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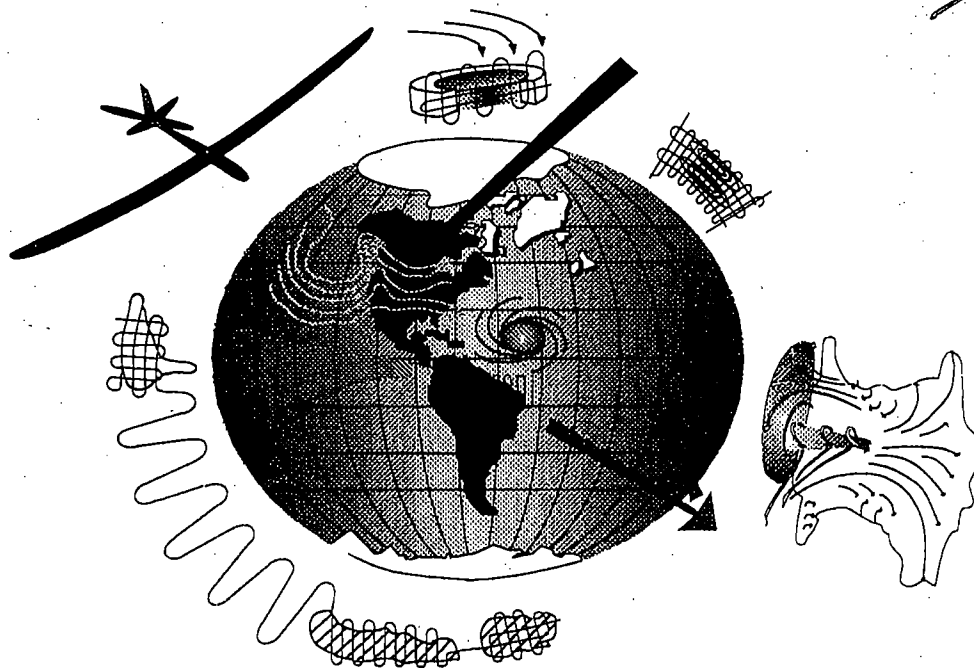
SECTION II

UNMANNED
AIRCRAFT

Unmanned Aircraft: An Essential Tool for Policy Decisions Regarding Global Change

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Planetary Science
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Alexandria, Virginia

1990 Commission
on Unmanned
Aircraft



Introduction

The 1980's brought dramatic evidence that the Earth system was susceptible to global-scale changes at rates unimagined ten years ago. The 1990s represent a critical period during which a profoundly deeper level of understanding is essential for predicting global change in the next century and for guiding policy decisions. Identifying the scale of the research effort - the intellectual disciplines, the human resources, the research facilities, the international agreements, etc. - is intricate yet essential problem facing us all.

We represent here selected examples of experiments designed to deepen our understanding of the structure of the atmosphere using a new research tool - the unmanned aircraft - that we believe will be crucial for untangling dominant scientific questions in the next decade. We identify here specific questions confronting the field that represent a small sample of the issues to be answered.

The presentation is divided into two parts. Section I presents a series of questions which constitute the foundation of research in global change but which we believe require the unmanned aircraft if results robust enough for policy decisions are to be obtained in the next decade. These include:

- **Atmospheric Radiation Measurements for Prediction of Global Warming**
- **Polar Ozone Depletion**
- **Global Sources and Sinks of CO₂ and CH₄**
- **Stratosphere/Troposphere Exchange**
- **Heterogeneous and Gas Phase Photochemistry of the Tropical Tropopause and Lower Stratosphere**
- **Hurricane Research and Forecasting**
- **Impact of High Altitude Supersonic Aircraft Flights on the Stratosphere**
- **Tropical Meteorology**
- **Operational Meteorology**
- **UARS and EOS Ground Truth**

Section II presents a description of technical advances leading to a family of aircraft proposed for the next three years of research:

- **Perseus**
- **Perseus B**
- **Perseus C**
- **Theseus**

Polar Ozone Depletion

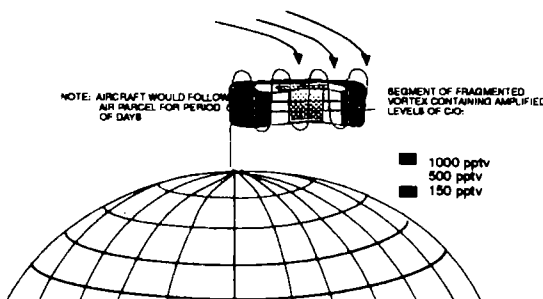
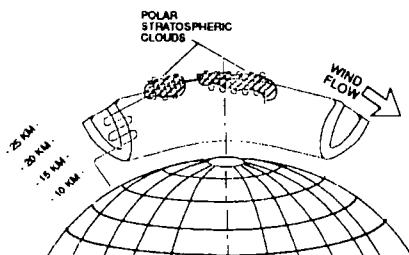
A series of related questions dominate the next five years of polar ozone depletion research. The emphasis will be on quantitative predictions of ozone depletion in both hemispheres. We select a sample of the more pressing issues:

- What evidence is there of ozone depletion by chlorine and bromine catalysis in the Arctic?
- Can we quantitatively account for ozone destruction within the Antarctic vortex above ER-2 altitudes and at latitudes $> 72^\circ \text{S}$?
- How do PSCs redistribute chlorine among the various reservoirs, specifically HCl , ClONO_2 , Cl_2 , ClOOCl and ClO ? On what time scale does this transition take place? How do nitrogen oxides reenter the system?
- To first order, the inner vortex (the chemically perturbed region) in the Antarctic is a reaction vessel, but the Arctic vortex is a flow reactor. What impact do these chemically perturbed regions have on ozone loss in their respective hemispheres?

Research Groups Expressing Commitment to Unmanned Experiments:

NOAA Aeronomy Laboratory
 NASA Jet Propulsion Laboratory
 Pennsylvania State University
 Massachusetts Institute of Technology
 Harvard University

Tuck, Fahey, Kelly
Webster
Brune
Molina
Anderson, Toohey



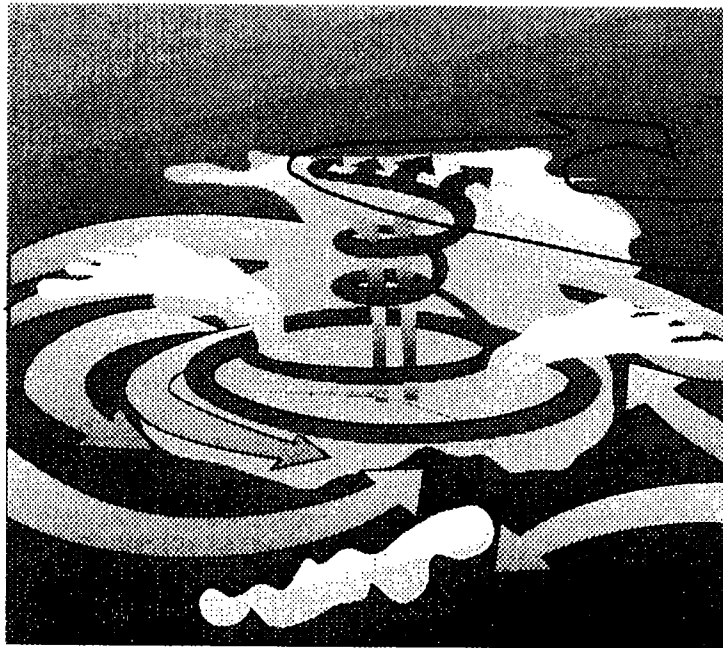
Hurricane Research and Forecasting

Of critical practical importance is the operational forecasting of hurricane tracks. Hurricanes are among the most destructive natural phenomena; the two deadliest natural catastrophes in U.S. history were both hurricanes. The 1989 Hurricane Hugo did \$7 billion damage in the U.S. Present forecasts are often uncertain enough that large stretches of coastline must be evacuated as a precaution. Routine sampling of the hurricane environment using a dropwindsonde-equipped, unmanned aircraft flying above the hurricane will lead to substantial improvements in hurricane track forecasts.

Research Groups Expressing Commitment to Unmanned Experiments:

Massachusetts Institute of Technology
Harvard University

K. Emanuel
B. Farrell



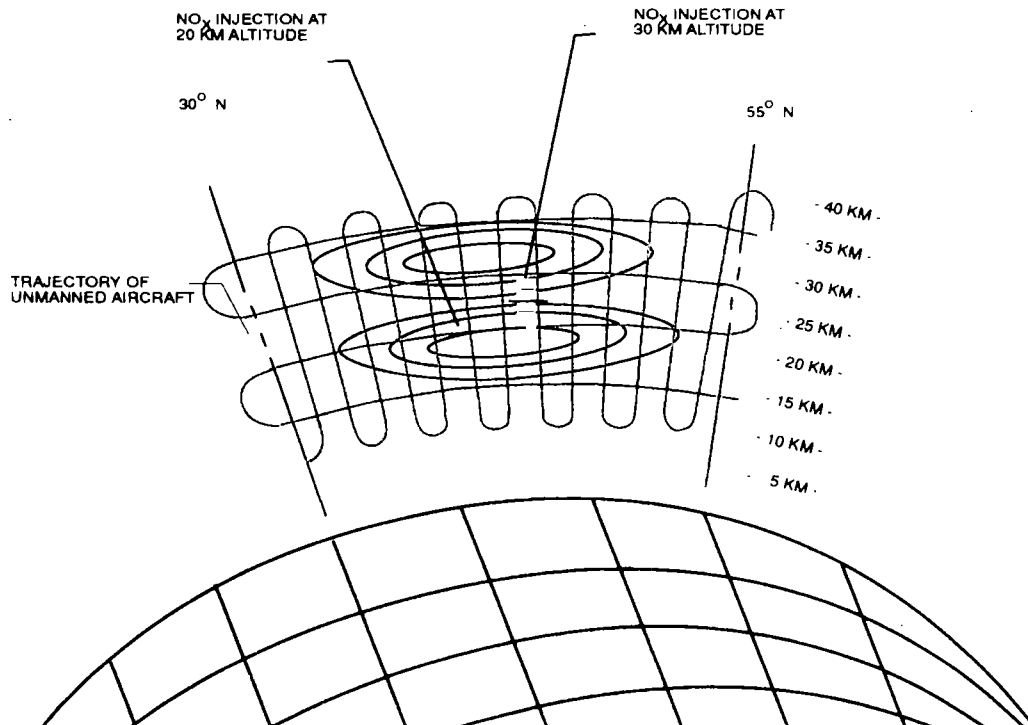
Impact of High Altitude Supersonic Aircraft Flights on the Stratosphere

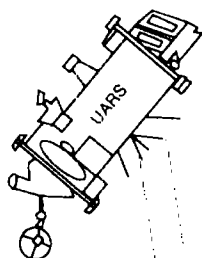
Three issues dominate studies of stratosphere perturbations resulting from the injection of exhaust gases from aircraft flying in the stratosphere. What material is injected and at what altitude? How is the injected material redistributed in the stratosphere and what chemical transformations occur? Finally, how do those distributed products affect the current photochemical, radiation and aerosol structure of the stratosphere. These questions can only be answered by in situ observation of NO, NO₂, HONO₂, OH, HO₂, H₂O, HCl, ClONO₂, ClO, O₃, P,T, wind fields, and infrared flux fields to altitudes of 30 KM.

Research Groups Expressing Commitment to Unmanned Experiments:

NOAA Aeronomy Laboratory
Harvard University
Penn State

Fahey
Anderson, Toohey, Wofsy
Brune





UARS and EOS' Accuracy and Precision Verification by Independent Observation

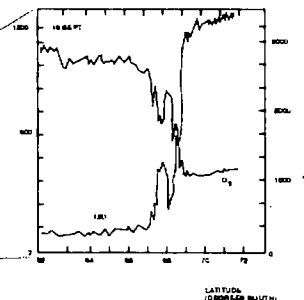
A very large fraction of our national resources for global change research have been directed towards large satellite programs. How accurate and precise are satellite observations of trace constituents in the stratosphere and troposphere? Consider, for example, the "UARS Validation Data Set" and the "UARS Complementary Data Set" which calls for observations of O_3 , H_2O_2 , NO_2 , HNO_3 , CO_2 , CFC-11, CFC-12, $ClONO_2$, HF , N_2O_5 , H_2O , N_2O , NO , CH_4 , ClO , HCl , aerosols, NO_3 , HO_2NO_2 , HO_2 , OH , BrO , $O(^3P)$, $HOCl$, and a number of important meteorological quantities. In order to test the accuracy and precision of UARS data sets, a serious research effort is required using techniques independent of those on the satellite, within volume elements observes simultaneously by both methods.

Research Groups Expressing Commitment to Unmanned Experiments:

Jet Propulsion LAB
NOAA Aeronomy LAB

Harvard University
Penn State University
University of Washington

C. Webster
D. Fahey, K. Kelly,
M. Proffitt
J. Anderson, D. Toohey
B. Brune
J. Holton



Unmanned Aircraft

Technology for the 1990's

Unmanned aircraft have been used by the military for many years, most notably by the Israelis, who have achieved impressive successes using these tools for surveillance, targeting, communications relays, jamming, and as decoys. Only recently have they matured to the point where they can be considered for civil applications. Aurora Flight Sciences is a new organization, derived from research groups at M.I.T. with long experience in low-speed aerodynamics, devoted specifically to developing unmanned aircraft as research platforms for the atmospheric science community. In the following pages we present three specific platforms currently under development. These platforms derive from a common technological base, namely:

- *Computational aerodynamics.* New computer algorithms developed by Prof. Mark Drela at MIT and validated on the MIT Daedalus program allow the accurate analysis and design of flows at low Reynolds number. The low air density at high altitudes produces Reynolds numbers approximately equivalent to those of the human-powered aircraft, allowing a direct transfer of existing codes and airfoils to the high-altitude low-speed regime.
- *Composite structures.* Lightweight structures made of high-modulus materials such as graphite-epoxy can be shaped and formed into accurate yet lightweight surfaces. The 1986 Voyager flight around the world illustrates both the performance attributes of these materials, and the way they can be constructed using a minimum of facilities.
- *Microelectronics.* The same revolution brought to personal computers by integrated circuits is now being brought to localized control systems. By replacing the pilot with microcomputers, servos, and sensors, remote or even autonomous control can be created for air vehicles, with a wider operating envelope than possible on a man-rated platform. Integrated design of structures and control system (for example, providing active control to relieve gusts or suppress flutter) offers further benefits.
- *Energy sources.* A variety of energy sources many developed during the 1960s for use in the space program have now reached the stage where they are practical propulsion alternatives for lightweight aircraft. These include high-energy density batteries, solid-polymer electrolyte fuel cells, and amorphous silicon solar cells.

As important as the performance benefits brought by these technologies, however, are the reductions in scale they make possible. Large, multimillion-dollar facilities are not needed; each of these are manageable on a small scale. Thus, costs can be kept low while flexibility and responsiveness are maximized.

These platforms are specifically designed to reduce the scale of operations required for the conduct of high-altitude scientific research, placing high performance within the reach of small research groups. All the vehicles shown here, for example, disassemble for shipment in a small trailer or for air shipment aboard commercial carriers of a C-130. They are designed for field assembly in remote locations, and for operation by small crews.

As versatile as these platforms are, however, they are only a sampling of what can be done. New, innovative uses of existing platforms, and totally new platforms such as solar or microwave powered aircraft, will continue to open new possibilities to the science community throughout the coming decade.

Perseus

Stratospheric Ozone Probe

Purpose

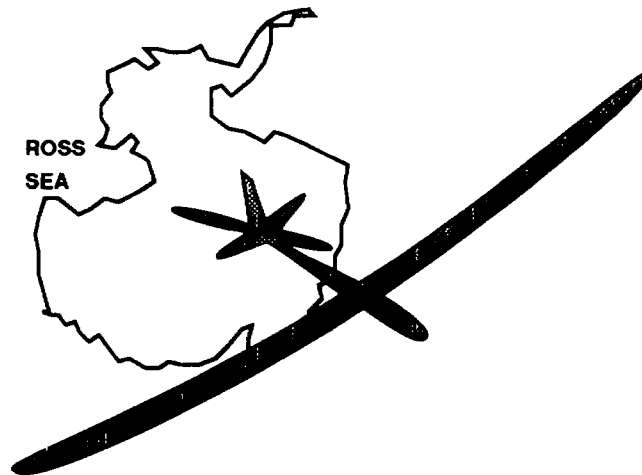
Perseus is an unmanned aircraft specifically designed for high-altitude atmospheric research. It combines the high-efficiency, computer-derived aerodynamics developed for the Daedalus human-powered aircraft project with lightweight composite structures, an electronic control site, and high performance batteries to provide a new research tool that is highly flexible, low in cost, and specifically tailored to the needs of global climate change research in the 1990's.

Specifications

Wingspan:	58.7 feet	17.9 meters
Wing area:	172 square feet	16.0 square meters
Take-off weight:	612 pounds	278 kilograms
Payload Weight:	110 pounds	50 kilograms
Altitude capability:	82,000 feet	25 kilometers

Program Status

A prototype (known as a "proof-of-concept" vehicle) is presently under construction using a combination of private venture, NASA, and NSF funding. Three aircraft are scheduled for delivery to Harvard University in 1991 for use in a NASA-NSF experiment to measure stratospheric ozone in Antarctica in 1992.

