling studies [Solomon et al., 1986; McElroy et al., 1986; Jones et al., 1989; Prather, 1992]. The efficiencies adopted are given in Table 4. The Hanson and Ravishankara [1991a] data are preferred for (5) through (8) because they were gathered at reactant concentrations approaching those of the real stratosphere. Hanson and Ravishankara were unable to detect the reaction of hydrochloric acid with N₂O₅ or ClONO₂ on water ice surfaces. The actual efficiencies may be finite, but in the absence of data and following Drdla et al. [1993], we take zero as a default. It is conceivable that stratospheric type II water ice becomes coated with nitric

acid trihydrate, so that it behaves toward the species in (5) through (8) as though it were type I. The heterogeneous reactions of ClONO₂ and N₂O₅ will often be fast enough to cover average type II surface areas with HNO₃ on short timescales [Hanson and Ravishankara, 1991a]. Drdla et al. [1993] argue that during water ice growth phases, any nitric acid trihydrate deposited is rapidly buried. During evaporation, coating seems a higher likelihood, but Drdla et al. [1993] postulate that it does not occur and spread condensing nitric acid evenly through the water ice solid. In this case, little is available at the surface. For present purposes we assume that type II particle surfaces are composed solely of water ice. We employ the collision rate equations in the work by Drdla and Turco [1991] and Drdla et al. [1993] to calculate overall reaction rates, taking the mean free path for 100 mbar from Turco et al. [1989].

Heterogeneous reactions on sulfate aerosols were included in the calculations. In the midlatitude stratosphere, background sulfate is thought to consist of liquid 60–80% H₂SO₄ by weight, with a surface area of about $5 \times 10^{-9} \text{cm}^2 \text{cm}^{-3}$ [Steele and Hamill, 1981; Hofmann and Solomon, 1989]. Several groups have measured rates for (7) and (8) on the corresponding sulfuric acid solutions [Mozurkewich and Calvert, 1988; Tolbert et al., 1988; Hanson and Ravishankara, 1991b]. The efficiency for chlorine nitrate hydrolysis rises rapidly with water content over the range 0.001–0.1, while N₂O₅ hydrolysis is roughly constant at 0.1. At the low temperatures of the polar stratosphere the sulfuric acid content of the aerosols can drop to 20–50% [Wolff and Mulvaney, 1991; Turco and Hamill, 1992]. The chlorine nitrate hydrolysis rate maximizes at these sulfate compositions [Tolbert et al., 1988; Hanson and Ravishankara, 1991b; Granier and Brasseur, 1992].

Watson et al. [1990], Wolff and Mulvaney [1991], and Hanson and Ravishankara [1991b] discuss the solubility of hydrochloric acid in the H₂SO₄ solutions. Little HCl will dissolve in the 60–80% range, but the solubility rises substantially below 50% sulfuric acid. Wolff and Mulvaney [1991] and Turco and Hamill [1992] explore the possibility that large HCl concentrations in the sulfate aerosol could lead to enhancements in (5) and (6), but experimentally, efficiencies are found to be low at stratospheric HCl concentrations [Hanson and Ravishankara, 1991b]. We follow Granier and Brasseur [1992] here and ignore hydrochloric acid reactions on the sulfate aerosols.

The physical state of sulfate aerosols at polar temperatures is uncertain. There is some theoretical evidence that the sulfuric acid solutions can freeze during the PSC period as temperatures drop far enough into the supercooled regime

Table 4. Reaction Efficiencies for Type I and Type II Materials

	Type I	Type II
HCl + ClONO ₂	0.3	0
HCl + N ₂ O ₅	0.003	0
H ₂ O + ClONO ₂	0.006	0.3
H ₂ O + N ₂ O ₅	0.0006	0.02
HOCl + HCl	0.2	0.2

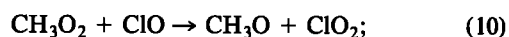
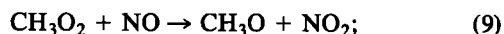
Values are taken from Hanson and Ravishankara [1991a] and Abbatt and Molina [1992].

[Jensen *et al.*, 1991; Luo *et al.*, 1991; Turco and Hamill, 1992]. Observations, however, are consistent with a liquid phase [Wolff and Mulvaney, 1991; Goodman *et al.*, 1989], and freezing is not instantaneous [Turco *et al.*, 1989]. Reactions (7) and (8) may be quite slow on frozen sulfate [Harker and Strauss, 1981; Mozurkewich and Calvert, 1988; Hanson and Ravishankara, 1991b]. Since only some of the background sulfuric acid in the Antarctic vortex may be liquid, we take a relatively low surface area estimate of $3 \times 10^{-9} \text{ cm}^2 \text{ cm}^{-3}$ [Wolff and Mulvaney, 1991; Goodman *et al.*, 1989]. Efficiencies for both (7) and (8) are set at 0.1. Sulfate particle concentrations are of the order of 10 cm^{-3} , which is generally much larger than the corresponding values for PSCs, so that the sulfuric acid surfaces are always left exposed [Turco *et al.*, 1989; Drdla and Turco, 1991]. The same bimolecular equivalent rate constant technique is applied to translate efficiencies and contact rates into photochemical rates.

Model Runs

We assume the conditions summarized here in Tables 1 through 4 to define a baseline ozone hole model. In our earlier study of the alkane mitigation concept, both ethane and propane were introduced into the calculations [Cicerone *et al.*, 1991]. From a qualitative standpoint the response of ozone to the two different organics was similar. In the present work we will report only upon ethane additions. Tests have verified that the key results would not be altered if the experiments were repeated with propane. Following simulations of the real ozone hole at zero alkane concentrations, ethane was initialized into the baseline along with the substances in Table 2. This would correspond to an alkane injection made early in the winter. Amounts of the hydrocarbon were varied to one and two inorganic chlorine atom equivalents, or to 2 and 4 ppbv.

Ethane was inserted not only into the baseline case but also into a set of variations upon it. The mechanisms through which organic oxidations lead to chlorine activation suggested several instructive sensitivity studies. Prather [1992] and Crutzen *et al.* [1992] have shown that the new heterogeneous process 3 enables HO_x radicals released from methane to convert hydrochloric acid to ClO_x . The kinetic channels for CH_4 breakdown within the ozone hole are outlined in Table 5. The chain is analogous to oxidation in more familiar areas of the atmosphere [Crutzen, 1988; Crutzen *et al.*, 1992] but with some exceptions. Chlorine monoxide acts as a surrogate for NO in peroxide consumption,



and a principal fate of HO_x is (4). In the portion of Table 5 labeled alkane oxidation/chlorine branch, (3) recreates ClO_x if it is lost during initial hydrogen abstraction. Formaldehyde photolysis to the formyl radical yields net activation of HCl. The competing photolysis to CO and molecular hydrogen is not shown but is null with respect to ClO_x . Chlorine attack on CH_2O is also null. Hydrogen abstraction by hydroxyl from either methane or formaldehyde can give net HCl conversion, but the chlorine atom reactions are usually more important because they have larger rate constants. Ethane

Table 5. Segments of the Methane Oxidation Sequence for a High ClO_x , Low NO_x Scenario Including the New Heterogeneous Reaction $\text{HCl} + \text{HOCl}$