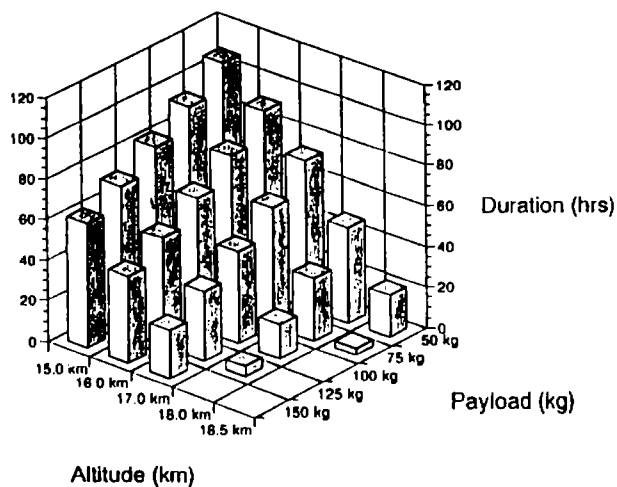


Perseus B

Low cost, Long-Duration Platform

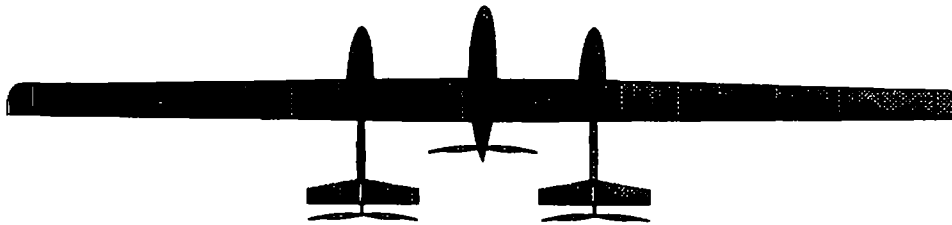


Perseus B is designed to provide larger payloads for longer durations while retaining maximum commonality in terms of tooling and control systems. Using an internal combustion engine with two stages of turbocharging, Perseus B can carry payloads of up to 150 kg (330 pounds) at altitudes of up to 18 km (59,000 feet). Durations of over 100 hours are possible with 50 kg (110 pound) payloads at 15 km (49,000 feet). Perseus B can be equipped with a variety of options, including a dropwindsonde dispenser, infrared flux and flux divergence measurement, particle measurement, water vapor, ozone, free radical, CO₂ and CH₄ detectors or a satellite data link for missions beyond the radio horizon. Perseus B deliveries will be available in 1991. A higher performance version (Perseus C) using the Arion propulsion system, is proposed for development in 1992.



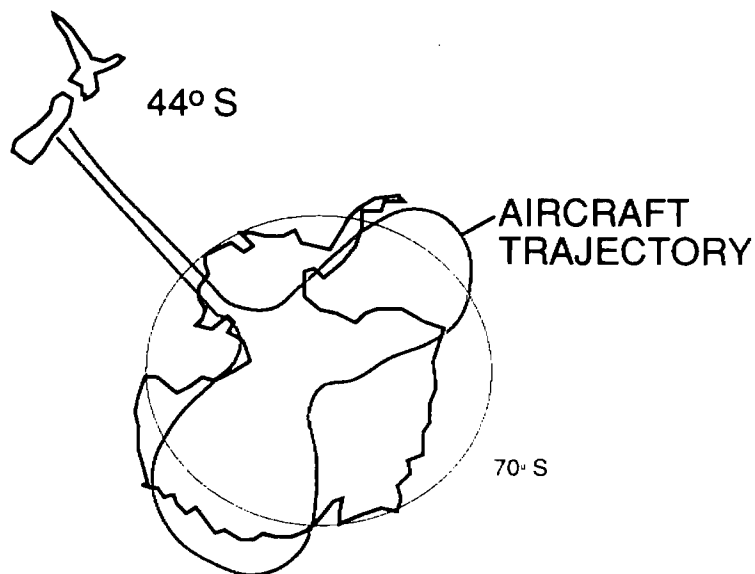
Theseus

Long-Range Scientific Platform

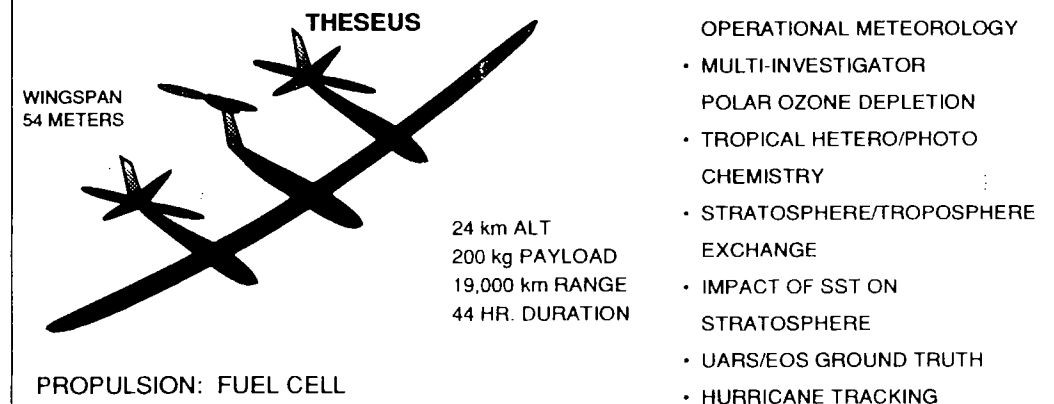
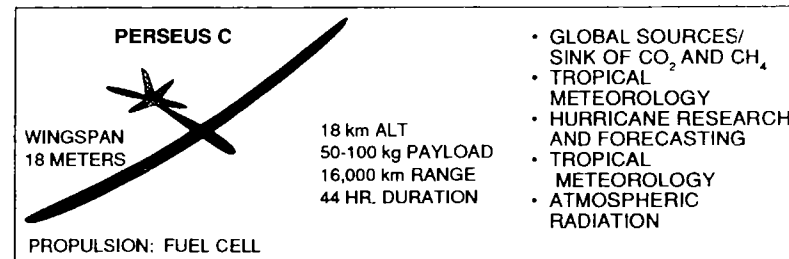
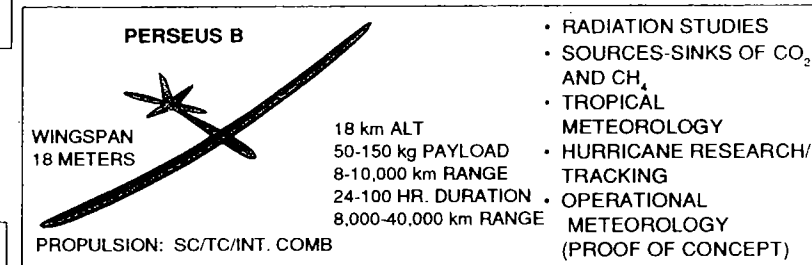
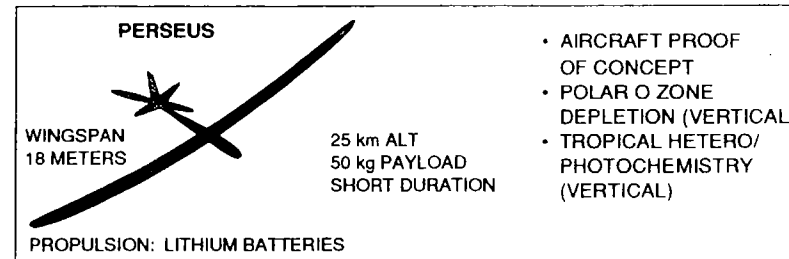


To provide the capabilities needed for extended missions such as polar stratospheric ozone research, hurricane tracking or operational meteorology, Aurora proposes to develop a larger platform known as Theseus.

Theseus is designed to carry 200 kg (440 lb.) payloads at altitudes of 24 km (80,000 feet) for ranges of up to 20,000 km (10,800 nm). The key to this performance is its use of liquid hydrogen and the Arion propulsion system, a proprietary system under development by Aurora. Three separate engines are used to provide engine-out capability and redundancy for long overwater missions and to provide commonality with a single-engine version used to power Perseus.



Lineage of Aircraft Design and Scientific Objectives



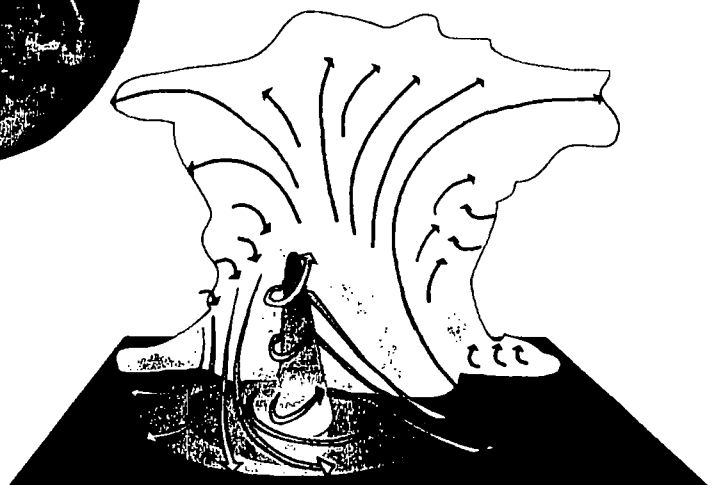
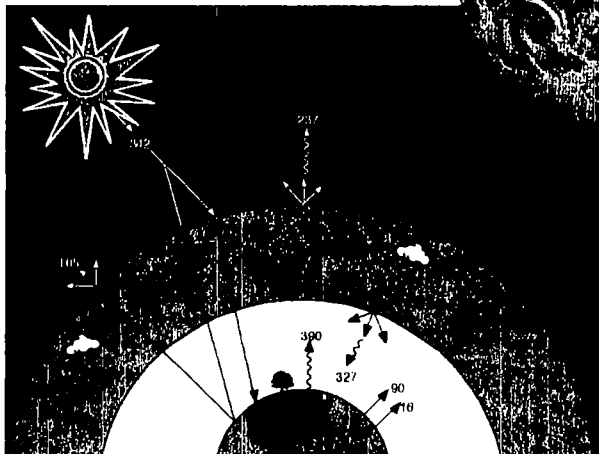
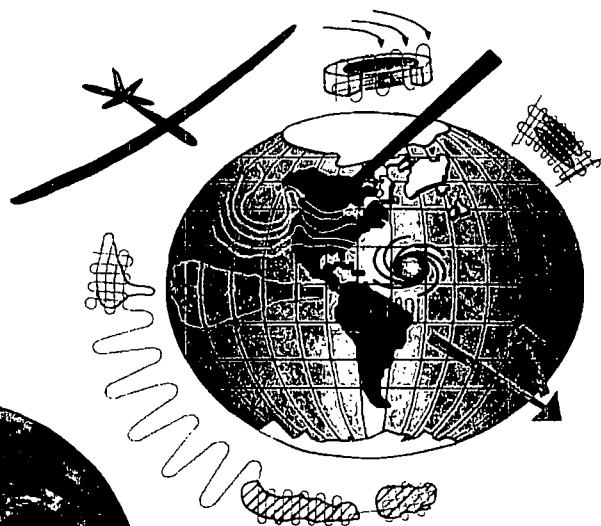
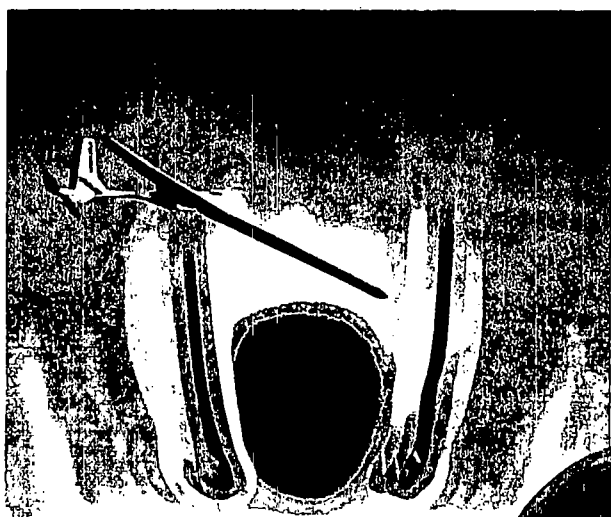
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1991
DOCUMENT ON
UNMANNED
AIRCRAFT
OTHER CHAPTERS
IN PREPARATION

Unmanned Aircraft: An Essential Component in Global Change Research

Edited By:

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Dr. John S. Langford
Aurora Flight Sciences



Introduction

1990's: DECADE OF NEW DISCOVERIES

The 1980's brought clear evidence that the earth system is susceptible to global-scale changes at rates unimagined ten years ago. The 1990's represent a critical period during which fundamental advances in our understanding of feedback processes which control global change rates must be quantified for informed policy decisions.

From a mechanistic point of view, much of the earth's atmosphere remains unexplored: Cloud/radiative feedback, sources and sinks of carbon, tropospheric oxidation, microphysics of tropical convection, free radical catalysis, stratosphere/troposphere exchange, to select a few. Implicit in what follows is the distinction between mechanistic or process oriented studies and observations of climatology. While both are essential for scientific progress, a balance must be struck in our national strategy. Identifying the scale and the blend of the research effort — the intellectual disciplines, the human resources, the research facilities, the international agreements, etc. — is an essential problem facing us all.

1990's: DECADE FOR A BALANCED SCIENTIFIC PROGRAM IN GLOBAL CHANGE

Why are unmanned aircraft an ideal companion to satellite programs in the nation's Global Change research program? In part, the answer hinges on the following points:

- 1. Unmanned aircraft provide immediate data addressing key questions on climate change, polar ozone depletion, tropospheric oxidation rates, impact of high-speed civil transports, and severe storms.**
- 2. Unmanned aircraft will provide complementary data to the current large satellite platforms. Specifically, in situ and remote high spatial and temporal resolution information on the global scales can be obtained from the ground to altitudes of 30—35 km.**
 - Radiation field measurements: Flux (and radiance) divergence and directionality with cloud properties and constituent concentrations from the surface to 30 km, which are essential for climate warming studies
 - Global carbon cycle: Sources/sinks of CO_2 and CH_4 over open ocean, ice pack, tundra, jungles, marshes, etc., which are required to identify key players in the carbon cycle
 - Ozone and water vapor: High accuracy/precision observations in the upper troposphere and in the stratosphere
 - Simultaneous high accuracy observations with high spatial resolution of the catalytically active species (in ozone destruction processes): OH , HO_2 , Cl , ClO , BrO , NO , NO_2 , $\text{O}(^1\text{P})$
 - Diagnostics for atmospheric dynamics: Atmospheric tracers (N_2O , CFC 11/12, CH_4) required to identify air parcel trajectories
 - Atmospheric structure: Winds, temperatures, lapse rates, potential vorticity, potential temperature, gravity waves
 - Reactive reservoir species H_2O , HONO_2 , HCl , ClONO_2 , ClOOCl , Cl_2
 - Particle size (0.01 μ to 20 μ), concentration, shape, composition
 - Cloud microphysical properties: cirrus, stratus, etc.

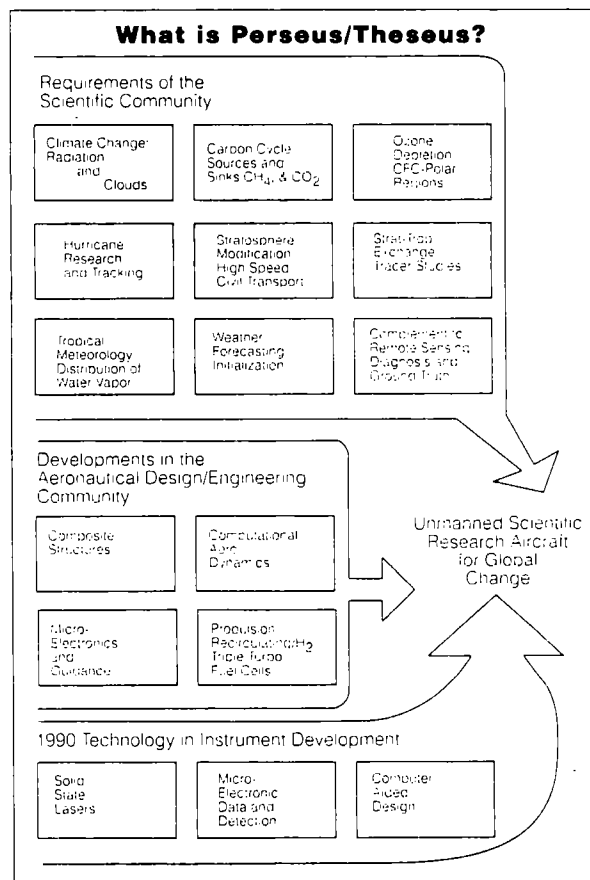
3. **Unmanned aircraft will revitalize the scientific core of observational global change studies while developing the next generation of scientists/engineers**
4. **Unmanned aircraft will establish scientific and technical leadership in a critical international area**
5. **Unmanned aircraft will attract a large number of scientists currently disenfranchised by Big Science projects which are incompatible with university, small business and government research labs.**

1990's: COALITION FOR THE DEVELOPMENT OF HIGH ALTITUDE, LONG DURATION, UNMANNED AIRCRAFT

Development of the Perseus/Theseus class of unmanned aircraft represents the union of three hitherto isolated technical domains:

1. **Careful articulation of first order scientific questions in global change.**
2. **Developments in the aeronautical design and engineering communities.**
3. **Technological developments in instrument design, notably micro optics and micro electronics.**

This emerging union can be summarized schematically in the adjoining diagram which outlines the major topic headings of this document.



1990's: THE DECADE OF RENEWED SCIENTIFIC AND TECHNICAL INFRASTRUCTURE

While research directly addressing the leading scientific issues surrounding Global Change is the focus of this document, there are important links to national scientific and technical vitality, education, economic competitiveness, and international leadership. Specifically, development of unmanned aircraft and associated instruments addressing Global Change research highlights:

1. Technological developments in the following areas:

- Optical imaging with electronic pattern recognition • Microelectronics
- Computer controlled laser systems • Communication and guidance systems
- High efficiency airfoil technology • Materials development
- Propulsion systems • Artificial intelligence • Analytical Instrumentation

With the strategy proposed herein, these development areas will be accessible to a new generation of scientists and engineers very early in their careers.

2. Education:

- Restructuring of universities to breakdown outmoded barriers between biology, chemistry, physics, computer sciences, materials research, and engineering
- Opportunities for imaginative experimental development placed in the hands of emerging leaders of science and technology: graduate students, postdoctoral students, and young faculty

3. Vitality in U.S. research and development programs:

- "Hands on" development of new instrumentation important to science and to global markets
- Testing of new ideas for instrumentation with low cost, rapid turn-around
- Close interaction between theory and experiment
- Unprecedented opportunities to explore the earth's environs using novel techniques to address internationally important issues

4. Timely exchange between science and public policy. For example, the evolution of the Montreal Protocol controlling CFC production, a reasoned international response driven by clearly defined scientific results, represents a paradigm for the approach presented here. Similar opportunities exist in cloud/radiative feedback, carbon sources, etc.

5. International economic competitiveness — either we will sell innovative new instrumentation and aircraft described herein on world markets or we will purchase them on world markets in the next decade.