Branch	Reaction	
<i>Alkane</i>		
Chlorine	$\text{CH}_4 + \text{Cl} \rightarrow \text{CH}_3 + \text{HCl}$	
	$\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{O}_2$	
	$\text{CH}_3\text{O}_2 + \text{ClO} \rightarrow \text{CH}_3\text{O} + \text{ClO}_2$	
	$\text{ClO}_2 \rightarrow \text{Cl} + \text{O}_2$	
	$\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$	
	$\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{HO}_2$	
	$\text{HO}_2 + \text{ClO} \rightarrow \text{HOCl} + \text{O}_2$	
	$\text{HOCl} + \text{HCl} \rightarrow \text{Cl}_2 + \text{H}_2\text{O}$	
	$\text{Cl}_2 + h\nu \rightarrow \text{Cl} + \text{Cl}$	
	$\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$	
	Sum	$\text{CH}_4 + 2\text{O}_3 \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O} + 2\text{O}_2$
		$\text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O}$
	Hydroxyl	$\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{O}_2$
		$\text{CH}_3\text{O}_2 + \text{ClO} \rightarrow \text{CH}_3\text{O} + \text{ClO}_2$
$\text{ClO}_2 \rightarrow \text{Cl} + \text{O}_2$		
$\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$		
$\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{HO}_2$		
$\text{HO}_2 + \text{ClO} \rightarrow \text{HOCl} + \text{O}_2$		
$\text{HOCl} + \text{HCl} \rightarrow \text{Cl}_2 + \text{H}_2\text{O}$		
$\text{Cl}_2 + h\nu \rightarrow \text{Cl} + \text{Cl}$		
$\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$		
Sum		$\text{CH}_4 + \text{OH} + \text{HCl} + 2\text{O}_3 \rightarrow \text{CH}_2\text{O} + 2\text{H}_2\text{O} + \text{Cl} + 2\text{O}_2$
<i>Aldehyde</i>		
Chlorine		$\text{CH}_2\text{O} + \text{Cl} \rightarrow \text{CHO} + \text{HCl}$
		$\text{CHO} + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2$
	$\text{HO}_2 + \text{ClO} \rightarrow \text{HOCl} + \text{O}_2$	
	$\text{HOCl} + \text{HCl} \rightarrow \text{Cl}_2 + \text{H}_2\text{O}$	
	$\text{Cl}_2 + h\nu \rightarrow \text{Cl} + \text{Cl}$	
	$\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$	
	Sum	$\text{CH}_2\text{O} + \text{O}_3 \rightarrow \text{CO} + \text{H}_2\text{O} + \text{O}_2$
		$\text{CH}_2\text{O} + \text{OH} \rightarrow \text{CHO} + \text{H}_2\text{O}$
	Hydroxyl	$\text{CHO} + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2$
		$\text{HO}_2 + \text{ClO} \rightarrow \text{HOCl} + \text{O}_2$
		$\text{HOCl} + \text{HCl} \rightarrow \text{Cl}_2 + \text{H}_2\text{O}$
		$\text{Cl}_2 + h\nu \rightarrow \text{Cl} + \text{Cl}$
		$\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$
		Sum
Photolysis		$\text{CH}_2\text{O} + h\nu \rightarrow \text{CHO} + \text{H}$
		$\text{H} + \text{O}_2 \rightarrow \text{HO}_2$
		$\text{HO}_2 + \text{ClO} \rightarrow \text{HOCl} + \text{O}_2$
		$\text{HOCl} + \text{HCl} \rightarrow \text{Cl}_2 + \text{H}_2\text{O}$
		$\text{Cl}_2 + h\nu \rightarrow \text{Cl} + \text{Cl}$
		$\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$
		$\text{CHO} + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2$
	$\text{HO}_2 + \text{ClO} \rightarrow \text{HOCl} + \text{O}_2$	
	$\text{HOCl} + \text{HCl} \rightarrow \text{Cl}_2 + \text{H}_2\text{O}$	
	$\text{Cl}_2 + h\nu \rightarrow \text{Cl} + \text{Cl}$	
	$\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$	
	Sum	$\text{CH}_2\text{O} + 2\text{HCl} + 2\text{O}_3 \rightarrow \text{CO} + 2\text{H}_2\text{O} + 2\text{Cl} + 2\text{O}_2$

reacts a thousand times more rapidly with chlorine than does methane [Demore *et al.*, 1990], and when it is inserted into the photochemical system at the parts per billion by volume level, multiple carbon chains with similar properties contrib-

Table 6. Segments of the Ethane Oxidation Sequence for a High ClO_x, Low NO_x Scenario Including the New Heterogeneous Reaction HCl + HOCl

Branch	Reaction
<i>Alkane</i>	
Chlorine	C ₂ H ₆ + Cl → C ₂ H ₅ + HCl
	C ₂ H ₅ + O ₂ → C ₂ H ₅ O ₂
	C ₂ H ₅ O ₂ + ClO → C ₂ H ₅ O + ClO ₂
	ClO ₂ → Cl + O ₂
	Cl + O ₃ → ClO + O ₂
	C ₂ H ₅ O + O ₂ → C ₂ H ₄ O + HO ₂
	HO ₂ + ClO → HOCl + O ₂
	HOCl + HCl → Cl ₂ + H ₂ O
	Cl ₂ + hν → Cl + Cl
	Cl + O ₃ → ClO + O ₂
Sum	C ₂ H ₆ + 2O ₃ → C ₂ H ₄ O + H ₂ O + 2O ₂
Hydroxyl	C ₂ H ₆ + OH → C ₂ H ₅ + H ₂ O
	C ₂ H ₅ + O ₂ → C ₂ H ₅ O ₂
	C ₂ H ₅ O ₂ + ClO → C ₂ H ₅ O + ClO ₂
	ClO ₂ → Cl + O ₂
	Cl + O ₃ → ClO + O ₂
	C ₂ H ₅ O + O ₂ → C ₂ H ₄ O + HO ₂
	HO ₂ + ClO → HOCl + O ₂
	HOCl + HCl → Cl ₂ + H ₂ O
	Cl ₂ + hν → Cl + Cl
	Cl + O ₃ → ClO + O ₂
Sum	C ₂ H ₆ + OH + HCl + 2O ₃ → C ₂ H ₄ O + 2H ₂ O + Cl + 2O ₂
<i>Aldehyde</i>	
Chlorine	C ₂ H ₄ O + Cl(+O ₂) → CH ₃ CO ₃ + HCl
	CH ₃ CO ₃ + ClO(+O ₂) → CH ₃ O ₂ + ClO ₂ + CO ₂
	ClO ₂ → Cl + O ₂
	Cl + O ₃ → ClO + O ₂
	CH ₃ O ₂ + ClO → CH ₃ O + ClO ₂
	ClO ₂ → Cl + O ₂
	Cl + O ₃ → ClO + O ₂
	CH ₃ O + O ₂ → CH ₂ O + HO ₂
	HO ₂ + ClO → HOCl + O ₂
	HOCl + HCl → Cl ₂ + H ₂ O
	Cl ₂ + hν → Cl + Cl
	Cl + O ₃ → ClO + O ₂
Sum	C ₂ H ₄ O + 3O ₃ → CH ₂ O + CO ₂ + H ₂ O + 3O ₂
Hydroxyl	C ₂ H ₄ O + OH(+O ₂) → CH ₃ CO ₃ + H ₂ O
	CH ₃ CO ₃ + ClO(+O ₂) → CH ₃ O ₂ + ClO ₂ + CO ₂
	ClO ₂ → Cl + O ₂
	Cl + O ₃ → ClO + O ₂
	CH ₃ O ₂ + ClO → CH ₃ O + ClO ₂
	ClO ₂ → Cl + O ₂
	Cl + O ₃ → ClO + O ₂
	CH ₃ O + O ₂ → CH ₂ O + HO ₂
	HO ₂ + ClO → HOCl + O ₂
	HOCl + HCl → Cl ₂ + H ₂ O
	Cl ₂ + hν → Cl + Cl
	Cl + O ₃ → ClO + O ₂
Sum	C ₂ H ₄ O + OH + HCl + 3O ₃ → CH ₂ O + CO ₂ + 2H ₂ O + Cl + 3O ₂

Table 6. (continued)

Branch	Reaction
<i>Aldehyde</i>	
Photolysis	C ₂ H ₄ O + hν(+O ₂) → CH ₃ O ₂ + CO + H
	H + O ₂ → HO ₂
	HO ₂ + ClO → HOCl + O ₂
	HOCl + HCl → Cl ₂ + H ₂ O
	Cl ₂ + hν → Cl + Cl
	Cl + O ₃ → ClO + O ₂
	CH ₃ O ₂ + ClO → CH ₃ O + ClO ₂
	ClO ₂ → Cl + O ₂
	Cl + O ₃ → ClO + O ₂
	CH ₃ O + O ₂ → CH ₂ O + HO ₂
	HO ₂ + ClO → HOCl + O ₂
	HOCl + HCl → Cl ₂ + H ₂ O
	Cl ₂ + hν → Cl + Cl
	Cl + O ₃ → ClO + O ₂
Sum	C ₂ H ₄ O + 2HCl + 3O ₃ → CH ₂ O + CO + 2H ₂ O + 2Cl + 3O ₂

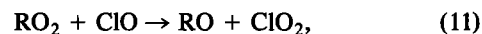
For CH₂O fragmentation, see Table 5.

ute to HO_x production (Table 6). The HO_x radicals enter Table 5 and Table 6 in the HO₂ form.

One variation on the baseline forms a conceptual bridge with our earlier study predating rate measurements for heterogeneous process 3 [Cicerone *et al.*, 1991]. It would be expected that if the HCl + HOCl reaction were inoperative, the Tables 5 and 6 chains would be halted at (4). Hydrochloric acid then functions as a real reservoir, enhancing prospects for mitigation. The efficiency of (3) is zeroed in one set of runs to demonstrate consistency with Cicerone *et al.* [1991]. These calculations are carried out for mechanistic analysis only and are not meant to represent any real physical situation in the stratosphere. Laboratory measurements of the new heterogeneous reaction clearly support near-unit efficiency [Abbatt and Molina, 1992].

It must also be the case that some finite timescale is involved in the release of all HO_x from the hydrocarbon skeletons. After the first hydrogen abstraction, an organic peroxy radical and then an aldehyde are likely to form quickly. The aldehyde, however, may be stable for days under the weak photolytic conditions of high-latitude winter. Early cloud evaporation could suspend (3) before the full hydrogen atom yield has been realized. Accordingly, another set of variants on the baseline adopts a brief PSC scenario. Only type I particles are simulated and only during the month of August. Because this situation may be representative of air parcels at the vortex edge where higher winter temperatures are maintained, we also turn off the denitrification process, so that NO_y remains near initial values into the spring [Fahey *et al.*, 1989a]. Water vapor concentrations are raised to their unperturbed levels [Fahey *et al.*, 1989a].

Critical branches in the Tables 5 and 6 schemes may occur at the homologous series



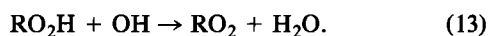
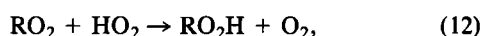
where R is a hydrocarbon grouping. Rate constants are still extremely uncertain even for the methyl peroxy radical reaction with ClO [Simon *et al.*, 1989; Demore *et al.*, 1990; Demore, 1991], and most of the processes represented by

Table 7. Final Ozone Concentrations

PSC	HCl + HOCl	RO ₂ + ClO	Scenario	Ethane		
				0	1	2
JAS	on	10 ⁻¹²	NO _x	0.07	0.04	0.05
			sulfate	0.19	0.10	0.11
JAS	off	10 ⁻¹²	NO _x	0.19	0.42	0.55
			sulfate	0.30	0.49	0.59
A	on	10 ⁻¹²	NO _x	0.89	0.97	0.99
			sulfate	0.88	0.98	1.00
JAS	on	10 ⁻¹³	NO _x	0.04	0.04	0.09
			sulfage	0.13	0.09	0.16

PSC, polar stratospheric cloud; JAS, PSC particles present in July, August, and September; A, PSC particles present in August. On – HCl + HOCl efficiencies as in the work of *Abbatt and Molina* [1992]. Off – HCl + HOCl efficiencies zeroed. RO₂ + ClO rate constants in units of cm³ molecule⁻¹ s⁻¹. Ethane concentrations given as inorganic chlorine atom equivalents; e.g., 1 = 2.0 ppbv. Ozone concentrations under ethane columns 0, 1, and 2 are in ppmv.

(11) have not been measured. With NO_x and so also NO levels depressed during the Antarctic winter, low rates for (11) allow the sequence



Cycling from (12) to (13) constitutes an HO_x sink [*Crutzen*, 1988] and could alter alkane-induced chlorine activation rates. The RO₂ + ClO rate constants were assigned the value 10⁻¹² cm³ molecule⁻¹ s⁻¹ in Table 1, a round figure extrapolated from *Simon et al.* [1989]. In a third variation on the baseline, all of the type (11) reactions including that of the methyl peroxy are slowed by an order of magnitude.

Results

Final ozone concentrations from the major runs are organized in Table 7. Time developments for ozone and the chlorine reservoirs HCl and ClONO₂ are illustrated for selected calculations in Figures 1 through 4.

The baseline case is meant to simulate major features of ozone hole chemistry, and so we have checked trace species concentrations from it against crucial measurement constraints. Perhaps the most important comparison is with ozone. Both final levels and the time development plotted in Figure 1 agree with balloon sonde measurements made from McMurdo sound, adjusted for earlier onset of irradiation at lower latitude [*Hofmann*, 1988; *Deshler and Hofmann*, 1991; *Crutzen et al.*, 1992]. Hydrochloric acid from the sulfate scenario is plotted in Figure 2; the NO_x calculation was similar. Activation by methane oxidation matches the models of *Prather* [1992] and *Crutzen et al.* [1992]. The jump in early October from reduced concentrations to the total inorganic chlorine amount is seen in column infrared measurements [*Murcray et al.*, 1989]. HOCl concentrations remained below 0.1 ppbv in all runs and so match a single data point for mid-September from the Jet Propulsion Laboratory group [*Toon and Farmer*, 1989; *Toon et al.*, 1989]. ClO radical maximizes at about one-half parts per billion by volume on September 1 and remains in this regime for several weeks. The concentrations agree well with the ER-2

measurements of *Brune et al.* [1989]. Chlorine nitrate levels are plotted along with HCl in Figure 2 for the sulfate run and again were similar for the NO_x initial concentrations. The ClONO₂ calculations are broadly consistent with several indications that NO_x must exist in the photochemical system during the month of September [*Fahey et al.*, 1989a; *Solomon et al.*, 1989].