Chapter I represents a compendium of leading scientific questions. This represents the major thrust of this report because experience has demonstrated that identification of the first order scientific questions must precede development of platforms, instruments, and program elements. This is an important departure from the past which has been characterized by the inheritance of platforms and programs for atmospheric science designed for other purposes. This chapter is evolving and growing. In this version we have selected the following topics and authors:

- Section I:** Cloud/Radiative Feedback
Author: Prof. V. Ramanathan, University of California—San Diego, Scripps Oceanographic Institution
- Section II:** Tropical Convection and Hurricane Research
Author: Prof. K. Emanuel, Director, Center for Meteorology and Physical Oceanography, Massachusetts Institute of Technology
- Section III:** Polar Ozone
Author: Prof. J.G. Anderson, Departments of Chemistry and Earth and Planetary Science, Harvard University
- Section IV:** Stratosphere/Troposphere Exchange
Author: Prof. J. Holton, Department of Atmospheric Sciences, University of Washington
- Section V:** Tropospheric Oxidation
Author: Prof. Wm. A. Brune, Department of Meteorology, Pennsylvania State University
- Section VI:** Stratospheric Impact of High Speed Civil Transport Aircraft
Author: Prof. D.W. Toohey, Department of Geosciences, University of California—Irvine
 Dr. S.C. Wofsy, Department of Earth \ Planetary Sciences, Harvard University
- Section VII:** Impact of Heterogeneous Reactions: The Global Ozone Budget
Author: Dr. M. Ko \ Dr. N. Dak Sze, AER, Cambridge, MA
- Section VIII:** Global Sources and Sinks of Carbon
Author: Prof. R.J. Cicerone, Department of Geosciences, University of California—Irvine
 Dr. R. Keeling, National Center for Atmospheric Research, Boulder, CO
- Section IX:** Ground Truth for the UARS and EOS Satellites
Author: Dr. M Kurylo, NASA Headquarters, Washington, DC
- Section X:** Impact of Polar Stratospheric Clouds on the Chemistry, Dynamics, and Radiation of High Latitudes
Author: Dr. O.B. Toone, NASA-Ames
 Dr. L. Poole, NASA-Langley

Chapter II reviews an array of unmanned aircraft which have been designed to address the scientific issues laid out in Chapter I. These developments join the emerging technologies of:

- Computational aerodynamics employed to optimize the low Reynolds number, high Mach number airfoils critical to the success of these aircraft
- Composite structures which are required to achieve high strength to weight ratios used in these designs
- Propulsion technology required to achieve the optimal combination of high altitude and long duration
- Guidance and control technology employing emerging technology in microelectronics.

Author: Dr. John Langford
 Aurora Flight Sciences
 Manassas, VA

Section III

POLAR OZONE DEPLETION

James G. Anderson

Departments of Chemistry

and

Earth and Planetary Science

Harvard University



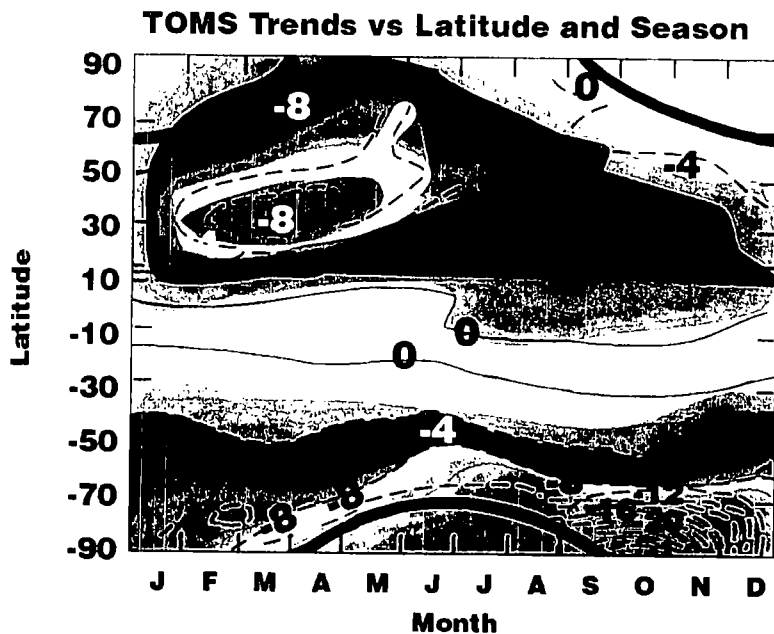
Perspective of the antarctic vortex showing Perseus superimposed on the wind field defining the polar jet, which provides containment of the amplified CIO concentrations.

I. Introduction

The sudden onset of ozone depletion in the antarctic vortex set a precedent for both the potential severity of global change and the time scale for the onset of such events. While we now know beyond any doubt that CFCs and halons are the source of halogen radicals that in turn control the rate of ozone destruction, we do not have answers to the following first-order questions:

- Will significant ozone erosion occur within the arctic vortex in the next ten years, as chlorine loading in the stratosphere approaches 5 ppbv? That is, will an “ozone hole” appear in the Northern Hemisphere by decade’s end?
- To what extent will the antarctic ozone hole expand and deepen with this increasing chlorine loading?
- Which mechanisms are responsible for the observed ozone erosion poleward of 30°N in the winter/spring northern hemisphere reported in satellite observations summarized in the figure on the following page.
- How will these large distortions in the global distribution of ozone affect UV penetration to the surface, heating rates in the upper troposphere and stratosphere, and lapse rate, surface temperatures, and general circulation?

The emphasis in our approach is to achieve a level of understanding adequate for prediction, and thus we focus on the processes that establish **cause and effect**.



Observed trends in ozone total column reported from the Total Ozone Mapping Spectrometry (TOMS) using observations obtained over the past 11 years. Recent improvements in the data analysis have led to a technique for determining and removing drift in the calibration such that the data at the end of 11-1/2 years is accurate to $\pm 1.3\%$ (2σ) relative to the data at the beginning of the record.

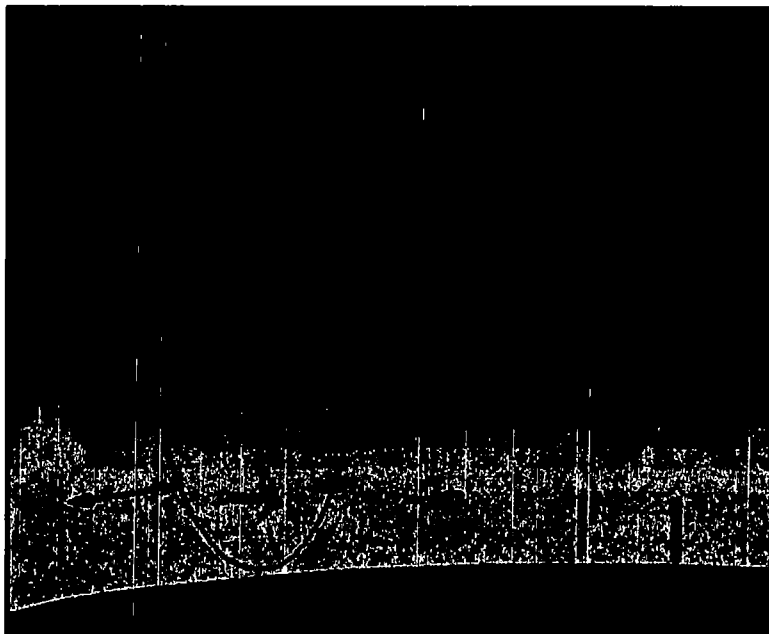
II. Scientific Questions

While there are literally dozens of specific questions that must be dealt with quantitatively, for the sake of coherence they can be categorized as follows:

Question 1. How do the meteorological (pressure, temperature, wind) fields, radiation (UV, VIS, IR) fields, tracer (N_2O , CH_4 , CFC-11) fields, and ozone, water vapor fields evolve during set up, maintenance, and break up of the vortex?

The thrust of this question is to define for the first time the structure of the stratosphere poleward of 40° latitude between altitudes of 10 and 30 km.

- When does diabatic cooling begin to distort the "normal" summertime tracer fields? What is the temporal evolution of potential temperature and potential vorticity fields as the polar jet develops?
- To what degree is there stratospheric-tropospheric exchange along isentropic surfaces?
- To what extent is there exchange between inner and outer vortex air during the lifetime of the vortex?
- What is the origin of air that occupies the core of the vortex?
- Do rates of subsidence reflected in distortions to the tracer fields match subsidence rates inferred for diabatic cooling rates determined from observations of radiant divergence?
- To what extent is the vortex stabilized by ozone loss from the core?
- What is the latitude and altitude (referenced, for example, to surfaces of constant N_2O) dependence of thermal tendency ($d\theta/dt$), eddy heat transport ($\overline{v'\theta_y'}$) and mean heat transport ($\overline{v\theta_y}$) from 40° to the pole in both hemispheres?



Tracer fields constitute the “coordinate system” within which all observables are interpreted. A minimum complement of tracers for such a coordinate system is CH_4 , N_2O , CFC-11, CO_2 , and PV, the potential vorticity. The large dynamic range in the rate of removal of CH_4 , H_2O , and CFC-11 above the tropopause coupled with high spatial resolution meridional transections of these species provide unique insight into processes involved in the production and destruction of tracer *variance*; CO_2 mixing ratios establish the lifetime of air parcels (i.e., the time between entry of the air through the Hadley-driven tropopause and the time of observation) and PV distinguishes between a tracer that is it *not* transported across isentropes by diabatic circulation (PV) and ones that are (CH_4 , N_2O , CFC-11).

Question 2. What are the threshold conditions for significant repartitioning of reactive species within the nitrogen, chlorine, bromine, and hydrogen families?

The thrust of this question is to understand how the reactive compounds, most notably the catalytically active free radicals, respond to the dropping temperatures that initiate polar stratospheric cloud formation both inside and within the environs of the vortex.

- What is the mechanism for the “Noxon cliff”—the removal of NO_x from the gas phase? Does the phenomenon require the presence of PSCs?
- What conditions (temperature, pressure, HONO_2 and H_2O , vapor pressure) trigger the formation of PSCs? At what threshold temperature do Type I and Type II PSCs form? Is temperature alone a valid indication of these phase transitions?
- Do NO , NO_2 , ClO , HONO_2 , and HCl concentration fields evolve in the temperature and PSC fields in a manner consistent with heterogeneous conversion of HCl and HONO_2 to gas phase Cl_2 and solid phase nitric acid trihydrate? How important is the $\text{N}_2\text{O}_5/\text{H}_2\text{O}$ reaction in the denitrification process?
- Do PSCs appear outside the vortex, for example, in gravity wave events? How important are these localized adiabatic processes to the overall effectiveness of halogen and nitrogen repartitioning?
- Which processes govern the transition from “normal” conditions to deNO_x ification (removal of NO_x from the gas phase), to denitrification (removal of NO_x from the gas phase), to dehydration (irreversible removal of H_2O in all phases)?
- What factors control the kinetics of $\text{HCl}/\text{ClONO}_2$ conversion to ClO ?
- What factors control growth rates and subsidence rates of PSCs?

Question 3. How do ozone loss rates resulting from free radical catalytic processes evolve with time as a function of altitude, latitude, and solar zenith angle? How much ozone is destroyed by chemical processes within the vortex?

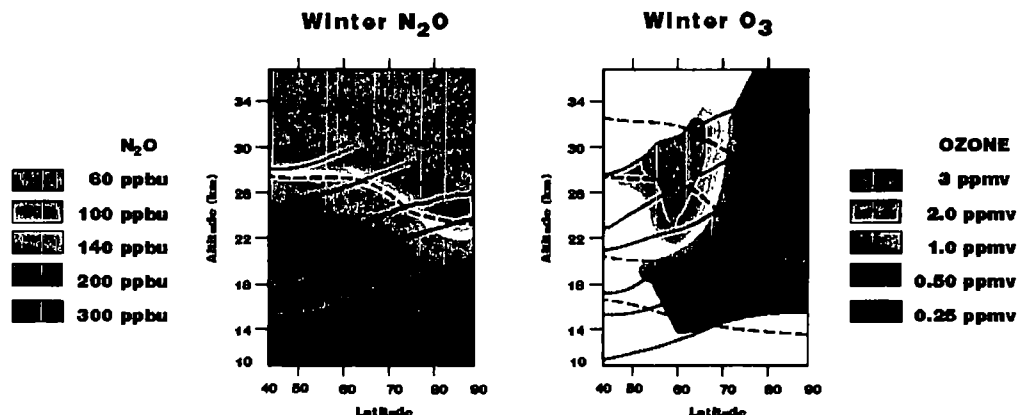
This question raises both (a) intravortex loss, which has been crudely quantified in a limited region within the antarctic vortex, as well as (b) more broadly distributed ozone erosion in the northern hemisphere well outside the arctic vortex. How will this situation evolve as chlorine loading approaches 5 ppbv?

- How do the concentration fields of the rate limiting radicals (ClO , BrO , NO_2 , OH , HO_2) evolve within time as a function of altitude, latitude, and solar zenith angle poleward of 40° ?
- Where do each of the rate limiting steps in the catalytic cycles peak as a function of altitude, latitude, region, and season?
- What is the evolution of the correlation of ozone versus the tracer fields (N_2O , CH_4 , CFC-11), potential temperature, and potential vorticity between altitudes of 10 and 30 km poleward of 40° ?
- Does the degree of ozone loss regressed against the tracer fields (N_2O , CH_4 , CFC-11), correspond to the ozone loss determined from $d\text{O}_3/dt$ surfaces using observed concentrations of the rate limiting radicals?
- How much air is “processed” within the vortex during its lifetime?
- At what rate and by what process does ClO return to “normal” levels of ClONO_2 and HCl ? What are the chemical and dynamical signatures of air as it spins out from the vortex following vortex break up?
- Why is enhanced ClO so smoothly distributed over large regions outside the vortex? Why is it “capped” at ~ 100 pptv?
- How will the picture change as the stratosphere approaches 5 ppbv of total chlorine?

III. Impact of Unmanned Aircraft

Impact On Question 1: Obtaining decisive answers to the specific scientific questions raised in Question 3 cannot be obtained with current platforms: satellite, ground based, balloon or manned aircraft. Effectiveness of previous studies has been seriously constrained by limitations on altitude, latitude, trajectory conditions (i.e., polar night), spatial resolution, and temporal coverage. This has prevented the quantification of vertical and horizontal advection, eddy mixing, subsidence as well as radiation heating and cooling rates, which constitute the foundation of efforts quantifying ozone loss.

The first order of business is to establish the time evolution of θ , PV, N_2O , CH_4 , CFC-11 , H_2O , and O_3 between 40° latitude and the pole, using aircraft-borne, in situ measurements between 10 and 30 km.

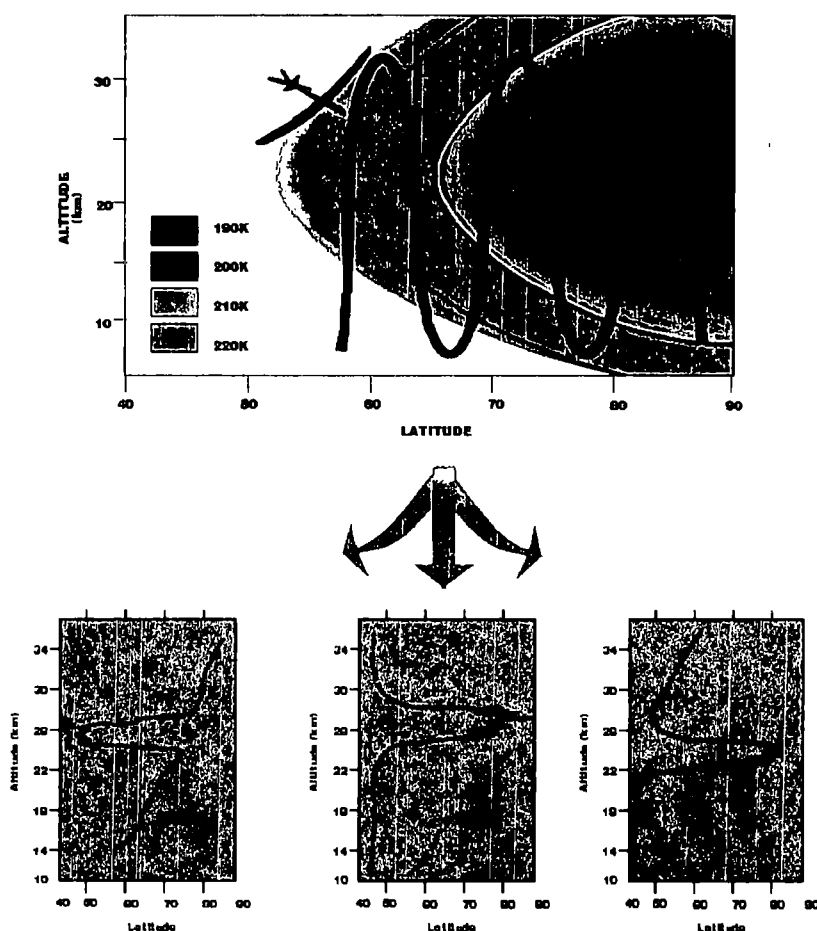


A critical unanswered question in polar studies is the consistency of evolving tracer fields with constituent fields (e.g., O_3 and NO_y) prior to precipitous changes initiated by phase changes (formation of PSC I and PSC II regions) and chemical catalysis, both heterogeneous and homogeneous. This demands detailed coverage, at high spatial resolution from the poleward edge of the subtropical jet ($\approx 40^\circ$) to the pole and from just below the tropopause to 30 km.

This series of experiments will first establish the relationship between the major tracers (N_2O , CH_4 , CFC-11) and the ozone field. Does the regression of O_3 against each of the tracers establish a consistent picture? Does the relationship between potential vorticity and N_2O substantiate the current conception that they are surrogates for each other?

Perhaps the most critical advance from this analysis, however, will be a mapping of ozone redistribution resulting from the motion of the atmosphere *per se*. This will be extracted from maps of zonally averaged meridional/subsidence defined by the evolving relationship between tracers and pressure surfaces.