The additions of one and two inorganic chlorine atom equivalents of ethane deepen both the NO_x and the sulfate concentration baselines. The hydrochloric acid time developments in Figure 2 show extensive chlorine activation even in the absence of the alkane but enhancement of conversion to ClO_x with ethane added. We have interpreted these effects largely through the mechanisms of Tables 5 and 6 and verified our analysis through comparison with model outputs of photochemical production and loss rates and individual species concentrations. In the zero ethane baseline, HCl loss during August can be attributed to hydrogen radicals created during methane oxidation initiated by chlorine atom attack. With the return of NO_x in September, reaction with chlorine nitrate contributes. In the ethane injection curve in Figure 2,

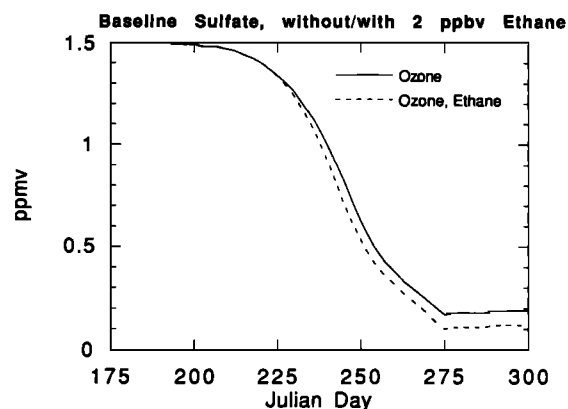


Figure 1. Ozone time development in the baseline model. Sulfate concentration set. Solid curve, no ethane added. Dashed curve, 2 parts per billion by volume (ppbv) ethane added.

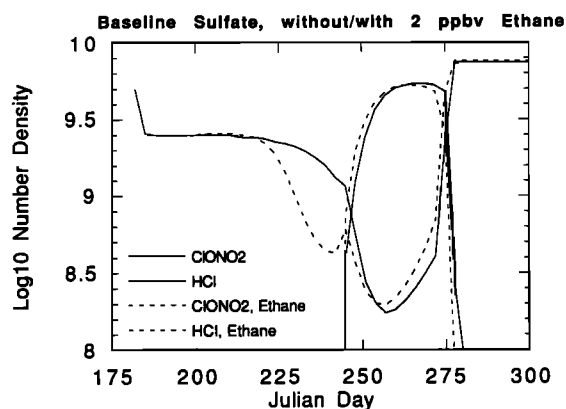


Figure 2. Hydrochloric acid and chlorine nitrate time developments in the baseline model. Sulfate concentration set. Chlorine nitrate initialized at zero. Solid curves, no ethane added. Dashed curves, 2 ppbv ethane added.

HCl concentrations rise slightly, while the days are short and the Sun is near the horizon, because hydrogen atoms build up in the acetaldehyde and formaldehyde reservoirs. As the aldehydes decompose, however, strong conversion to ClO_x through (3) increases ozone depletions. The baseline NO_x scenario gives larger ozone losses overall because N_2O_5 photolysis early in the winter activates a small amount of HCl before organic oxidation begins.

The test case with (3) suppressed confirms the major results of *Cicerone et al.* [1991]. Parts per billion by volume levels of ethane again decrease ozone depletions. Time developments are illustrated for ozone in Figure 3 and for the chlorine reservoirs in Figure 4. The zero ethane versions are shallower than in the baseline case because methane now constitutes a small source of hydrogen atoms which can create HCl instead of a means for converting it to the active radicals. Ethane acts as a hydrogen source as well. The plugging effect is less dramatic than in the work of *Cicerone et al.* [1991]. The calculations here emphasize production of NO_x in late winter because nitric acid concentrations are higher at 70° than at 80° and PSC particles more ephemeral.

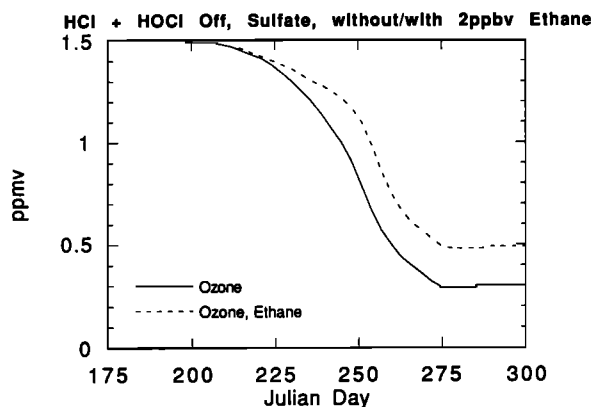


Figure 3. Ozone time development with the HCl + HOCl heterogeneous reaction inoperative. Sulfate concentration set. Solid curve, no ethane added. Dashed curve, 2 ppbv ethane added.

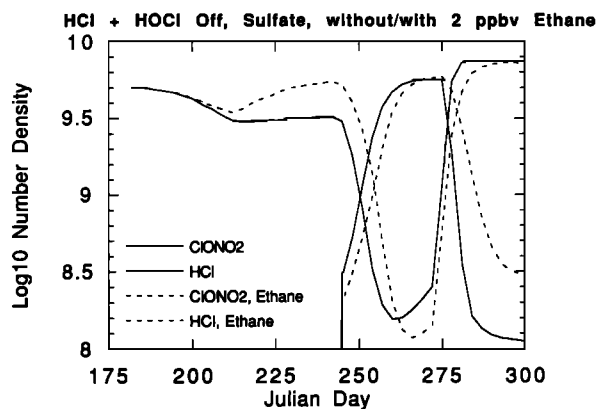


Figure 4. Hydrochloric acid and chlorine nitrate time developments with the HCl + HOCl heterogeneous reaction inoperative. Sulfate concentration set. Chlorine nitrate initialized at zero. Solid curves, no ethane added. Dashed curves, 2 ppbv ethane added.

Activation of HCl through (5) following nitric acid photolysis dominates overall ozone depletion.

Restricting polar stratospheric clouds to the type I form and to the month of August reduces ozone depletion in the absence of alkane. Final ozone concentrations are about 0.9 ppmv and are very similar in the NO_x and sulfate concentration sets because sulfate aerosols are present in the model for a month in July prior to the appearance of the clouds. Chlorine nitrate is converted rapidly to HOCl through reaction on the sulfate and, likewise, N_2O_5 to nitric acid. Ethane oxidation fails to activate HCl because hydrogen atoms which get caught in the aldehyde reservoirs are partly released after PSC evaporation, when the Tables 5 and 6 chains end at (4). Short PSC periods will tend to favor plugging of the ozone hole by alkanes but also render mitigation less critical since losses are small to begin with.

In the last run detailed in Table 7, rates for the class of reactions $\text{RO}_2 + \text{ClO}$ were lowered an order of magnitude relative to the baseline. Ozone concentrations were not sensitive to peroxy radical processes over this range. In separate experiments not tabulated, setting rate constants for all of the set 11 to 0 returned the plugging capabilities of the alkanes. The reaction sequence (12) and (13) destroys hydrogen radicals and so prevents them from activating chlorine in (3) and (4). The HO_x production mechanism familiar from NO_x rich tropospheric situations [*Crutzen*, 1988] is damped because ClO does not take the place of NO. In another set of untabulated results, 2 ppbv ethane injections were either delayed until August 1 or else repeated every 2 weeks throughout August and September. In both cases, deepening was even stronger than in the baseline. Additions of tens of parts per billion by volume alkane eventually reverse the deepening trend but probably would not be feasible to deliver to the stratosphere [*Cicerone et al.*, 1991, 1992].

Discussion

Our latest simulations of engineered Antarctic chemistry indicate that (3) counteracts the ability of alkanes to sequester chlorine atoms by channeling HO_x of organic origin into

HCl activation. In baseline runs and others, alkane injections can actually increase ozone depletions. The chain of events leading from initial hydrogen abstraction through hydrocarbon oxidation to net chlorine activation can be understood in terms of the reactions in Table 6.

A number of large uncertainties bear on these conclusions. Some are common to polar stratospheric chemistry models in general. Laboratory data for the known heterogeneous reactions still cannot be translated to the stratosphere with complete confidence because real atmospheric conditions and surfaces are difficult to duplicate [Hanson and Ravishankara, 1991a, b; Drdla et al., 1993]. It is also possible that the list of surface processes which must be considered in stratospheric models will grow longer. The recent measurements of high HCl + HOCl efficiencies opened up entirely new kinetic channels to investigation and both motivated and necessitated the present work [Abbatt and Molina, 1992; Prather, 1992; Crutzen et al., 1992]. Efficiencies for (5) and (6) on water ice surfaces are especially poorly known [Hanson and Ravishankara, 1991a]. We have ignored them here primarily for lack of data. There may be some justification for doing so; it has been pointed out that the HCl content of the ice matrix must be very low [Wolff et al., 1989; Elliott et al., 1990, 1991; Tabazadeh and Turco, 1993]. Details of the crystalline structure of PSC particles remain obscure, however, and have not been factored into theoretical analyses.

Microphysical models of polar stratospheric clouds are still under development, and uncertainties in them feed back directly into the chemistry. Calculations of surface area are probably only accurate on an order of magnitude basis [Drdla and Turco, 1991; Drdla et al., 1993]. The nature of the surface is often in question at very fundamental levels. Type II PSC particles may or may not be coated with nitric acid trihydrate [Hanson and Ravishankara, 1991a; Drdla et al., 1993]. Background sulfate aerosols may or may not be frozen in the Antarctic winter [Turco et al., 1989; Goodman et al., 1989; Wolff and Mulvaney, 1991; Turco and Hamill, 1992; Drdla et al., 1993].

Measurements which could be applied to constrain the photochemical models are scarce. Autumn observations of a few key species could facilitate the construction of initial concentration sets for polar calculations [Rodriguez et al., 1991; Prather, 1992; Crutzen et al., 1992] and would also be revealing in terms of preprocessing on sulfate prior to PSC appearance [Wolff and Mulvaney, 1991; Turco and Hamill, 1992]. Even where measurements are available, large uncertainties must be continually dealt with. For example, new high-latitude HCl data suggest that models of stratospheric chlorine chemistry may be incomplete (C. Webster and M. Prather, personal communication, 1993).

Simulations of the real ozone hole can treat some of the uncertainties through sensitivity tests [Rodriguez et al., 1989; Drdla and Turco, 1991; Prather, 1992; Crutzen et al., 1992]. In our engineered calculations this becomes more difficult, because we must place a high priority on varying quantities associated with the alkane injections. The amount and conditions of hydrocarbon introduction must be adjusted and tested. Errors inherent in rate constants along the organic oxidation sequence must be dealt with. The parameter space which could be explored is greatly expanded. We have chosen here to construct a very generalized representation of PSC microphysics and ozone hole chemistry meeting a broad set of measurement constraints. Our resolution

of some issues is necessarily coarse. It would be valid, for example, to ask whether nitric acid photolysis overlapping the type II period would alter our results. The effect of mixing with vortex external, NO_x rich air masses could also be debated. Growth of the model parameter space would seem to be a general problem in evaluating environmental engineering propositions. The natural atmosphere alone can push our computational capabilities to their limits. Engineered versions magnify the modeling challenges.

The relationship between our older and more recent simulations illustrates an even more crucial problem in assessing concepts for large-scale environmental engineering. The addition of a single reaction to the photochemical system has altered the major results. Our experience demonstrates that the atmosphere can hold surprises, no matter how sophisticated models may be. The ozone hole itself is, of course, another case in point.

Summary

The scientific community has been confronted with several propositions for direct intervention into the terrestrial environmental system to reverse large-scale pollution phenomena [e.g., Stix, 1989; Martin et al., 1990; Hansen, 1991; Cicerone et al., 1992]. We have investigated a concept for remediation of the Antarctic ozone hole. Early calculations showed that injection of parts per billion by volume levels of the light alkanes ethane and propane could scavenge ozone destructive ClO_x radicals and convert them to the reservoir hydrochloric acid [Cicerone et al., 1991]. As long as the chlorine atoms remained in the HCl form, massive spring-time ozone depletions were mitigated. Laboratory measurements of near-unit efficiencies for the PSC surface process HCl + HOCl → H₂O + Cl₂ later raised the prospect of conversion of the hydrochloric acid back to ClO_x [Abbatt and Molina, 1992]. The new heterogeneous reaction is driven by HO_x radicals [Prather, 1992; Crutzen et al., 1992], several of which can be released during a stratospheric alkane oxidation sequence.

In the present work, HCl + HOCl has been included in the original photochemical model along with ethane, and a series of simulations of ozone hole chemistry performed first without and then with alkane additions. The model is situated at 70°S latitude so that intermittent irradiation occurs throughout most of the winter, and much of nitric acid resists denitrification and can photolyze to generate NO_x. A baseline case computation yields concentrations for key inorganic chlorine- and nitrogen-containing species which are broadly consistent with results of Antarctic measurement campaigns [Brune et al., 1989; Fahey et al., 1989a, b; Murcray et al., 1989; Solomon et al., 1989; Toon and Farmer, 1989; Deshler and Hofmann, 1991]. Addition of ethane produces a net activation of hydrochloric acid and increased ozone depletions. The effect can be explained in terms of HO_x radicals generated along the ethane oxidation chain. Tropospheric nonmethane hydrocarbons influence HO_x through a similar set of reactions [Crutzen, 1988; Crutzen et al., 1992].

If the HCl + HOCl process is suppressed in the model, the connection between HO_x and chlorine activation is broken, and the ozone hole plugging capabilities of ethane are restored. Reduction in polar stratospheric cloud duration and intensity gives a shallower set of depletions, but they

can be reduced by ethane because some hydrogen atoms are stored as intermediates along the oxidation chain until evaporation takes place. Ozone behavior is insensitive to a collective factor of 10 reduction in rate constants for the organic peroxy radical reactions with ClO, from 10^{-12} to 10^{-13} $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. When the $\text{RO}_2 + \text{ClO}$ reactions are ignored altogether, ethane mitigates ozone losses once again because cycling from peroxy radicals to hydroperoxide species removes HO_x which would otherwise lead to chlorine activation.

Uncertainties within the model include those common to other ozone hole studies; heterogeneous reaction rates are not well known and observational data are relatively sparse. We have focused sensitivity testing to some extent on parameters associated directly with the alkane additions. Amounts and timing of ethane introduction were varied, along with the peroxy rates. Centering on the alkane chemistry led necessarily to sacrifices in tests of other quantities, particularly those describing clouds and heterogeneous reactions. We suggest that models of environmental engineering will find this a typical difficulty. Schemes such as vortex alkane injection will generally bring with them a set of uncertainties which must be superimposed on those of the natural system. A more critical dilemma in the assessment of engineered solutions to large-scale pollution problems is highlighted by the contrast between our first and second set of ozone hole calculations. Introduction of a single new photochemical reaction forced major revisions to our original conclusions. It is evident that even state of the art atmospheric models cannot be expected to anticipate all ramifications of an intervention concept.