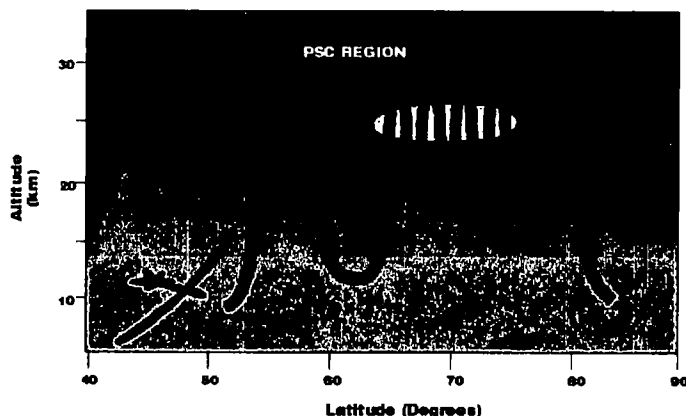
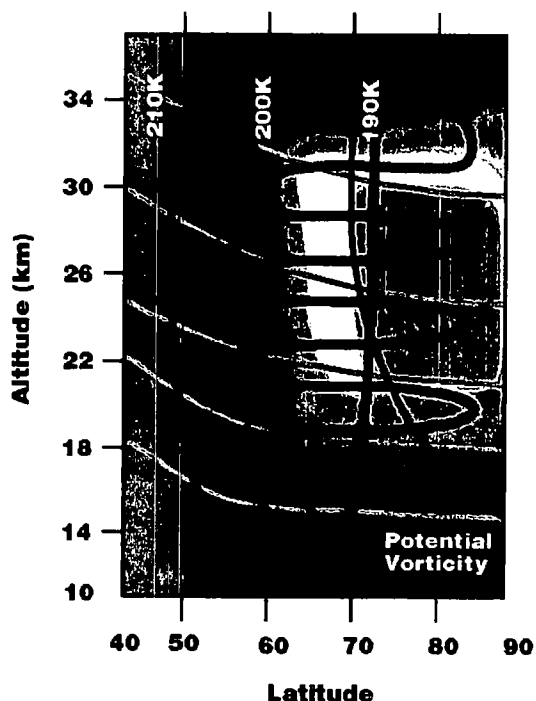
Stratospheric warmings, particularly in the northern hemisphere, have a dramatic effect on the PV, θ , N_2O , CH_4 , CFC-11, H_2O , and O_3 fields. These events will be characterized for the first time with unmanned aircraft because the length scales of interest range from 0.1 km to 100 km, an regime inaccessible to any other technology.



The regions of low temperature that develop first in the vicinity of 25 km. They are highly localized and, in their initial stages, go undetected at spatial resolutions of 0.1 km and greater. As the vortex evolves through the winter, these PSC regions spread horizontally and vertically, typically moving down to ER-2 altitudes (19 km) in their latter stages. Growth of ice—Nitric acid trihydrate (PSC II) particles to sizes $1-3\mu$ also redistributes NO_y by particle subsidence. Thus, it is critical to observe the evolution of the system from the threshold conditions to a fully mature, chemically perturbed vortex.

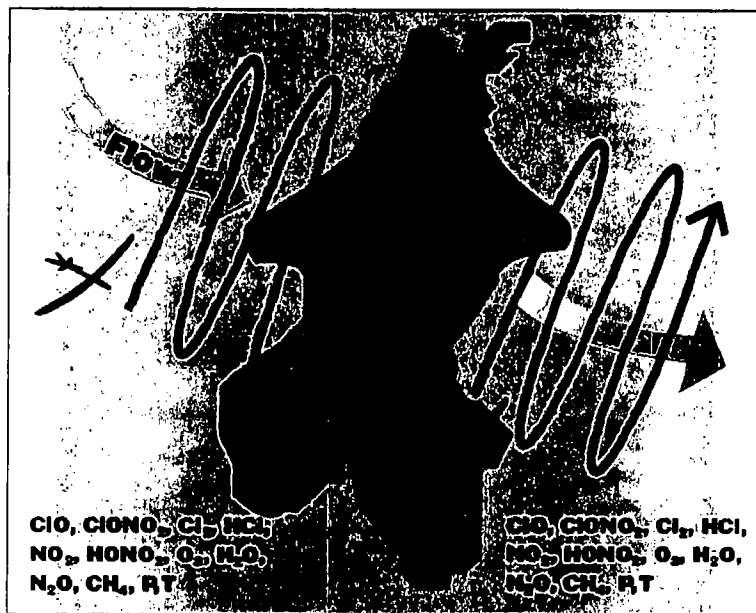
Impact On Question 2: The key criteria for a measurement strategy to diagnose threshold conditions (i.e., during polar night). The unmanned aircraft provides this capability for the first time.

A critical advantage of the unmanned aircraft in addition to altitude, frequency of coverage, accessibility to polar night conditions, etc., is its ability to control its own trajectory based on real-time observations. For example, the detection of PSC regions provides the input for a guidance algorithm to redirect the aircraft trajectory back through the region of greatest interest.

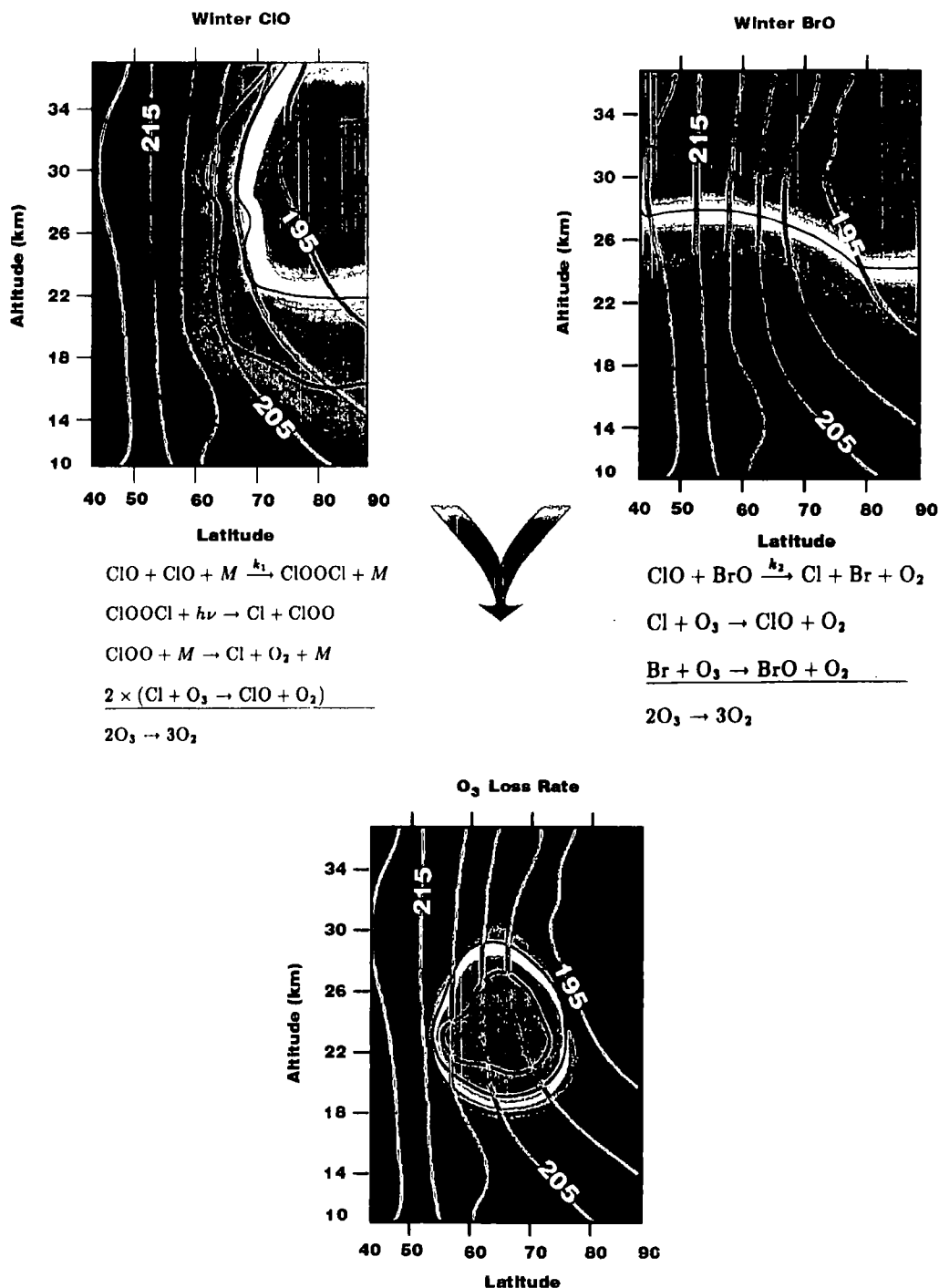


The existence of highly perturbed regions imbedded in the atmosphere, whether they be PSCs, vortex edges, or regions of highly perturbed free radical concentrations, requires a level of "onboard" intelligence capable of optimizing the trajectory. This approach heightens the ability of unmanned aircraft to address mechanistic issues in a manner unavailable to conventional aircraft.

Given (1) that PSC formation and the impact of PSCs on gas phase chemistry constitutes the initiation steps leading to dramatically amplified halogen free radical concentrations, and thereby defines the probability for large ozone loss rates in future years, and (2) these processes occur in the depths of polar night for relatively brief periods at high altitudes over dangerous regions of the globe, the unmanned aircraft presents truly unique opportunities for observations. A specific example involves the adiabatically driven PSC formation regions over the Northern Scandinavian Peninsula. There is a critical need to map the **kinetics** of chlorine repartitioning by such events.



Impact On Question 3: The climatology of free radicals, which control the rate of ozone destruction, is an essential component in any quantification of ozone loss—yet even a first-order estimate in the real atmosphere has eluded us using satellites and balloons. This failure is a result of inaccessibility of the region of interest (detailed, high frequency) meridional coverage to altitudes of at least 30 km, coupled with appropriate instrumentation for the in situ detection of ClO, BrO, NO₂, OH, and HO₂. An example isolating just the two major halogen radical catalytic cycles is displayed below.



The simultaneously observed ClO and BrO fields provide the critical input to the ozone loss rate "field", as shown below, and are then calculated from the expression

$$-\left(\frac{\Delta \text{O}_3}{\Delta t}\right) = 2 \int k_1 [\text{ClO}]^2 dt / \Delta t + 2 \int k_2 [\text{ClO}] [\text{BrO}] dt / \Delta t$$

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ARCTIC AND ANTARCTIC OZONE DEPLETION

HEARING

BEFORE THE

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SPACE

OF THE

COMMITTEE ON COMMERCE,
SCIENCE, AND TRANSPORTATION
UNITED STATES SENATE

ONE HUNDRED FIRST CONGRESS

FIRST SESSION

ON

ARCTIC AND ANTARCTIC OZONE DEPLETION

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IN ARCTIC

STRATOSPHERE

IN SITU OBSERVATIONS OF ClO IN THE ARCTIC STRATOSPHERE:
ER-2 AIRCRAFT RESULTS FROM 59°N TO 80°N LATITUDE

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Abstract. Large abundances of ClO were observed inside the arctic polar vortex during 14 flights of the NASA ER-2 aircraft from Stavanger, Norway (59°N, 6°E) to 80°N latitude. Flights were conducted at altitudes between 14 and 20 km when the solar zenith angle was between 79° and 101°. Data are reported for three flights, January 6, January 16, and February 10, that represent the main features observed during the mission. ClO mixing ratios were typically less than 50 parts per trillion by volume (pptv) outside the vortex and exceeded 100 pptv inside the vortex for all flights. ClO mixing ratios were more than 500 pptv for four days in a row in early February, reaching 1130 pptv on February 10, at an altitude of 19 km (potential temperature of 460 K). Peak ClO mixing ratios in early February were ~ 100 times larger than those observed at mid-latitudes for all altitudes surveyed between 15 and 19 km. These data, comparable to those obtained in the antarctic ozone hole, indicate that the springtime arctic polar vortex was extensively perturbed by heterogeneous chemistry and contained enough ClO to catalytically destroy ozone rapidly.

Introduction

The dramatic depletion of ozone in the antarctic polar vortex has been shown to result from the presence of highly elevated abundances of ClO. While no such massive depletion has been observed in the Arctic, the potential for ozone loss in the arctic vortex needs to be understood. Substantial amounts of ozone can be lost by halogen catalysis only if the mixing ratios of ClO remain high (≥ 1000 pptv) for at least two to three weeks. Thus for the Arctic we must, first, determine if ClO levels are elevated and, in addition, if BrO is present; second, quantify the rates of ozone loss using the observed levels of ClO and BrO; and, finally, see if the conditions in the Arctic are similar to those observed in the Antarctic. In the absence of observed ozone loss, elevated abundances of ClO are the strongest signature of potential ozone depletion.

We discuss here in situ measurements of ClO made as part of the Airborne Arctic Stratospheric Experiment (AASE) during January and February, 1989. Measurements of BrO are described in a companion letter [Toohey et al., 1990]. The instrument was mounted on the NASA ER-2 high-altitude aircraft, which was flown from Stavanger, Norway, toward the arctic polar vortex on 14 flights. Observations from three of those flights are described. Unlike measurements in the Antarctic in 1987,

which were all made when air in the vortex was sunlit, those in the Arctic were often made when the sun was below the horizon. The observed ClO abundances depend on the position of the vortex, the solar zenith angle (SZA), and the history of temperatures and sunlight along the trajectory of the air masses. We will use these three flights to illustrate the main features of ClO formation and evolution during the six-week mission.

Experiment

The basic goals of the AASE mission were to determine if the wintertime arctic stratosphere is perturbed, as is the antarctic stratosphere, and to learn more about the perturbing mechanisms. The AASE mission consisted of 14 flights from Stavanger, Norway, toward the arctic polar vortex, and four transit flights, two each direction, between Moffett Field, California, and Stavanger. The 14 flights from Stavanger were conducted on the following dates: January 3, 6, 7, 12, 16, 19, 20, 24, 25, 30, and February 7, 8, 9, and 10. The transit flights were flown on December 29 and 31, and, for the return, on February 20 and 21. Data are reported in this letter for the flights on January 6 and 16, and February 10.

The Harvard University ClO-BrO instrument was mounted in a pod under the left wing of the NASA ER-2, and was part of the 15-instrument complement. Fairly detailed discussions of this instrument have been presented [Brune et al., 1989], and a brief summary is presented here. ClO and BrO are detected simultaneously as the free air stream is decelerated from 200 m sec⁻¹ to 20 m sec⁻¹ and passes in a laminar stream through the instrument. ClO is not detected directly, but rather is chemically converted to Cl atoms by a reaction with reagent NO that is added near the inlet to the measurement flow tube. These chlorine atoms are then detected by resonance fluorescence [Brune et al., 1989]. The ClO concentration is proportional to the difference between the signal when NO is added to the flow and the signal when it is not. Nitric oxide is added during a 32-s cycle, and ClO levels of 2 pptv can be detected at a signal-to-noise ratio of two for each of these cycles. The absolute calibration is estimated to be $\pm 25\%$ at the 2 σ confidence level. ClO abundances in this paper reflect the most recent understanding of our calibrations. ClO data reported by other investigators involved in the AASE mission have typically not been updated, and may be 10-35% different.

The ER-2 was usually flown on isentropic surfaces between 420 and 500 K to and from the arctic vortex, which was most often located north of Stavanger (59°N, 6°E). A rapid descent to ~ 380 K followed by a rapid ascent to often another constant potential temperature surface was included on the return leg, usually just south of the solar terminator. This pattern was not the only one used, but it was used for all the flights described here.

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Results

January 6, 1989. The first flight to penetrate the arctic polar vortex occurred on January 6, 1989. The ER-2 was flown up the Norwegian coast, over the sea to (74°N, 21°E), and back again. Contained in Figures 1a-c are the SZA, the potential temperature at the aircraft (denoted as theta), and the observed ClO abundance. At a potential temperature of ~470 K, ClO mixing ratios were less than 30 pptv, even for SZAs less than 90°. As the aircraft penetrated the wall of the vortex, at ~70°N for this flight, the ClO abundance rose rapidly to more than 250 pptv. The SZA for maximum ClO was 92.5°, which was also the SZA at which the sun was 2° above the horizon at 20 km altitude. Most of the elevated values of ClO were observed in the dark and decreased as the aircraft flew further into polar night. Shortly after the aircraft was turned south, the pilot executed a dive to the 390 K surface at 15 km altitude, and then rose to a constant 410 K surface for the remainder of the flight. ClO changed a factor of six between the 460 and 390 K surfaces inside the vortex, and fell off to values of ~10 pptv just outside the vortex. The slow rise in ClO for the remainder of the flight, outside the vortex, agrees with the change in ClO expected from the exchange of chlorine between ClO and ClONO₂ reservoirs [Brune et al., 1990].

We can draw three conclusions from these observations. First, the air inside the vortex, even in early January, had already been perturbed, presumably by a sequence of PSC activity followed by sunlight to create these large levels of ClO. Second, the amount of NO₂ inside the vortex was substantially less than that of ClO. Otherwise, at these high SZAs, ClO would combine with NO₂ to form ClONO₂ in less than an hour. Such low values of NO₂ are confirmed by the measurements of NO [Fahey et al.,

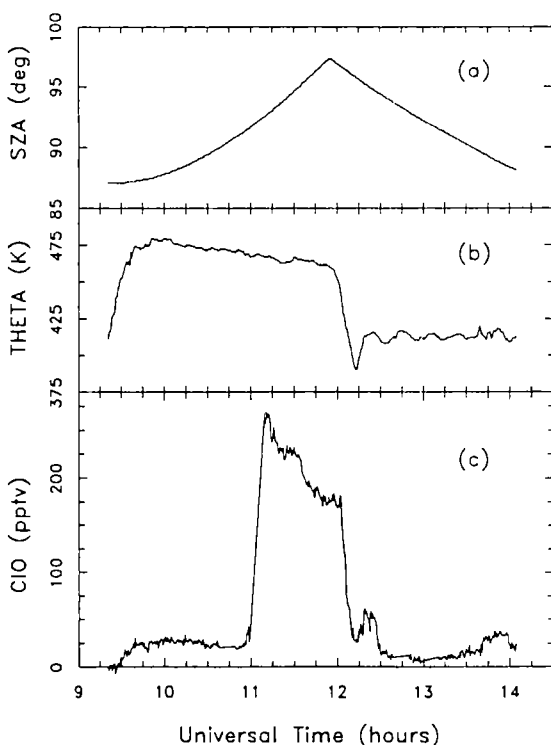


Fig. 1. Observed ClO mixing ratios plotted against Universal Time for January 6, 1989. Solar zenith angle (degrees), potential temperature (K), and ClO mixing ratio (pptv) are plotted in Figures 1a, 1b, and 1c, respectively.

1990]. And third, the total amount of chlorine converted from HCl and ClONO₂ into more reactive chlorine was more than the 250 pptv of ClO observed at the vortex edge, since, at these SZAs, much of the reactive chlorine would be in the form of the ClO dimer, Cl₂O₂.

January 16, 1989. The sharp rise in the ClO mixing ratio at the edge of the vortex followed by a slow decrease north of the terminator is more evident on January 16, when the flight path extended to 78°N, over Spitzbergen Island. The SZA, potential temperature, and observed ClO mixing ratios are shown in Figures 2a-c, respectively. The SZA varied from 90° to 100°, and the potential temperature was a constant 445 K until the dive to the 380 K surface at 12:45 UT. The peak ClO mixing ratio was 175 pptv at a SZA of 93° and a potential temperature of 445 K, entirely consistent with the value observed during the January 6 flight at the same potential temperature.