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References

- Abbatt, J. P. D., and M. J. Molina, The heterogeneous reaction of $\text{HOCl} + \text{HCl}$ on ice and nitric acid trihydrate: Reaction probabilities and stratospheric implications, *Geophys. Res. Lett.*, **19**(5), 461–464, 1992.
- Aikin, A. C., J. R. Herman, E. J. Maier, and C. J. McQuillan, Atmospheric chemistry of ethane and ethylene, *J. Geophys. Res.*, **87**(C4), 3105–3118, 1982.
- Aikin, A. C., J. R. Herman, E. J. R. Maier, and C. J. McQuillan, Influence of peroxyacetyl nitrate on odd nitrogen in the troposphere and lower stratosphere, *Planet. Space Sci.*, **31**(9), 1075–1082, 1983.
- Anderson, D. E., The troposphere-stratosphere radiation field at twilight: A spherical model, *Planet. Space Sci.*, **31**(12), 1517–1523, 1983.
- Anderson, D. E., and S. A. Lloyd, Polar twilight UV-visible radiation field: Perturbations due to multiple scattering, ozone depletion, stratospheric clouds, and surface albedo, *J. Geophys. Res.*, **95**(D6), 7429–7434, 1990.
- Anderson, J. G., D. W. Toohey, and W. H. Brune, Free radicals within the Antarctic vortex: The role of CFCs in antarctic ozone loss, *Science*, **251**, 39–46, 1991.
- Atkinson, R., and A. C. Lloyd, Evaluation of kinetic and mechanistic data for modeling of photochemical smog, *J. Phys. Chem. Ref. Data*, **13**(2), 315–439, 1981.
- Atkinson, R., and J. N. Pitts, Kinetics of the reactions of the OH radical with HCHO and CH_3CHO over the temperature range 299–426 K, *J. Chem. Phys.*, **68**(8), 1978.
- Baulch, D. L., R. A. Cox, R. F. Hampson, J. A. Kerr, J. Troe, and R. T. Watson, Evaluated kinetic and photochemical data for atmospheric chemistry: Supplement II, *J. Phys. Chem. Ref. Data*, **13**, 1259–1273, 1984.
- Brasseur, G., A. De Rudder, and P. C. Simon, Implication for stratospheric composition of a reduced absorption cross section in the Herzberg continuum of molecular oxygen, *Geophys. Res. Lett.*, **10**, 20–23, 1983.
- Broecker, W. S., Comment on "Iron deficiency limits phytoplankton growth in Antarctic waters" by John H. Martin et al., *Global Biogeochem. Cycles*, **4**(1), 3–4, 1990.
- Brune, W. H., J. G. Anderson, and K. R. Chan, In situ observations of ClO in the Antarctic: ER-2 aircraft results from 54 to 72 degrees south latitude, *J. Geophys. Res.*, **94**(D14), 16,649–16,664, 1989.
- Chatfield, R. B., and A. C. Delany, Convection links biomass burning to increased tropical ozone: However, models will tend to overpredict ozone, *J. Geophys. Res.*, **95**(D11), 18,473–18,488, 1990.
- Cicerone, R. J., S. Elliott, and R. P. Turco, Reduced Antarctic ozone depletions in a model with hydrocarbon injections, *Science*, **254**, 1191–1194, 1991.
- Cicerone, R. J., S. Elliott, and R. P. Turco, Global environmental engineering, *Nature*, **356**, 472, 1992.
- Coffey, M. T., W. G. Mankin, and A. Goldman, Airborne measurements of stratospheric constituents over Antarctica in the austral spring, 1987, 2, Halogen and nitrogen trace gases, *J. Geophys. Res.*, **94**(D14), 16,597–16,613, 1989.
- Crutzen, P. J., Tropospheric ozone: An overview, in *Tropospheric Ozone*, edited by I. S. A. Isaksen, D. Reidel, Norwell, Mass., 1988.
- Crutzen, P. J., I. S. A. Isaksen, and J. R. McAfee, The impact of the chlorocarbon industry on the ozone layer, *J. Geophys. Res.*, **83**, 345–362, 1978.
- Crutzen, P. J., C. Bruhl, U. Schmailzl, and F. Arnold, Nitric acid haze formation in the lower stratosphere: A major contributing factor to the development of the Antarctic ozone hole, in *Aerosols and Climate Change*, edited by P. V. Hobbs and M. P. McCormick, pp. 287–304, Deepak, Hampton, Va., 1988.
- Crutzen, P. J., R. Muller, C. Bruhl, and T. Peter, On the potential importance of the gas phase reaction $\text{CH}_3\text{O}_2 + \text{ClO} \rightarrow \text{ClOO} + \text{CH}_3\text{O}$ and the heterogeneous reaction $\text{HOCl} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{Cl}_2$ in "ozone hole" chemistry, *Geophys. Res. Lett.*, **19**(11), 1113–1116, 1992.
- Demore, W. B., Tests of stratospheric models: The reactions of atomic chlorine with O_3 and CH_4 at low temperature, *J. Geophys. Res.*, **96**(D3), 4995–5000, 1991.
- Demore, W. B., M. J. Molina, R. T. Watson, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, and A. R. Ravishankara, Chemical kinetics and photochemical data for use in stratospheric modeling, in Evaluation 6, *JPL Publ. 83-62*, Jet Propul. Lab., Pasadena, Calif., 1983.
- Demore, W. B., S. P. Sander, D. M. Golden, M. J. Molina, R. F. Hampson, M. J. Kurylo, C. J. Howard, and A. R. Ravishankara, Chemical kinetics and photochemical data for use in stratospheric modeling, in Evaluation 9, *JPL Publ. 90-1*, Jet Propul. Lab., Pasadena, Calif., 1990.
- Deshler, T., and D. J. Hofmann, Ozone profiles at McMurdo Station, Antarctica, the austral spring of 1990, *Geophys. Res. Lett.*, **18**, 657–660, 1991.
- Drdla, K., and R. P. Turco, Denitrification through PSC formation: A 1D model incorporating temperature oscillations, *J. Atmos. Chem.*, **12**, 319–366, 1991.
- Drdla, K., R. P. Turco, and S. Elliott, Heterogeneous chemistry on Antarctic PSCs: A microphysical estimate of the extent of chemical processing, *J. Geophys. Res.*, **98**(D5), 8965–8981, 1993.
- Elliott, S., R. P. Turco, O. B. Toon, and P. Hamill, Incorporation of stratospheric acids into water ice, *Geophys. Res. Lett.*, **17**, 425–428, 1990.
- Elliott, S., R. P. Turco, O. B. Toon, and P. Hamill, Application of physical adsorption thermodynamics to heterogeneous chemistry on polar stratospheric clouds, *J. Atmos. Chem.*, **13**(3), 211–224, 1991.
- Fahy, D. W., D. M. Murphy, K. K. Kelly, M. K. W. Ko, M. H.

- Proffitt, C. S. Eubank, G. V. Ferry, M. Loewenstein, and K. R. Chan, Measurements of nitric oxide and total reactive nitrogen in the Antarctic stratosphere: Observations and chemical implications, *J. Geophys. Res.*, **94**(D14), 16,665–16,681, 1989a.
- Fahey, D. W., K. K. Kelly, G. V. Ferry, L. R. Poole, J. C. Wilson, D. M. Murphy, M. Loewenstein, and K. R. Chan, In situ measurements of total reactive nitrogen, total water, and aerosol in a polar stratospheric cloud in the Antarctic, *J. Geophys. Res.*, **94**(D9), 11,299–11,315, 1989b.
- Gardner, E. P., R. D. Wijayarathne, and J. G. Calvert, The primary quantum yields of photodecomposition of acetone in air under tropospheric conditions, *J. Phys. Chem.*, **89**, 5069–5076, 1984.
- Goodman, J., O. B. Toon, R. F. Pueschel, K. G. Snetsinger, and S. Verma, Antarctic stratospheric ice crystals, *J. Geophys. Res.*, **94**, 11,285–11,297, 1989.
- Granier, C., and G. Brasseur, Impact of heterogeneous chemistry on model predictions of ozone changes, *J. Geophys. Res.*, **97**(D16), 18,015–18,033, 1992.
- Gutman, D., N. Sanders, and J. E. Butler, Kinetics of the reactions of methoxy and ethoxy radicals with oxygen, *J. Phys. Chem.*, **86**, 66–70, 1982.
- Hansen, J. R., Can climate be engineered?, *Eos Trans. AGU*, **72**(44), Fall Meeting suppl., 60, 1991.
- Hanson, D. R., and K. Mauersberger, Laboratory studies of the nitric acid trihydrate: Implications for the south polar stratosphere, *Geophys. Res. Lett.*, **15**, 855–858, 1988.
- Hanson, D. R., and A. R. Ravishankara, The reaction probabilities of ClONO₂ and N₂O₅ on polar stratospheric cloud materials, *J. Geophys. Res.*, **96**, 5081–5090, 1991a.
- Hanson, D. R., and A. R. Ravishankara, The reaction probabilities of ClONO₂ and N₂O₅ on 40 to 70% sulfuric acid solutions, *J. Geophys. Res.*, **96**(D9), 17,307–17,314, 1991b.
- Hanson, D. R., and A. R. Ravishankara, Investigation of the reactive and nonreactive processes involving ClONO₂ and HCl on water and nitric acid doped ice, *J. Phys. Chem.*, **96**, 2682–2691, 1992.
- Harker, A. B., and D. R. Strauss, Kinetics of the heterogeneous hydrolysis of dinitrogen pentoxide over the temperature range 214–263 K, *Fed. Aviat. Admin. Publ. FAA-EE-81-3*, Rockwell Int. Sci. Cent., Thousand Oaks, Calif., 1981.
- Heidt, L. E., J. F. Vedder, W. H. Pollock, R. A. Lueb, and B. E. Henry, Trace gases in the Antarctic atmosphere, *J. Geophys. Res.*, **94**(D9), 11,599–11,611, 1989.
- Hofmann, D. J., Balloon borne measurements of middle atmosphere aerosols and trace gases in Antarctica, *Rev. Geophys.*, **26**(1), 113–130, 1988.
- Hofmann, D. J., and S. Solomon, Ozone destruction through heterogeneous chemistry following the eruption of El Chichon, *J. Geophys. Res.*, **94**(D4), 5029–5041, 1989.
- Hofmann, D. J., J. W. Harder, S. R. Rolf, and J. M. Rosen, Balloon-borne observations of the development and vertical structure of the Antarctic ozone hole in 1986, *Nature*, **326**, 59–62, 1987.
- Hofmann, D. J., J. M. Rosen, J. W. Harder, and J. V. Hereford, Balloon borne measurements of aerosol, condensation nuclei, and cloud particles in the stratosphere at McMurdo station Antarctica during the spring of 1987, *J. Geophys. Res.*, **94**(D9), 11,253–11,269, 1989.
- Horowitz, A., and J. G. Calvert, Wavelength dependence of the primary processes in acetaldehyde photolysis, *J. Phys. Chem.*, **86**, 3105–3114, 1982.
- Jensen, E. J., O. B. Toon, and P. Hamill, Homogeneous freezing nucleation of stratospheric solution droplets, *Geophys. Res. Lett.*, **18**(10), 1857–1861, 1991.
- Jones, R. J., et al., Lagrangian photochemical modeling studies of the 1987 Antarctic spring vortex, 1, Comparison with AAOE observations, *J. Geophys. Res.*, **94**, 11,529–11,558, 1989.
- Kanakidou, M., H. B. Singh, K. M. Valentin, and P. J. Crutzen, A two dimensional study of ethane and propane oxidation in the troposphere, *J. Geophys. Res.*, **96**(D8), 15,395–15,413, 1991.
- Kasting, J. F., and H. B. Singh, Nonmethane hydrocarbons in the troposphere: Impact on the odd hydrogen and odd nitrogen chemistry, *J. Geophys. Res.*, **91**, 13,239–13,256, 1986.
- Keys, J. G., and P. V. Johnston, Stratospheric NO₂ and O₃ in Antarctica: Dynamic and chemically controlled variations, *Geophys. Res. Lett.*, **13**(12), 1260–1263, 1986.
- Ko, M. K. W., N. D. Sze, M. Livshits, M. B. McElroy, and J. A. Pyle, The seasonal and latitudinal behavior of trace gases and ozone as simulated by a two dimensional model of the atmosphere, *J. Atmos. Sci.*, **41**, 2381–2408, 1984.
- Ko, M. K. W., K. K. Tung, D. K. Weisenstein, and N. D. Sze, A zonal mean model of stratospheric tracer transport in isentropic coordinates: Numerical simulations for nitrous oxide and nitric acid, *J. Geophys. Res.*, **90**, 2313–2329, 1985.
- Luo, B. P., T. Peter, and P. J. Crutzen, Maximum supercooling of H₂SO₄ aerosol droplets, paper presented at the Bunsen Meeting, Schliersee, Germany, October 6–9, 1991.
- Martin, J. H., S. E. Fitzwater, and R. Michael Gordon, Iron deficiency limits phytoplankton growth in Antarctic waters, *Global Biogeochem. Cycles*, **4**(1), 5–12, 1990.
- McCormick, M. P., and C. R. Trepte, SAM II measurements of Antarctic PSC's and aerosols, *Geophysical Res. Lett.*, **13**(12), 1276–1279, 1986.
- McCormick, M. P., H. M. Steele, P. Hamill, W. P. Chu, and T. J. Swissler, Polar stratospheric cloud sightings by SAM II, *J. Atmos. Sci.*, **39**, 1387–1397, 1982.
- McCormick, M. P., C. R. Trepte, and M. C. Pitts, Persistence of polar stratospheric clouds in the southern polar region, *J. Geophys. Res.*, **94**(D9), 11,241–11,251, 1989.
- McElroy, M. B., R. J. Salawitch, S. C. Wofsy, and J. A. Logan, Reductions of Antarctic ozone due to synergistic interactions of chlorine and bromine, *Nature*, **321**, 759–762, 1986.
- Molina, M. J., Heterogeneous chemical processes in ozone depletion, in *Ozone Depletion, Greenhouse Gases, and Climate Change*, National Research Council, National Academy Press, Washington, D. C., 1989.
- Mozurkewich, M., and J. G. Calvert, Reaction probability of N₂O₅ on aqueous aerosols, *J. Geophys. Res.*, **93**(D12), 15,889–15,896, 1988.
- Murcray, F. J., A. Goldman, and R. Blatherwick, HNO₃ and HCl amounts over McMurdo during the spring of 1987, *J. Geophys. Res.*, **94**(D14), 16,615–16,618, 1989.
- Ogawa, T., and T. Shimazaki, Diurnal variations of odd nitrogen and ionic densities in the mesosphere and lower thermosphere: Simultaneous solution of photochemical diffusive equations, *J. Geophys. Res.*, **80**, 3945–3960, 1975.
- Peng, T. H., and W. S. Broecker, Dynamical limitations on the Antarctic iron fertilization strategy, *Nature*, **349**, 227–229, 1991.
- Plumb, I. C., K. R. Ryan, J. R. Steven, and M. F. R. Mulcahy, Kinetics of the reaction of C₂H₃O₂ with NO at 295 K, *Int. J. Chem. Kinet.*, **14**, 183–194, 1982.
- Prather, M. J., More rapid polar ozone depletion through the reaction of HOCl with HCl on polar stratospheric clouds, *Nature*, **355**, 534–537, 1992.
- Rodriguez, J. M., et al., Nitrogen and halogen species in the spring Antarctic stratosphere: Comparison of models with AAOE observations, *J. Geophys. Res.*, **94**(D14), 16,683–16,703, 1989.
- Rodriguez, J. M., M. K. W. Ko, and N. D. Sze, Role of heterogeneous conversion of N₂O₅ on sulphate aerosols in global ozone losses, *Nature*, **352**, 134–137, 1991.
- Rowland, F. S., Some aspects of chemistry in the springtime Antarctic stratosphere, in *The Changing Atmosphere*, John Wiley, New York, 1987.
- Sarmiento, J., Slowing the buildup of fossil carbon dioxide in the atmosphere by iron fertilization: A comment, *Global Biogeochem. Cycles*, **5**(1), 1–2, 1991.
- Simon, F. G., J. P. Burrows, W. Schneider, G. K. Moortgat, and P. J. Crutzen, Study of the reaction ClO + CH₃O₂ → products at 300 K, *J. Phys. Chem.*, **93**, 7807–7813, 1989.
- Singh, H. B., and P. L. Hanst, Peroxyacetyl nitrate in the unpolluted atmosphere: An important reservoir for nitrogen oxides, *Geophys. Res. Lett.*, **8**(8), 941–944, 1981.
- Solomon, S., The mystery of the Antarctic ozone hole, *Rev. Geophys.*, **26**(1), 131–148, 1988.
- Solomon, S., R. R. Garcia, F. S. Rowland, and D. J. Wuebbles, On the depletion of Antarctic ozone, *Nature*, **321**, 755–757, 1986.
- Solomon, S., R. W. Sanders, M. A. Carroll, and A. L. Schmeltkeopf, Visible and near ultraviolet spectroscopy at McMurdo Station Antarctica, 5, Observations of the diurnal variations of BrO and OClO, *J. Geophys. Res.*, **94**(D9), 11,393–11,403, 1989.
- Steele, H. M., and P. Hamill, Effects of temperature and humidity