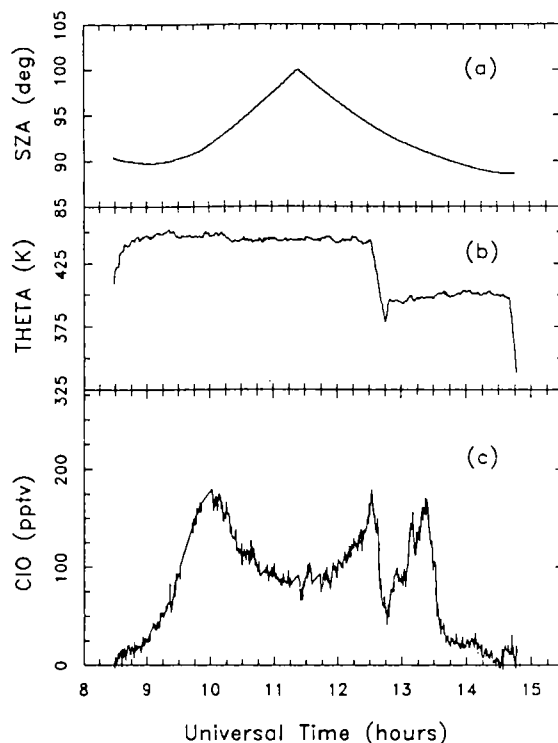


Fig. 2. Observed ClO mixing ratios plotted against Universal Time for January 16, 1989. Individual graphs are as in Figure 1.

ClO dropped by a factor of four between the 445 and 380 K surfaces inside the vortex, from 175 to 45 pptv, but recovered to 160 pptv at the 400 K surface an hour later. This asymmetry in the "dog dish" profile for ClO has two causes. First, the time constants for exchange of chlorine between ClO and the other chlorine reservoirs are almost a day. Second, the total exposure of the air to sunlight increases during the day at a given latitude. So, for the same SZA, ClO will be greater in the afternoon, when more of it has been shifted from its nighttime reservoirs into ClO, than in the morning.

A striking feature of the ClO profile is that substantial ClO, 80 pptv, was observed even when the SZA was 100°. Trajectory analyses from the U. K. Meteorological Office show that the air sampled at the highest latitudes could not have been exposed to sunlight at a SZA of less than 96° for the previous 40 hours (R. L. Jones, private communication). This observation of ClO in the dark is

even stronger proof than the results of January 6 that, inside the vortex, NO_2 was very low and that ClO was being exchanged with the ClO dimer. And, since this air mass had remained at high SZAs for almost two days, the ClO could exist in observable amounts only if it was in thermal equilibrium with the dimer.

The amount of dimer (Cl_2O_2) in thermal equilibrium with the observed ClO can be determined if the temperature of the air parcel is known. However, the temperature at the time of observation may not be the appropriate one if the air parcel had experienced temperature variations during the previous day, because the time for ClO and the dimer to establish thermal equilibrium after a temperature change is ~ 20 hours. By using a photochemical model that is moved along the trajectory, we can find the temperature that was experienced by the air parcel prior to our observation, and for which the dimer and observed ClO concentrations were effectively in thermal equilibrium. The effective equilibrium temperature so determined is 189.7 K, which is 0.6 K lower than the observed temperature obtained at the ER-2 simultaneously with the ClO observation. The ClO dimer mixing ratio implied from the ClO concentration (1.6×10^8 molecules cm^{-3}) and the equilibrium constant of Cox and Hayman [1988] is 910 pptv. Thus, the total chlorine in ClO and the dimer is 1900 pptv. An error of 1 K in the derived temperature would alter this value by 400 pptv.

ClO was observed inside the vortex at SZAs exceeding 94.5° on eight other flights, and the total chlorine in ClO and the dimer derived from the observed levels of ClO and temperatures exceeded 1100 pptv for all of them. While the temperature histories along the trajectories and the photolysis rates for the ClO dimer at high SZAs must be known to derive more exact numbers, the consistently high values for ClO and the dimer indicate either that much of the inorganic chlorine was shifted into ClO and the dimer as early as January 6, or that, in fact, the mixing ratios for the dimer were lower, and thus the equilibrium constant is lower than that determined by Cox and Hayman [1988]. If chlorine was converted to ClO and the dimer in early winter, then ozone loss could occur earlier than currently thought. If the equilibrium constant is lower, perhaps by a factor of two, then more Cl_2O_2 would thermally dissociate, and less would be photolyzed than is currently calculated for arctic stratospheric temperatures. As a result, less ozone would be destroyed by the dimer mechanism in the early spring. We are conducting studies to see if the dimer was detected in our instrument during some thermal diagnostic tests that were periodically performed during flight, and if absolute Cl_2O_2 values can be determined.

In late January, temperatures were low enough for the formation of water ice PSCs (Type II), and these PSCs were pervasive over Scandinavia and Siberia (R. L. Jones, private communication). The peak ClO mixing ratios for the final five flights, January 30 and February 7, 8, 9, and 10, all exceeded 500 pptv. These observations were made inside the vortex with the SZA less than 90° . The first four of these flights were to Spitzbergen Island at 78°N and back. ClO has the same features on these four flights that it did on January 16: a sharp rise at the vortex edge, evening values higher than morning values for the same SZA, and a decrease toward the northern latitudes and higher SZAs. The ClO mixing ratios outside the vortex edge are typically less than 50 pptv, but show some rapid increases to more than 100 pptv for short intervals. These small features may represent vortex air that was spun off of the vortex, and had not yet mixed with the surrounding air that was advected from mid-latitudes. The elevated levels of ClO on the last four consecutive days confirm that the vortex was extensively perturbed by the second week in February.

February 10, 1989. All previous flights had been flown to the north of Stavanger, toward polar night. However, in early February, the vortex was becoming distorted and, by February 10, was actually closer to Stavanger in the west-northwest direction than to the north. The flight trajectory on February 10 was across Iceland to Greenland, up the coast of Greenland, and returned by the same path. Thus the northernmost latitude sampled was 72°N , but the vortex was encountered for roughly half the flight. The vortex edge, defined by elevated ClO, was crossed as the aircraft passed over Iceland. The observed vortex air was illuminated during the entire flight, since the SZA was always less than 89° . Under sunlit conditions, the conversion of reservoir chlorine to radical chlorine could be better determined, since more chlorine would be in ClO and less in the nighttime reservoirs, particularly the ClO dimer.

The observed abundances of ClO are greater than 1100 pptv on the 470 K potential temperature surface, well inside the vortex, as shown in Figure 3. The sharp boundary at the vortex edge still persists, and the profile shows both vertical and horizontal structure. This profile for ClO looks very similar to those obtained over Antarctica during the Airborne Antarctic Ozone Experiment in August and September, 1987, which were obtained with similar flight altitude profiles [Brune et al., 1989]. For ClO levels to be this elevated, about one half of the total inorganic chlorine must have been in the form of ClO.

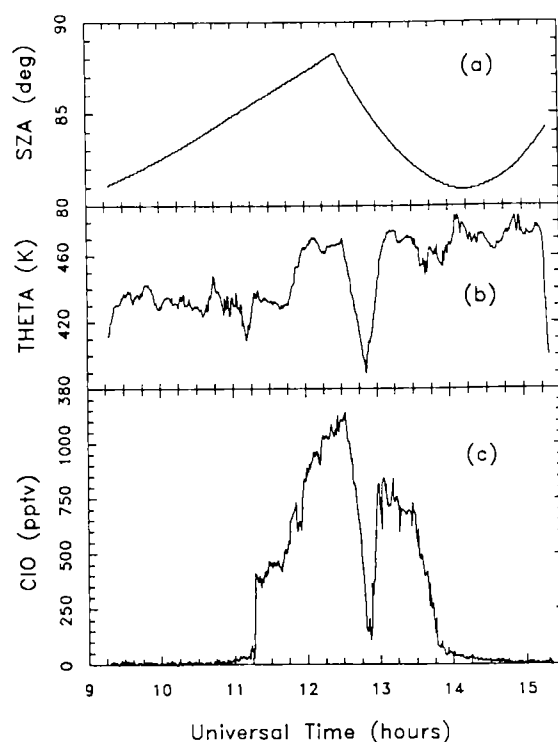


Fig. 3. Observed ClO mixing ratios plotted against Universal Time for February 10, 1989. Individual graphs are as in Figure 1.

The vertical distribution of ClO, taken during the dive inside the vortex on February 10, is shown in Figure 4. In addition, vertical distributions are shown for the flights of August 28, 1987, and February 13 and 19, 1988. The profile from August 28 was measured inside the antarctic polar vortex at 71°S . The profile from February 19 was obtained over Moffett Field, California, and is representative of mid-latitude profiles for that time of year. The

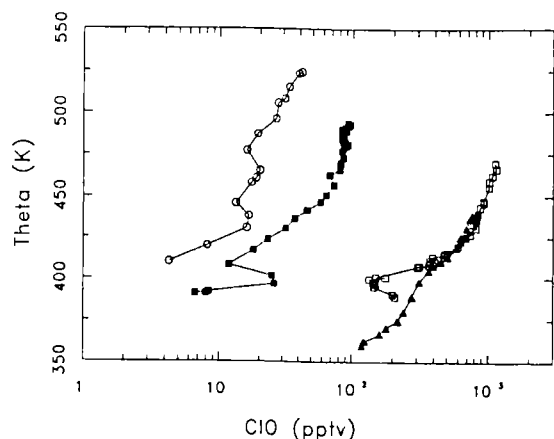


Fig. 4. ClO mixing ratio versus potential temperature for four flights. Data are shown for February 10, 1989, 70°N, inside the vortex (open squares); February 13, 1988, 61°N, outside the vortex (solid squares); February 19, 1988, 35°N, a typical mid-latitude profile (open circles); and an Antarctic flight on August 23, 1987, 72°S, inside the vortex (triangles).

profile from February 13 was obtained at 61°N, in a region slightly outside the arctic vortex. (The ClO levels for February 13 are ~30% larger than reported in Brune et al. [1988] because of an improved calibration.)

We draw four conclusions from these profiles. First, the ClO mixing ratios inside the arctic polar vortex are ~100 times larger than the mid-latitude abundances at all altitudes. Second, the ClO mixing ratios observed in the arctic vortex above a potential temperature of 400 K are comparable to those observed in the antarctic vortex. Thus, for chlorine, the arctic polar vortex appears to be as perturbed in 1989 as the antarctic vortex was in 1987. Third, the ClO mixing ratio decreases more rapidly at lower potential temperatures in the arctic than in the antarctic. These differences reflect the generally higher altitude of formation of PSCs in the northern hemisphere [McCormick et al., 1988]. Finally, the observed ClO mixing ratios for February 13, 1988, which are more than 80 pptv, were produced by heterogeneous chemistry on PSCs in the arctic polar vortex, and did not result from wintertime, high latitude gas-phase photochemistry [Brune et al., 1988]. The ClO mixing ratios observed outside the polar vortex during the AASE mission, which were typically less than 50 pptv, indicate how much ClO that gas-phase chemistry alone can produce.

Summary

The ClO mixing ratios exceeding 1000 pptv and the sharp edges in the elevated ClO distributions are strong evidence that heterogeneous processes have altered the partitioning of species in the chlorine and odd-nitrogen chemical families. The sequencing of heterogeneous conversion followed by exposure to sunlight was capable in early 1989 of perturbing a large portion of the arctic polar vortex, extending from above the ER-2 flight altitudes down to 15 km. Evidence of heterogeneous processes was found on the first flight that penetrated the vortex, January 6, and on all subsequent flights that sampled vortex air. The arctic vortex was extensively perturbed, both horizontally and vertically. Such large abundances of

ClO in concert with BrO, HO₂, and $\tilde{\text{O}}$, are capable of depleting ozone at rates comparable to those observed over Antarctica, ~1% per day [see, for example, Anderson et al., 1989], and some small loss of ozone must certainly have occurred.

Acknowledgments. A mission of this scale is possible only by the dedication and hard work of a large number of people. Excellent support and advice were given by members of the Atmospheric Research Project at Harvard University, particularly those who worked in Norway—Nate Hazen, Maria Mueller, and Norton Allen—but also Joyce Makrides, Joe Demusz, Elliot Weinstock, Bob Heroux, and others. The pilots, crews, and management of the NASA ER-2 were always helpful and performed well in less-than-ideal circumstances. Estelle Condon and Steve Wegener were always available to smooth logistical tangles, and members of the NOAA Aeronomy Laboratory provided excellent facilities. We also acknowledge the many thoughtful discussions with the other scientists on this mission. This work was supported by the NASA Upper Atmospheric Program under grants NASW 3960 and NAGW 1465.

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STATEMENT OF SENATOR ALBERT GORE
HEARING ON ARCTIC AND ANTARCTIC OZONE DEPLETION
SENATE SUBCOMMITTEE ON SCIENCE, TECHNOLOGY, AND SPACE
FEBRUARY 23, 1989

Today, the Senate Science, Technology, and Space Subcommittee will examine one of the most serious environmental threats that our planet faces - the depletion of the stratospheric ozone layer. The ozone layer forms a shield which protects us, and all other life on earth, from harmful ultraviolet radiation. Since UV radiation can cause skin cancer and cataracts, stunt crop growth, and damage marine ecosystems, we need the protection this shield of ozone provides. Unfortunately, man-made pollutants threaten this shield and researchers are starting to document the damage. The most startling evidence for ozone layer depletion has come from the polar regions.

We have all heard about ozone depletion over Antarctica. Today we will be hearing about new research which indicates that we should be worried about Arctic ozone depletion as well. In addition, the Subcommittee will examine what is being done to get rid of the

chlorofluorocarbons (CFCs) which are at the root of the problem.

We have with us three researchers from the recently-completed Airborne Arctic Stratospheric Expedition. More than 100 scientists spent the last two months in Norway, Greenland, and other parts of the Arctic, looking for evidence of an Arctic ozone hole. Today we will hear a summary of their findings along with an update on the Antarctic ozone hole.

We all remember the surprising discovery of the Antarctic ozone hole a few years back. NASA satellite photos revealed a hole in the ozone layer centered around the South Pole. It was huge, larger than the United States. Within the hole, ozone levels were half their normal levels. Apparently, hundreds of millions of people using aerosol deodorants can do a lot of damage.

Some have dismissed the Antarctic ozone hole since no one really lives in Antarctica. Most of the continent is cold, bleak, and lifeless. And there certainly aren't many voters there. But even in the Antarctic, ozone depletion can cause problems. The Antarctic Sea is teeming with marine life which may be impacted by the UV radiation streaming through the ozone hole. Scientists are only now starting to assess the possible impact of the ozone depletion in Antarctica and elsewhere.

And ozone depletion over Antarctica contributes to ozone depletion elsewhere. Not all the ozone lost in Antarctica is

being replaced. Our first witness, Dr. Robert Watson, was chairman of the Ozone Trends Panel which last March reported that ozone depletion was a global problem. There has been a two to three percent decrease in ozone concentrations over the U.S. since 1969. That doesn't sound like much, but even such a small drop could lead to millions of additional cases of skin cancer. It now appears that much of this decrease is due to ozone depletion over Antarctica.

So it is clear that we must understand the roles of the poles in ozone depletion. That's why I went to Antarctica last year to learn about the research being done there. I found that much has been learned, but many questions remain. The Airborne Arctic Stratospheric Expedition was organized to answer some of these questions.

Scientists like those here today represent our first defense against global environmental threats like ozone depletion. If we don't know what our pollution is doing to our planet, we cannot take measures to halt the damage. Without adequate research we won't recognize the threat until it is too late. We need a broad, international effort to monitor and understand our planet, in order to respond wisely to threats like ozone depletion, global warming, acid rain, deforestation, and rising sea levels.

The Science Subcommittee is responsible for authorizing funds for global change research programs at the National Science Foundation and at NASA. These programs, along with programs at the National Oceanic and Atmospheric

Administration, have provided us with much of what we know about the way our planet works. NSF and NASA have funded many of the long-term studies required to document man's impact on our planet. The pictures of the Antarctic ozone hole came from NASA's TOMS satellite. For years, NSF has funded atmospheric scientists working at on increasingly sophisticated computer models to predict the effects of greenhouse warming. In addition to research focused on global change, NSF and NASA fund millions of dollars of basic research in other fields which provide data and equipment which can be used to understand global change. A discovery made in a physics lab may have little impact on the field of physics, but it may lead to a new sensor that allows atmospheric chemists to make great strides in the study of trace gases in the air. Or a mathematician might prove a theorem which will allow a computer scientist to write better software which a meteorologist could then use to better understand the weather conditions that lead to formation of the ozone hole. Such cross-fertilization is a key part of science.

It is critical that we take into account these interrelationships. The success of the Arctic ozone expedition was due not just to atmospheric scientists. They relied upon physicists, programmers, electronic engineers, and scientists from dozens of other disciplines. One of the lessons such an expedition teaches us is that we must have a balanced, healthy research program which covers all

scientific disciplines. It would be a mistake to increase funding for research on ozone depletion at the expense of other discipline. This is a new problem, we will need new money to assess and address it.

In the months ahead, the Science Subcommittee will consider the NASA budget. There are numerous NASA satellites which provide data that researchers need to monitor the health of our planet. Needless to say, I feel strongly that these NASA programs should be well-funded. The "Mission to Planet Earth" proposed by the Ride Report will provide badly-needed data about our planet. In the months ahead, the Subcommittee will have to decide how much money we have to spend on these programs. The budget deficit will force some tough choices. But when it comes to the global environment we don't have a choice. Good planets are hard to find. We must take good care of the one we've got.

After the researchers on our first panel discuss the disturbing results of their expedition and update us on the threat that CFCs pose to the ozone layer, we will hear from three manufacturers and users of CFCs. They will discuss the progress that has been made so far in finding replacements for CFCs. Replacing CFCs will not be easy. They are used in your refrigerator and in your car air conditioner. They're used to make computer chips, rubber foam, and plastics.

No, it won't be easy to replace CFCs and yet it is essential that we do. And we must do it as soon as possible.

I had hearings on ozone depletion more than five years ago when I was in the House. It was clear to me then that it was going to be necessary to control production of CFCs. Unfortunately, world production of CFCs has increased markedly since then.

We have made some progress. The Montreal Protocol, which the Senate ratified last year, put in place international limits on CFC production. Unfortunately, it does not go far enough. The Protocol calls for a 50% reduction in CFC emissions by 1999. This is too little and too late.