- on the growth and optical properties of sulphuric acid-water droplets in the stratosphere, *J. Aerosol Sci.*, **12**, 517–528, 1981.
- Stix, T. H., Removal of chlorofluorocarbons from the earth's atmosphere, *J. Appl. Phys.*, **66**(11), 5622–5626, 1989.
- Tabazadeh, A., and R. P. Turco, A model for heterogeneous chemical processes on the surfaces of ice and nitric acid trihydrate particles, submitted to *J. Geophys. Res.*, **98**, 12,727–12,740, 1993.
- Thompson, A. M., and R. J. Cicerone, Possible perturbations to atmospheric CO, CH₄, and OH, *J. Geophys. Res.*, **91**(D10), 10,852–10,864, 1986.
- Tolbert, M. A., M. J. Rossi, and D. M. Golden, Heterogeneous interactions of chlorine nitrate, hydrogen chloride, and nitric acid with sulfuric acid surfaces at stratospheric temperatures, *Geophys. Res. Lett.*, **15**(8), 847–850, 1988.
- Toon, G. C., and C. B. Farmer, Detection of HOCl in the Antarctic stratosphere, *Geophys. Res. Lett.*, **16**(12), 1375–1377, 1989.
- Toon, G. C., C. B. Farmer, L. L. Lowes, P. W. Schaper, J. F. Blavier, and R. H. Norton, Infrared aircraft measurements of stratospheric composition over Antarctica during September 1987, *J. Geophys. Res.*, **94**(D14), 1989.
- Toon, O. B., E. V. Browell, S. Kinne, and J. Jordan, An analysis of lidar observations of polar stratospheric clouds, *Geophys. Res. Lett.*, **17**(4), 393–396, 1990.
- Trainer, M., E. Y. Hsie, S. A. McKeen, R. Tallamrajo, D. D. Parrish, F. C. Fehsenfeld, and S. C. Liu, Impact of natural hydrocarbons on hydroxyl and peroxy radicals at a remote site, *J. Geophys. Res.*, **92**(D10), 11,879–11,894, 1987.
- Turco, R. P., The photochemistry of the stratosphere, in *The Photochemistry of Atmospheres*, edited by J. S. Levine, Academic, San Diego, Calif., 1985.
- Turco, R. P., and P. Hamill, Supercooled sulfuric acid droplets: Perturbed stratospheric chemistry in early winter, *Ber. Bunsen Ges. Phys. Chem.*, **96**, 323–334, 1992.
- Turco, R. P., and R. C. Whitten, A comparison of several computational techniques for solving some common aeronomic problems, *J. Geophys. Res.*, **79**, 3179–3185, 1974.
- Turco, R. P., and R. C. Whitten, The NASA Ames Research Center one and two dimensional stratospheric models, 1, The one dimensional model, *NASA Tech. Publ. TP-1002*, 1977.
- Turco, R. P., O. B. Toon, and P. Hamill, Heterogeneous physico-chemistry of the polar ozone hole, *J. Geophys. Res.*, **94**(D14), 16,493–16,510, 1989.
- Vaghjiani, G. L., and A. R. Ravishankara, Absorption cross sections of CH₃OOH, H₂O₂, and D₂O₂ vapors between 210 and 365 nm at 297 K, *J. Geophys. Res.*, **94**(D3), 3487–3492, 1989.
- Watson, L. R., J. M. Van Doren, P. Davidovits, D. R. Worsnop, M. S. Zahniser, and C. E. Kolb, Uptake of HCl molecules by aqueous sulfuric acid droplets as a function of acid concentration, *J. Geophys. Res.*, **95**(D5), 5631–5638, 1990.
- Watterson, I. G., and A. F. Tuck, A comparison of the longitudinal distributions of polar stratospheric clouds and temperatures for the 1987 Antarctic spring, *J. Geophys. Res.*, **94**(D14), 16,511–16,526, 1989.
- Weaver, J., J. Meagher, and J. Heicklen, Photo-oxidation of CH₃CHO vapor at 3130 Angstroms, *J. Photochem.*, **6**, 111–126, 1976.
- Wolff, E. W., and R. Mulvaney, Reactions on sulphuric acid aerosol and on polar stratospheric clouds in the Antarctic stratosphere, *Geophys. Res. Lett.*, **18**(6), 1007–1010, 1991.
- Wolff, E. W., R. Mulvaney, and K. Oates, Diffusion and location of hydrochloric acid in ice: Implications for polar stratospheric clouds and ozone depletion, *Geophys. Res. Lett.*, **16**, 487–490, 1989.
- R. J. Cicerone, Department of Geosciences, University of California, Irvine, CA 92717.
- K. Drdla, A. Tabazadeh, and R. P. Turco, Department of Atmospheric Sciences, University of California, Los Angeles, CA 90024.
- S. Elliott, Institute of Geophysics and Planetary Physics, Los Alamos National Laboratory, Los Alamos, NM 87544.

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