Last month, I introduced S. 201, the World Environment Policy Act of 1989. Title III called for a total phaseout of the six most important ozone-depleting chemicals by 1996. Such a phaseout will cause some hardship. But that hardship will be minor compared to the hardship that people around the world will suffer if CFC production and ozone depletion continues unabated. Certainly it is worth the inconvenience and added cost of having to replace the CFCs in our refrigerators if it means we can save the lives of thousands of Americans who would otherwise die of skin cancer.

The good news is that progress is being made in the search for replacements for CFCs. The witnesses on our second panel represent companies which are spending more than \$100 million a year looking for ways to make and use CFC alternatives. The National Institute of Standards and Technology has recently expanded its program to evaluate CFC

alternatives. Many companies in the air conditioning industry see a CFC phase-down as a challenge rather than a threat and they are working to produce equipment that is CFC-free. Together, the CFC manufacturers and users and the Federal government are finding ways to do without CFCs.

I think today's hearing will give us even more reason to be concerned about the threat that CFCs posed to the ozone layer. However, I hope that we will also hear some good news, good news about the progress that is being made to get rid of the CFCs that are the root of the ozone depletion problem.

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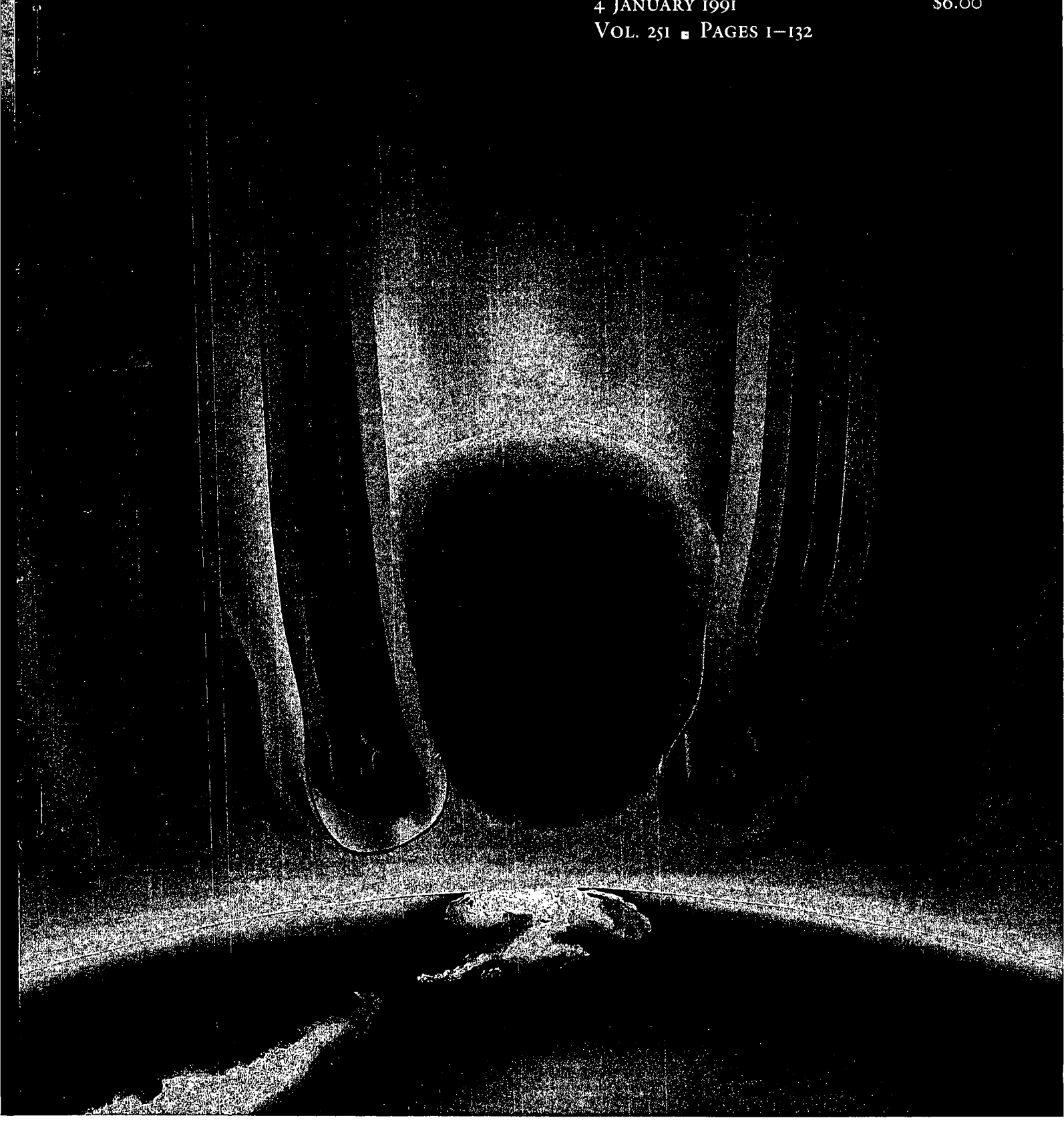
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In Situ Observations of ClO in the Antarctic: ER-2 Aircraft Results From 54°S to 72°S Latitude

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Results from a series of 12 ER-2 aircraft flights into the Antarctic polar vortex are summarized. These in situ data define the spatial and temporal distribution of ClO as the aircraft flew at an altitude of ~ 18 km from Punta Arenas (54°S latitude, 70°W longitude) to the base of the Palmer Peninsula (72°S latitude, 75°W longitude) and back. At the southern extremity of the flight trajectory the aircraft descended to ~ 13 km, turned north, and ascended to 18 km. A general pattern in the ClO distribution is reported: mixing ratios of approximately 10 parts per trillion by volume (pptv) are found at cruise altitude in the vicinity of 55°S increasing to 50 pptv at 60°S. In the vicinity of 65°S latitude a steep gradient in the ClO mixing ratio is observed. At a fixed potential temperature, the ClO mixing ratio increases by an order of magnitude within a very few degrees of latitude through this sharp transition, thus defining the edge of a "chemically perturbed region." From the edge of that region to the southern extension of the flights, 72°S, a dome of slowly increasing ClO best describes the distribution. Peak mixing ratios at 18 km at the southern extension of the flight track increased from 800 pptv on August 23 to 1100 pptv in early September and then increased slowly to 1200 pptv by the end of the mission on September 22.

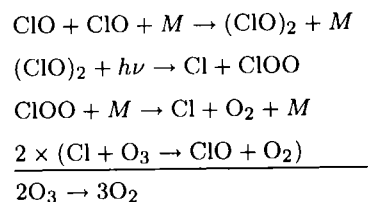
INTRODUCTION

Chlorine radicals, most notably Cl and ClO, have occupied center stage in more than a decade of intense study treating the coupling between chemically catalyzed ozone loss in the stratosphere and release of chlorofluorocarbons (CFC) at the surface. These studies emanated from the original work by *Molina and Rowland* [1974], which addressed the central question of CFC photolysis in the stratosphere fueling the catalytic reaction couplet $\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$ followed by $\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2$. This mechanism is of primary importance in the middle and upper stratosphere (~ 40 km). It is rate limited by oxygen atoms, which decrease in concentration dramatically with decreasing altitude. The discovery by *Farman et al.* [1985] of serious ozone loss within the Antarctic polar vortex, which subsumes a region the size of the Antarctic continent [*Stolarski et al.*, 1986] and is confined to the altitude region between 16 and 22 km [*Hofmann et al.*, 1987], forced a more thorough analysis of possible mechanisms joining chlorine catalysis to ozone loss.

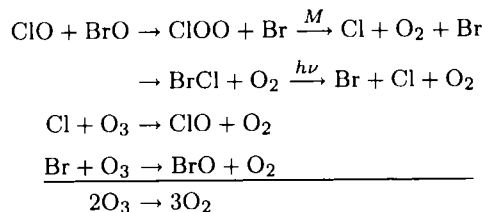
In addition, initial ground-based data obtained at McMurdo Station (77°S latitude) during the austral spring of 1987 indicated decided perturbations to the column content of several key halogen compounds. *S. Solomon et al.* [1987] reported column OClO concentrations enhanced by more than an order of magnitude, *Farmer et al.* [1987] reported decided changes in the HCl and ClONO₂ column concentra-

tions, and *P. Solomon et al.* [1987] and *deZafra et al.* [1987] reported enhanced ClO concentrations below 20 km altitude.

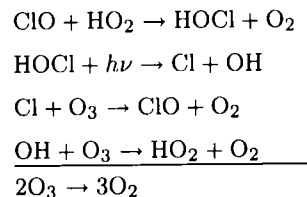
What evolved from the initial observations by *Farman et al.* [1985] and *Stolarski et al.* [1986] was a new class of catalytic processes involving halogen radicals that were not rate limited by atomic oxygen. *Molina and Molina* [1987] made the critically important suggestion that ClO could react in a termolecular process to form a symmetric dimer of ClO that could photolyze to yield a catalytic cycle converting O₃ to O₂:



A second cycle, involving both ClO and BrO in the rate-determining step, was suggested by *McElroy et al.* [1986]:



A third cycle joining the chlorine and hydrogen families has been suggested by *Solomon et al.* [1986]:



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A common thread through each of these proposed mechanisms is that they are all thought to be rate limited by the concentration of ClO. It was thus decided, in order to diagnose the cause of Antarctic ozone depletion, to build an instrument that could detect both ClO and BrO, in situ, from the ER-2 aircraft. A detection threshold adequate to detect ClO in the "normal" atmosphere at altitudes of 18 km was an important requirement. For purposes of design, this corresponds to approximately 1 part per trillion by volume (pptv) for both ClO and BrO. The objective, therefore, was to couple the high-altitude (18 km) observations of ClO and BrO with simultaneous, in situ observations of O₃, NO, NO_y, H₂O, N₂O, *T*, pressure, etc. (as described by Tuck *et al.* [1989]) so as to diagnose first whether the mechanism was dynamical or chemical, and second to isolate the specific chemical mechanism if catalytic processes were implicated.

An instrument was designed for the left wing pod of the ER-2 to meet these specifications for the in situ detection of ClO and BrO. The first results obtained with the instrument were in the mid-latitude, northern hemisphere region (27°N to 43°N) and are reported elsewhere [Brune *et al.*, this issue]. What we report here are in situ measurements of ClO between 54°S and 72°S latitude, which correspond to vortex penetration distances between 2° and 10° in latitude, depending primarily on the position of the vortex. Results from 12 flights of the ER-2 are summarized. A brief description of the instrument is offered first. This will serve as the experimental section for both papers contained in this issue that refer to these observations.

Three other papers serve as companions to work described herein. The first [Brune *et al.*, this issue], describes the measurements of BrO obtained simultaneously with these ClO measurements. The second [Anderson *et al.*, 1989a] defines the kinetics of O₃ loss within the vortex based on the observed ClO measurements, and the third [Anderson *et al.*, 1989b] defines the temporal evolution of the anticorrelation between ClO and O₃.

EXPERIMENT

The mechanism used for ClO radical detection is a chemical kinetic-spectroscopic technique in which the oxygen atom is extracted from the ClO radical by nitric oxide, leaving the naked Cl atom, which, in turn, is detected by atomic resonance scattering. A fortuitous overlap involving a minimum in the O₂ absorption cross section in the vicinity of 119 nm, corresponding to the $^2D_{5/2} - ^2P_{3/2}$ transition at 118.9 nm, preordains the appropriate spectroscopic choice of the three available vacuum-ultraviolet multiplets of atomic chlorine for this experiment. High-purity O₂/N₂ gas, "zero air," is passed through magnesium fluoride windowed cells in front of both the low-pressure, radio-frequency sustained discharge lamps used to generate the beam of resonant photons and the potassium-bromide-cathode photomultiplier tubes used to detect atomic resonance scattering from Cl atoms in the atmospheric sample. This technique has been discussed in depth elsewhere [Anderson *et al.*, 1980; Brune and Anderson, 1986] with respect to balloon-borne experiments and more recently [Brune *et al.*, 1988] with respect to aircraft-borne experiments.

Figure 1 presents a perspective schematic of the ClO instrument that occupied the left wing pod of the ER-2 aircraft for this airborne mission. The double-duct approach was designed to simultaneously achieve laminar and decel-

erated flow. A large, 20-cm outside diameter, 10 cm inside diameter, annular primary duct protruding from the wing pod extracts unperturbed air on axis with the airstream, stepping the velocity down from 200 m s⁻¹ to 60 m s⁻¹. Boundary layer depths of < 1 cm are achieved [see Brune *et al.*, 1988] within the primary duct. Seventy centimeters behind the leading edge of the primary duct, a secondary duct extracts the laminar core of the primary flow, simultaneously controlling the depth of the boundary layer and decelerating the flow yet again, from 60 m s⁻¹ to 20 m s⁻¹. Throttle valves at the downstream end of both ducts allow the on-board computer to control the flow velocity in each duct independently and over a large dynamic range for diagnostic analysis. Two planar arrays of 0.010-inch bead thermistors in the primary and secondary ducts combined with ohmic heating at the duct walls provide a sensitive characterization of the flow. In brief, the concept, developed by P. Soderman [see Brune *et al.*, 1988], of a primary-secondary duct to control fluid flow provided superb isolation of the core flow in both ducts such that the laminar core extended past the final bank of thermistors placed behind the last optical axis in the secondary duct.

An array of Teflon tubes 2 mm in diameter, perforated at 4-mm intervals, provided a uniform, planar distribution of injected NO, 25 cm behind the leading edge of the secondary duct, as shown in Figure 1. Three identical optical axes, containing a lamp module, optical baffling, and detector, are placed 12.5, 30, and 47.5 cm downstream of the NO injection plane.

Nitric oxide is added at three different flow rates through fritted discs in series with solenoid valves such that, in each 32-s addition cycle, NO is maintained at flow rates of 3.0, 1.2, and 0.5 standard temperature and pressure (STP) cm³ s⁻¹; 6 s, 4 s, and 4 s each, respectively. A clearing pulse of zero air is added for 5 s, then a 13-s period with NO off is maintained.

Figure 2 displays the resulting waveform from the second axis obtained within the Antarctic vortex. Note in particular the sharp transition at the leading and trailing edge and the slight decrease in observed signal at the lowest NO concentration. This demonstrates that the conversion of ClO to Cl is virtually complete, that the observed signal is independent of NO concentration, and that the rate of the reaction between NO and the chlorine-containing compound producing Cl atoms is that of the reaction $\text{ClO} + \text{NO} \rightarrow \text{Cl} + \text{NO}_2$. These conclusions hold over a ClO concentration range from the detection limit of the instrument (< 1 pptv) to the largest detected concentration within the Antarctic vortex (~1.0 ppbv).

The design of the optical axes, while derived from our previous balloon-borne systems, was unique in a number of ways. First, Rayleigh scattering of the lamp beam was the dominant source of background detector counts (in the absence of Cl atoms) rather than chamber scatter from the instrument walls, which dominates in the low-pressure regime (< 20 torr total pressure) appropriate to balloon systems. Second, optical penetration of resonant photons at 119 nm through O₂ becomes a significant consideration in the altitude region between 12 and 20 km. Therefore the total optical path from lamp to detection volume and from detection volume to detector was made as short as possible. Third, fluid dynamical constraints on wall-induced flow perturbations eliminated the possibility of using optical cavities

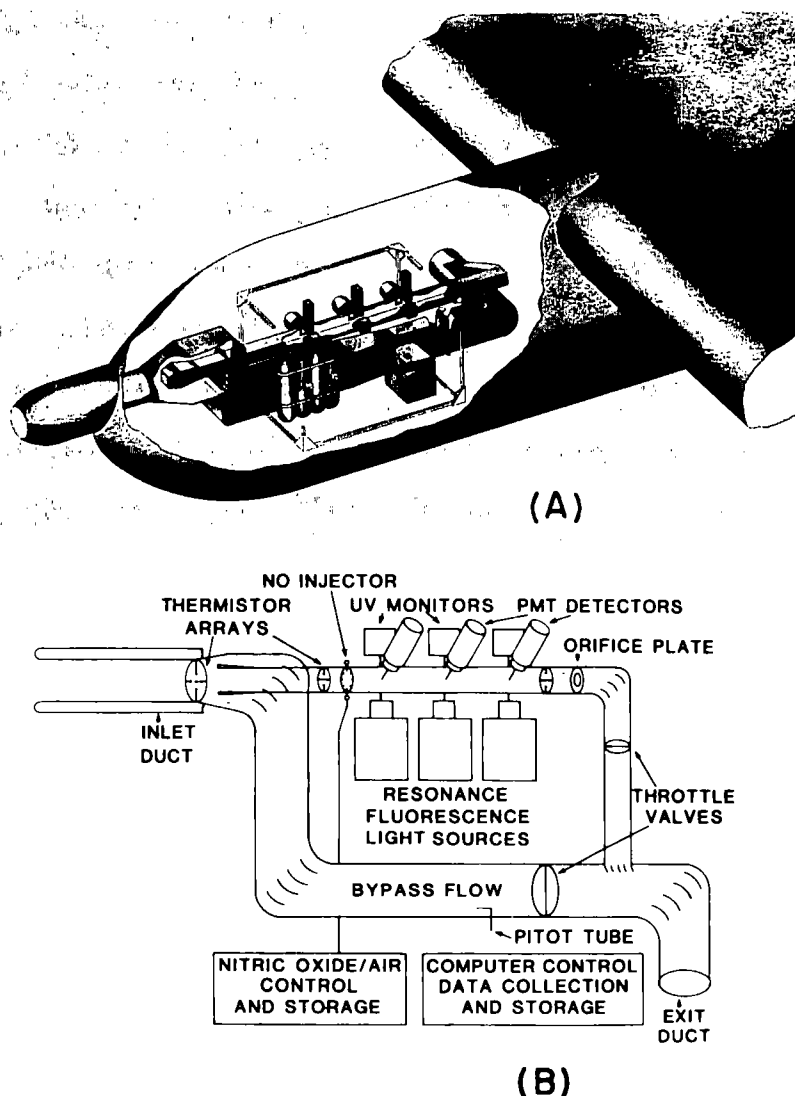


Fig. 1. (a) Perspective of the instrument architecture showing the primary duct (20 cm outside diameter and 10 cm inside diameter) protruding from the ER-2 wing pod. A secondary duct extracts a laminar core from the primary duct, passing that flow through three optical axes, each of which is capable of detecting either Cl or Br atoms. Nitric oxide (NO) is added to the flow in the secondary duct upstream of the optical axes to convert ClO to Cl. (b) Schematic of the major instrument subsystem including lamp modules, detectors, gas addition systems, primary-secondary ducting, throttle valves and thermistor arrays.

to either trap photons from the lamp beam or remove the wall from the field of view of the detector. These considerations dictated the square cross section (51 mm on a side) of the secondary duct and the extensive use of stainless steel razor blade baffle arrays to minimize the grazing incidence surface area opposite the lamp and the detector, as shown in Figure 3.

Calibration of the instrument is significantly simplified by the presence of observable Rayleigh scatter because the absolute sensitivity of each optical axis is directly proportional to the slope of the Rayleigh scatter signal with respect to pressure. This can be seen easily by considering the total signal S_{tot} as the sum of four parts:

$$S_{\text{tot}} = S_{\text{ch}} + S_{\text{Ray}}(M) + S_{\text{rs}}^{\text{Cl}} + S_{\text{dark}} \quad (1)$$

where S_{ch} is the pressure-independent component resulting from scattering of the lamp beam from the chamber walls; $S_{\text{Ray}}(M)$ is the pressure-dependent Rayleigh scatter contri-

bution to the total count rate; $S_{\text{rs}}^{\text{Cl}}$ is the Cl atom resonance scattering contribution; and S_{dark} is the detector "dark" count rate with the lamp off.

The dark count of the tube is less than one count per second and is insignificant. If the detector count rate in the absence of Cl formed from the chemical conversion of ClO to Cl is regressed against pressure, the intercept at zero pressure will be S_{ch} and the pressure dependent component will be given by

$$S_{\text{Ray}}(M) = (F_{119} + F_{122})\sigma_{\text{Ray}}[M](\epsilon\tau\eta)V \quad (2)$$

where F_{119} is the lamp flux of the Cl resonance line at 119 nm; F_{122} is the residual lamp flux of Lyman- α radiation at 122 nm, the only other emission from the lamp within the bandpass of the detector; σ_{Ray} is the weighted average Rayleigh scattering cross section of N_2 and O_2 ; $[M]$ is the total atmospheric density in molecules per cubic centimeter; ϵ is the collection efficiency of the detector; τ is the trans-

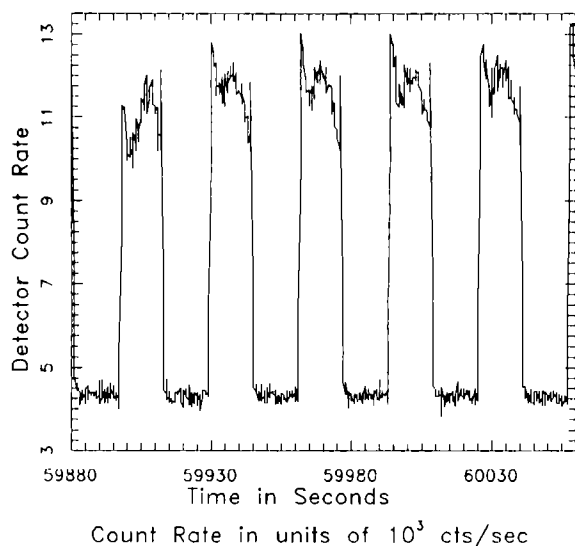


Fig. 2. Raw data showing the waveforms at the second optical axis. The first third of the waveform represents the clearing pulse of zero air added at the peak NO addition rates with a brief subsequent minimum which reflects the $\text{NO} + \text{Cl} + \text{M} \rightarrow \text{NOCl} + \text{M}$ "back reaction." The next third of the waveform is at an NO flow rate sufficient to convert 95% of the ClO to Cl. The final third of the waveform droops in response to reduced NO since at that NO concentration there is insufficient reaction time to fully convert ClO to Cl.

mission of the detection optics; η is the phototube quantum efficiency; and V is the volume (in cubic centimeters) of the scattering element defined by the intersection of the lamp beam and the detector field of view.

The resonance scattering contribution to the total count rate is given by [see Anderson *et al.*, 1980]

$$S_{\text{rs}}^{\text{Cl}} = \left[\int_{\text{line}} F_{119}(\lambda) \sigma(\lambda) d\lambda \right] [\text{Cl}] (\epsilon \tau \eta) V \quad (3)$$

where $F(\lambda)$ is the wavelength (or frequency) dependent lamp flux; $\sigma(\lambda)$ is the wavelength-dependent atomic absorption cross section; and $[\text{Cl}]$ is the chlorine atom concentration.

It has been demonstrated that the lamps used in this experiment are optically thin [see Schwab and Anderson, 1982] and thus exhibit Doppler emission profiles. The overlap integral in equation (3) can thus be simply integrated to give

$$\int_{\text{line}} F_{119}(\lambda) \sigma(\lambda) d\lambda = F_{119} \sigma_0 \left(\frac{T_A}{T_L + T_A} \right)^{1/2} \quad (4)$$

where T_L and T_A are the temperature of the lamp and of the absorber, respectively, and σ_0 is the atomic absorption cross section at the line center.

Inserting the right-hand side of (4) into (3), we have

$$S_{\text{rs}}^{\text{Cl}} = F_{119} \sigma_0 \left(\frac{T_A}{T_L + T_A} \right)^{1/2} [\text{Cl}] (\epsilon \tau \eta) V \quad (5)$$

Rewriting (2) in terms of F_{119} and the ratio $R = F_{122}/F_{119}$, the ratio of lamp flux at Lyman- α to that at 119 nm, we have

$$S_{\text{Ray}} = F_{119} (1 + R) \sigma_{\text{Ray}} [M] (\epsilon \tau \eta) V \quad (6)$$

Calibration proceeds as follows: The three optical axes are removed as a unit from the secondary duct of the flight instrument and are vacuum sealed into a flow reactor. A Leybold-Heraeus Roots blower (model RA-7001) backed by a forepump is used to establish pressure and flow velocity combinations (50–180 torr, 5–20 m s^{-1}) in the flow reactor that correspond to the conditions encountered in the ER-2 flight profiles. Trace amounts of Cl are added to the flow reactor (10^9 – 10^{10} cm^{-3}) using a thermal discharge source to convert Cl_2 to Cl. The amount of Cl in the flow is determined using atomic absorption spectroscopy at both 118.9 nm ($^2D_{5/2} - ^2P_{3/2}$) and 134.7 nm ($^2P_{3/2} - ^2P_{3/2}$). The oscillator strengths for both these transitions have been previously established [Schwab and Anderson, 1982] using a similar arrangement. We determine the absolute calibration of all three axes simultaneously by measuring $[\text{Cl}]$, $S_{\text{rs}}^{\text{Cl}}$, R , and the slope of S_{Ray} as a function of pressure.

Thus from equation (5), we have

$$S_{\text{rs}}^{\text{Cl}} / [\text{Cl}] = F_{119} \sigma_0 \left(\frac{T_A}{T_L + T_A} \right)^{1/2} (\epsilon \tau \eta) V$$

and from equation (6) we have

$$[\Delta S_{\text{Ray}} / \Delta M]_{\text{lab}, M} = F_{119} \sigma_{\text{Ray}} (\epsilon \tau \eta) V (1 + R)$$

Given that the O_2 absorption cross section at line center (118.9 nm) is small but not zero, a correction for pressure is necessary to accurately relate $[\Delta S / \Delta M]_{\text{flt}}$ obtained under flight conditions to the absolute calibration normalization obtained in the lab. In practice, $[\Delta S / \Delta M]_{\text{lab}, M}$ obtained in the lab calibration is regressed against pressure to estab-

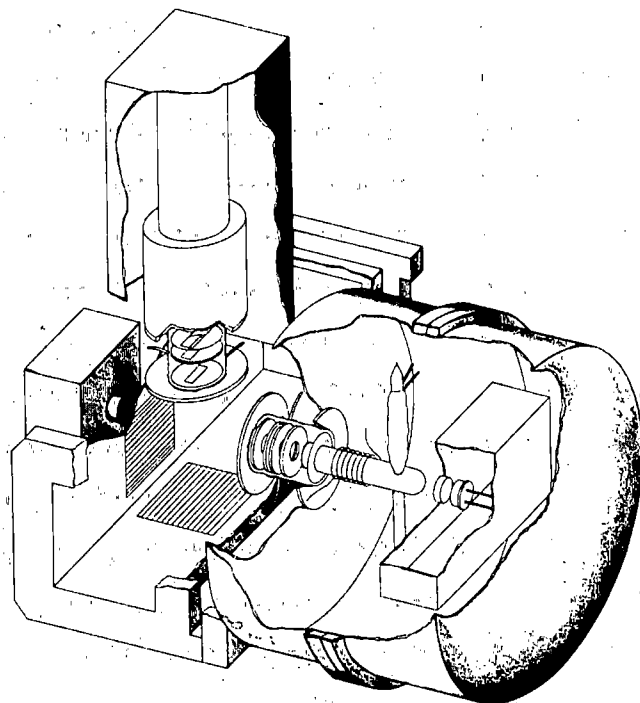


Fig. 3. Cutaway perspective of the optical axis design showing the lamp module, PMT housing, beam collimators, field of view baffles, razor blade light traps, ultraviolet diode and secondary duct cross section.

lish the slope and intercept. Then, given $[\Delta S/\Delta M]_{\text{flt}}$, we determine the proportionality between $[\text{Cl}]$ and $S_{\text{rs}}^{\text{Cl}}$ from

$$C_{\text{cal}} = \left(\frac{1}{1+R} \right) \left(\frac{[\Delta S/\Delta M]_{\text{flt}}}{[\Delta S/\Delta M]_{\text{lab},M}} \right) \times 10^{-5} (\text{counts s}^{-1}) / (\text{atm cm}^{-3}) \quad (7)$$

using the same concentration interval for both where $[\Delta S/\Delta M]_{\text{lab},M}$ is determined for an instrument sensitivity of 1 count s^{-1} for a Cl atom concentration of 10^5 atoms cm^{-3} .

While this simple normalization to Rayleigh scatter can be used without correction when the optical chamber is pristine following laboratory preparation, as the optics degrade through a flight series, the chamber scatter becomes a significant part of the detected signal in the absence of NO. Under these conditions, O_2 absorption of photons scattered from the optical chamber wall will serve to decrease the slope $[\Delta S/\Delta M]_{\text{flt}}$ observed in flight. This effect can be accounted for directly by writing the background detector count rate, S_{bkg} , in the absence of NO, as

$$S_{\text{bkg}} = S_{\text{ch}}^{\text{air}} + S_{\text{Ray}}^{\text{[M]}}$$

where $S_{\text{ch}}^{\text{air}}$ is the apparent chamber scatter in air at zero pressure. Then by defining a quantity

$$Q = \frac{\partial S_{\text{bkg}} / \partial M}{S_{\text{ch}}^{\text{air}}}$$

we account for this degradation by replacing $[\Delta S/\Delta M]_{\text{flt}}$ by $(Q+J)S_{\text{ch}}^{\text{air}}$ where J is a constant representing the absorption of 119 nm photons by air (a value that agrees well with calculations using known O_2 absorption cross sections at 1188 Å). In the same spirit, $[\Delta S/\Delta M]_{\text{lab}}$ is replaced in equation (7) by $(S[M]+I)$ where S is the slope and I is the intercept of a plot of $(\partial S/\partial M)_{\text{air}}/C_{\text{Cl}}$ measured in the laboratory. Finally, drift in instrumental sensitivity during a given flight, which is monotonic and < 10%, is accounted for by replacing $S_{\text{ch}}^{\text{air}}$ by $S_{\text{bkg}}/(Q[M]+1)$. Thus equation (7) becomes

$$C_{\text{cal}} = \left(\frac{1}{1+R} \right) \left\{ \frac{(Q+J)S_{\text{bkg}}}{(S[M]+1)(Q[M]+1)} \right\}$$

in units of $10^{-5} (\text{counts s}^{-1}) / (\text{atom cm}^{-3})$.

In practice, we have two more issues to confront that affect the absolute calibration at the $\pm 10\%$ level. The first is that the laboratory calibration is not carried out with the instrument and sample flow at the same temperature as that of the aircraft-borne observations. It is straightforward to demonstrate that this effect can be corrected for by multiplying C_{cal} in equation (7) by

$$\left(\frac{T_{\text{lamp}}^{\text{lab}} + T_{\text{abs}}^{\text{lab}}}{T_{\text{lamp}}^{\text{duct}} + T_{\text{abs}}^{\text{duct}}} \right)^{1/2}$$

This amounts to a correction of $\sim 8\%$ to the absolute calibration. The second issue involves the imperfect conversion of ClO to Cl via the forward reaction $\text{ClO} + \text{NO} \rightarrow \text{Cl} + \text{NO}_2$. This rapid bimolecular process does not provide unity yield of Cl because the termolecular reaction $\text{NO} + \text{Cl} + M \rightarrow \text{NOCl} + M$ and, to a lesser extent, the bimolec-

ular reaction $\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$ suppress the Cl yield by approximately 10% at the second optical axis (the first optical axis is positioned such that the ClO to Cl conversion is incomplete in the forward direction) and 20% at the third optical axis. Considerable care has been taken with the kinetics of the ClO to Cl conversion; we have done computer simulations of the system, laboratory studies of each reaction, and extensive experiments that examine both the mixing and reaction sequence. A major diagnostic tool is provided by the multiple optical axes. By adding NO at three different concentrations and observing the Cl atom yield at three different reaction times following the addition of NO, we can verify that the period of mixing is short compared with the reaction time and that the ClO to Cl conversion is approaching completeness by the first optical axis.

We thus insert a kinetic correction term K , which ranges between 1.1 and 1.2 depending on the optical axis in question, into the expression for the mixing ratio, such that our working expression for the ClO mixing ratio is

$$[\text{ClO}]/[\text{M}] = \frac{K S_{\text{rs}}^{\text{Cl}} (T_{\text{lamp}}^{\text{duct}} + T_{\text{abs}}^{\text{duct}} / T_{\text{lamp}}^{\text{lab}} + T_{\text{abs}}^{\text{lab}})^{1/2}}{9.66 \times 10^{18} (P_{\text{duct}}/T_{\text{duct}}) C_{\text{cal}}}$$

OBSERVATIONAL RESULTS

We can define a canonical summertime ClO distribution for the northern mid-latitudes based on the combined aircraft and balloon in situ observations presented by Brune *et al.* [1988]. Those results are summarized in Table 1 with emphasis on the aircraft altitude regime. This gives us a basis for comparison with the results of flights into the vortex region.

Twelve flights of the ER-2 aircraft were completed from Punta Arenas through the course of the mission from August 17 to September 22, 1987. Aircraft trajectories were established within an envelope defined by aircraft performance and safety to best confront scientific needs that drew upon experience gained during the mission and the coupled requirements to test dynamical and chemical theories simultaneously. Following the first two flights on August 17 and 18, which were cut short by extreme cold encountered at 67°S latitude, a "standard" flight profile was adopted, with minor tuning for specific issues that arose during the course of the mission.

The "standard" flight profile adhered to for the 10 flights from August 23 to September 22 (August 23, 28, and 30, and September 2, 4, 9, 16, 20, 21, and 22) involved a rapid

TABLE 1. Summary of the Vertical Distribution of ClO in the Mid-Latitude Northern Hemisphere

Altitude, km	ClO Mixing Ratio, pptv
17	0.3
18	1.0
19	3.0
20	6.0
25	40
30	200
35	500
40	500

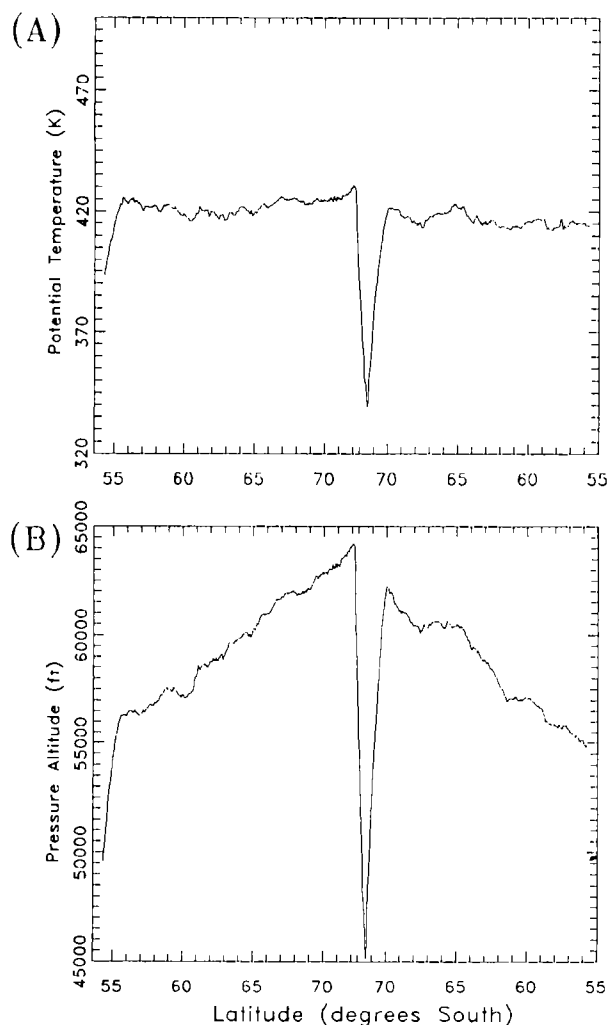


Fig. 4. (a) Typical potential temperature versus latitude pattern. While these data were taken from the August 28 flight, they are typical. (b) Altitude versus latitude dependence for the same flight.

climb to altitude following departure from Punta Arenas, adherence to an isentropic surface (either 430 K or 450 K, typically ~ 18.5 km) south to 72°S latitude, achievement of maximum altitude at 72°S before descending rapidly to ~ 13 km, usually in a northerly direction. This dive segment was followed immediately by an ascent to an altitude corresponding to a potential temperature of 430 or 450 K (typically ~ 18 km), with subsequent adherence to an isentropic surface northward to Punta Arenas, then rapid descent for landing.

Figure 4 defines these phases in two panels, one representing altitude as a function of latitude, the other potential temperature as a function of latitude. The major transitions are defined in Figure 4. While there were deviations from this pattern, there was consistency to first order on all 10 flights from August 23 to September 22.

We consider, in order, the ClO observations obtained on the 12 flights. The flights of August 17 and 18 were terminated at 67°S latitude because of extreme cold. The extremely low temperatures exposed a faulty coaxial connector in our instrument. The interrupt line between the computer in the aft of the wing pod and the data bus at the instrument in the forward bay of the wing pod affected the last segment

of data on August 17 and much of the data on August 18. Those results are summarized in Figure 5.

While the data from these two flights are incomplete, they are of considerable importance. First, they represent the first in situ observations of dramatically enhanced ClO. Chlorine monoxide concentrations of 20 pptv were observed immediately as the aircraft reached flight altitude (17 km) at 55°S latitude. At 64°S latitude a rapid increase to 70 pptv was observed. From 63°S to 66°S the ClO mixing ratio exhibited variability of $\pm 15\%$ with a monotonic increase in the mean to 125 pptv. Thus on this first flight, ClO mixing ratios approximately 50 times normal (i.e., mid-latitude) values were obtained. It is clear, however, that the data in Figure 5 did not represent a clear penetration of the vortex region.

Diagnostic software was installed between the return of the aircraft on August 17 and its departure on August 18. Information obtained from that diagnostic routine isolated the faulty component on August 18. Following replacement of the intermittent connector, the instrument performed flawlessly. The next available flight day, August 23, began the series of 10 flights that both reached the 72°S latitude limit of the aircraft and provided the vertical scan at the southern extension of the run. We consider each of these flights in detail.

August 23, 1987

Figure 6 summarizes data from the flight showing ClO mixing ratio versus latitude (Figure 6a), potential temperature versus latitude (Figure 6b), and potential temperature versus ClO (Figure 6c). The pattern displayed in Figure 6a represents what was to become the classic profile of ClO versus latitude at an approximately constant potential temperature to the southern extremity of the flight profile, where the dive in altitude and climb out to the north were executed. While quantitative details of the profiles changed in important ways, this flight was the portent of things to come. When the aircraft reached cruise altitude just south of Punta Arenas, the observed ClO mixing ratio was not

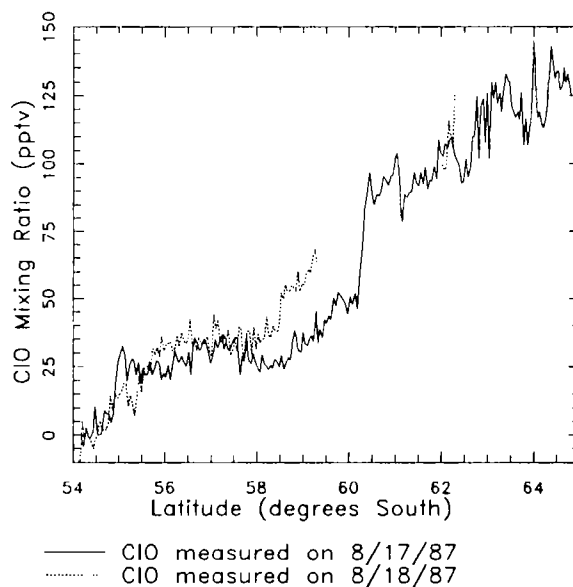


Fig. 5. Composite display of August 17 and 18 data. During the data collection period on these two flights the chemically perturbed region (CPR) was not penetrated.

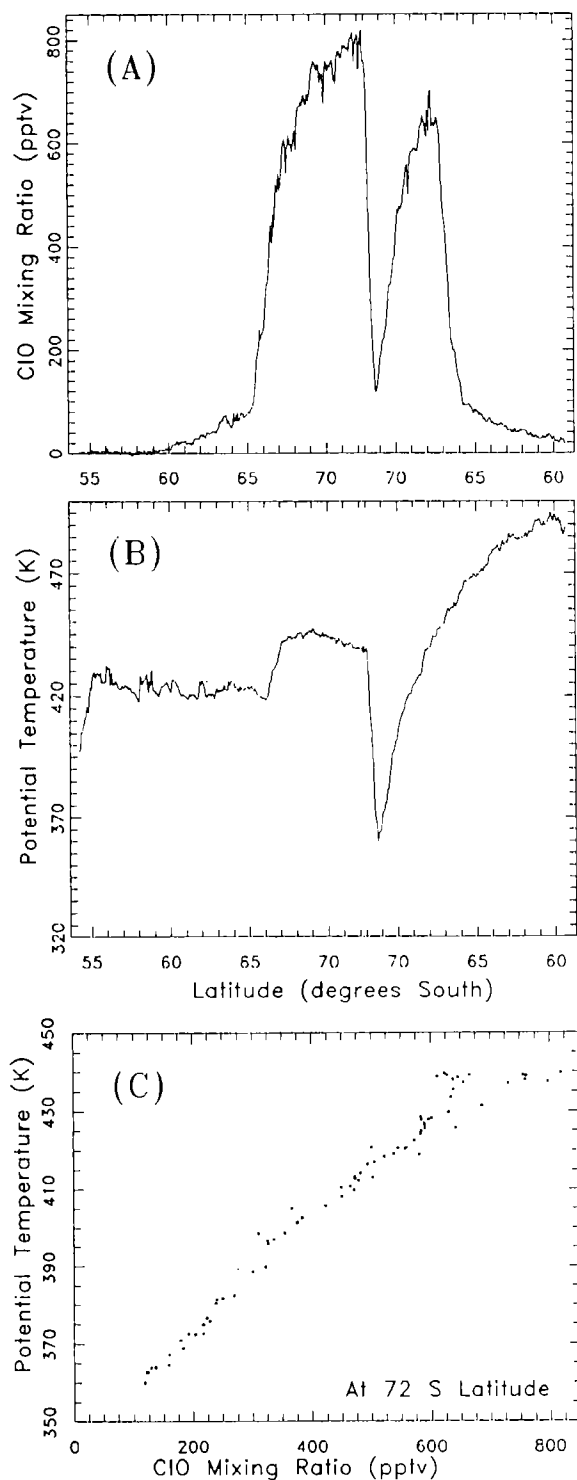


Fig. 6. (a) A survey of the observed CIO mixing ratio as a function of latitude for the August 23 flight, (b) the potential temperature for the flight as a function of latitude, and (c) the CIO mixing ratio as a function of potential temperature. Note that the vertical profile of CIO shown in Figure 6c corresponds to the southernmost point of flight trajectory, typically 72°S latitude.

atypical of mid-latitudes, 3 pptv. At 62°S latitude the mixing ratio reached 10 pptv and slowly increased to 40 pptv by 63°S latitude. Between 64° and 67°S latitude, the CIO mixing ratio increased by approximately an order of magnitude to 600 pptv. This "wall" in the CIO distribution was our first clear delineation of a distinct entity that we will refer to as the "chemically perturbed region," hereinafter CPR. At

67°S latitude the aircraft climbed rapidly, then leveled off until it reached 72°S. Peak mixing ratios of 800 pptv were obtained at the far southern extremity of the flight profile at the maximum height obtained. Thus CIO mixing ratios 400 times mid-latitude values were observed on August 23.

The rapid dive-ascent phase at the southern limit of the flight track provided the first definitive altitude profile of the mission, defining the steep ledge in mixing ratio that marked all subsequent observations. Figure 6c summarizes the vertical distribution. It is important to note that even at the bottom end of the profile, the observed CIO mixing ratio exceeds the detection threshold of the experiment by a factor of 10.

The asymmetry of the CIO in Figure 6a results not from variation in the CIO distribution going into and coming out of the vortex, but rather from the fact that both the dive and ascent segments were executed as the aircraft headed north. This points to the fact that CIO increases both with altitude and with penetration into the vortex.

The monotonic increase in potential temperature on the northbound leg reflects the attempt to reach the highest possible altitude and demonstrates that the steep gradient in CIO exists independent of the sign in the derivative of CIO with respect to potential temperature. The somewhat higher mixing ratio of CIO north of 66°S on the return leg, when compared with a similar latitude on the southbound leg, reflects the high potential temperature (altitude) surface on the homebound leg.

A particularly critical question regarding the CIO profile with potential temperature in the dive segment at 72°S latitude is both the steepness of the fall off between 450 and 350 K (13 km) and the absence of large variation about the mean CIO concentration in the vertical distribution.

August 28, 1987

The flight of August 28 marked the first attempt to predict and adhere to flight trajectories along isentropic surfaces. Results from that flight are displayed in Figure 7. Figure 7a reveals the limited penetration of the aircraft into the region defined by high CIO concentrations. This was characteristic of those flights which occurred when a high-pressure ridge occurred over Punta Arenas, a condition which forced the vortex southward toward the base of the Palmer Peninsula. This flight also was unique in that the wall in CIO showed a double shoulder, the second part of which was not entirely traversed at 72°S latitude. Peak mixing ratios of 600 pptv were reached; but the gradient in mixing ratio was so steep at 72°S that this cannot represent typical CIO mixing ratios within the CPR. In addition the "wings" of the CIO distribution outside the CPR are very broad.

Figure 7b demonstrates that the attempt to adhere to an isentropic surface on the outbound and inbound legs was very successful. On the southbound leg between 56°S and 72°S the potential temperature was 420 ± 5 K. Northbound the potential temperature was 416 ± 5 K. In the dive segment, a minimum potential temperature of 340 K was attained.

Figure 7c defines the dependence of CIO on potential temperature (altitude) at 72°S latitude. While the shape of CIO versus temperature matches that obtained on August 23 to first order, there is a clear ledge in the distribution at 400 K. The appearance of such a ledge was unusual. Given that the CPR wall shifts poleward with decreasing potential temper-

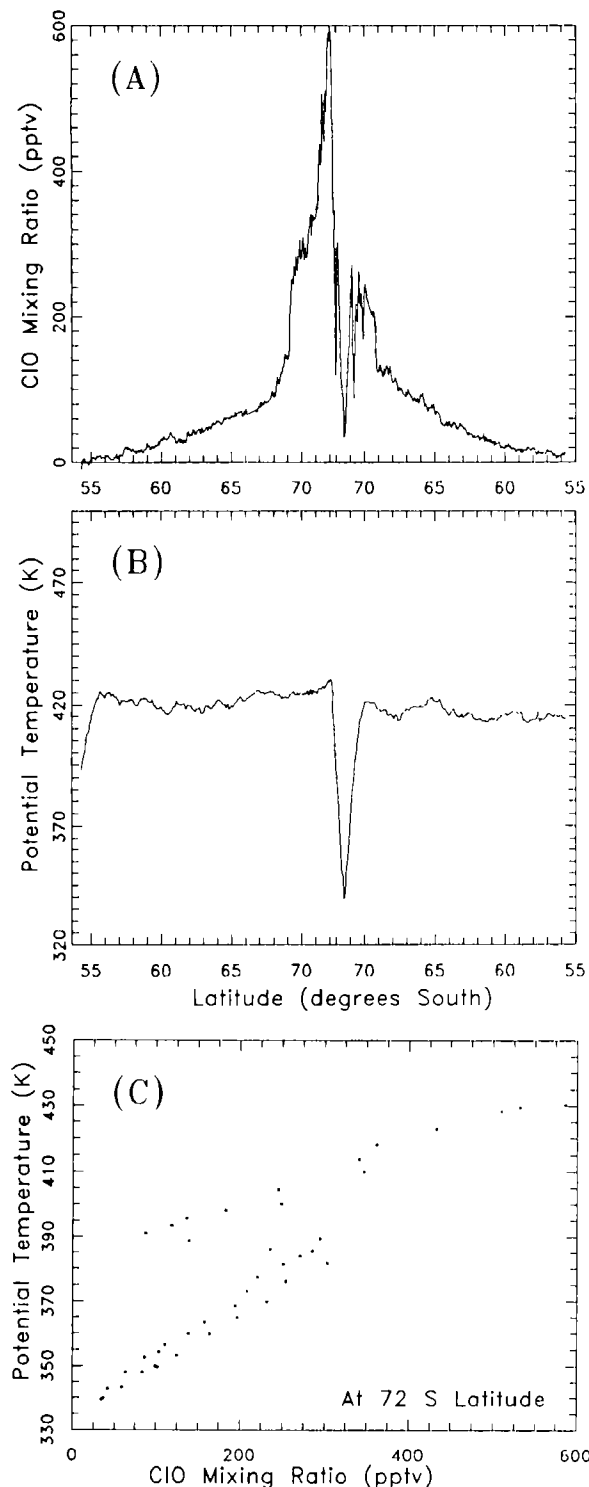


Fig. 7. (a) A survey of the observed CIO mixing ratio as a function of latitude for the August 28 flight, (b) the potential temperature for the flight as a function of latitude, and (c) the CIO mixing ratio as a function of potential temperature. Note that the vertical profile of CIO shown in Figure 7c corresponds to the southernmost point of the flight trajectory, typically 72°S latitude.

ature, it is dangerous to draw conclusions from such a small penetration distance into the vortex. The asymmetry in the CIO distribution was caused by the dive-ascent segment of the flight occurring in the northbound leg.

There is an interesting comparison to be made between the data of August 17 and those of August 28. Figure 8

superposes the southbound data from August 17 and August 28, demonstrating the similarity of the first shoulder region of the August 28 data with those of August 17. Both days, in contrast to most of the CIO observations, exhibited broad "wings" in the CIO distribution equatorward of the first large gradient in CIO and roughly equivalent mixing ratios on the first "plateau". This is interesting because it suggests that CIO concentrations obtained on August 17 were not values typical of the interior of the CPR.

August 30, 1987

The profile flown on August 30 was again a reasonable approximation to an isentropic surface on both the southbound (424 ± 5 K) and northbound (420 ± 7 K) legs, punctuated by a rapid scan down to 360 K, an extended residence time at 360 K, and back up to 420 K at 72°S latitude. These results are summarized in Figures 9a–9c.

Penetration of the CPR was significant on this flight. Nearly 7° latitude of penetration was achieved, and several clear conclusions can be drawn. First, the free radical concentration poleward of the CPR edge increased monotonically with latitude on a surface of fixed potential temperature. Second, there was a steep gradient in CIO with increasing altitude (potential temperature) at 72°S. This was revealed dramatically by the final climb executed just prior to the dive segment. For a 10 K change in potential temperature, the CIO mixing ratio increased from 600 pptv to 750 pptv, an increase of 25%. If that gradient were to hold, the CIO mixing ratio would reach 1 ppbv ~ 20 K above the aircraft flight track.

The vertical profile of CIO between 360 and 440 K at 72°S was extremely well behaved with no evidence of layering as was observed on August 28.

September 2, 1987

Although an attempt was made to adhere to an isentropic surface on this flight, large excursions from a mean of 430 K on the southbound and northbound legs were realized.

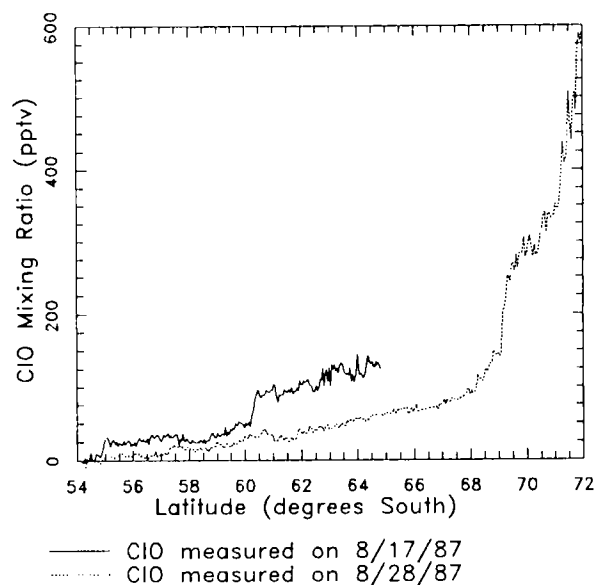


Fig. 8. Superposed CIO mixing ratio data from August 17 and 28. Evidence indicates that the data obtained on August 17 did not represent any significant penetration into the chemically perturbed region (CPR).

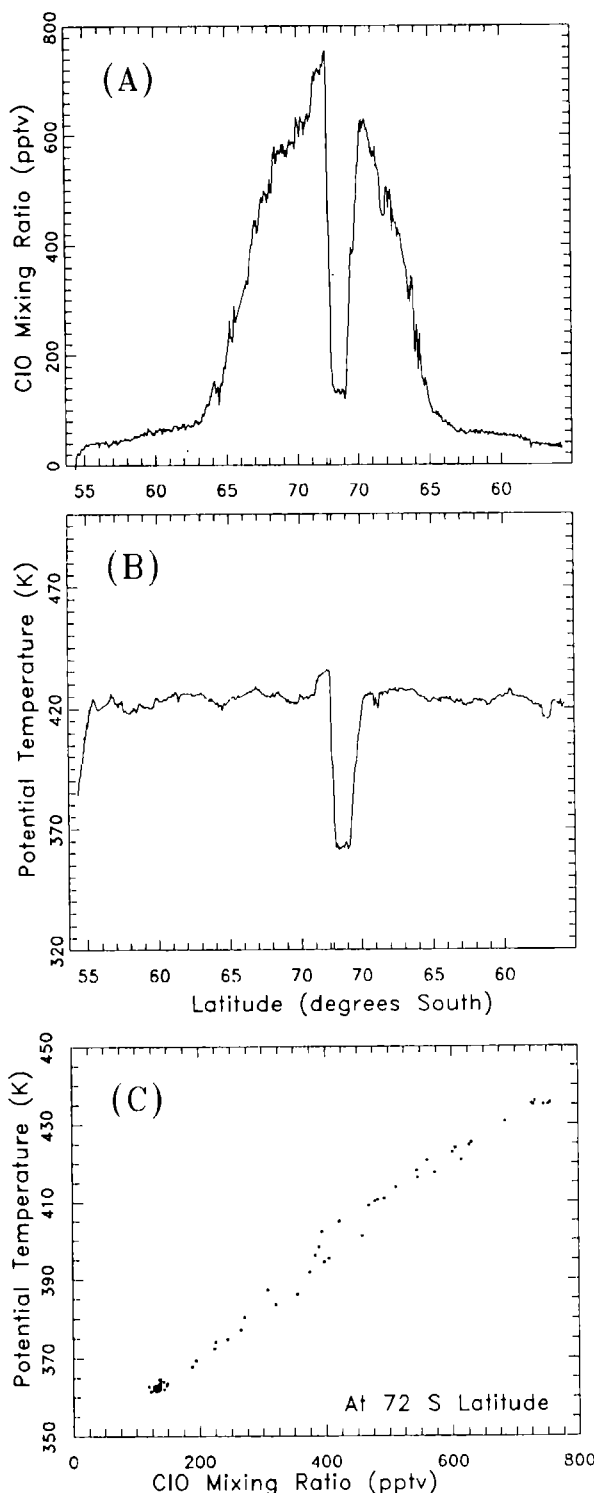


Fig. 9. (a) A survey of the observed CIO mixing ratio as a function of latitude for the August 30 flight, (b) the potential temperature for the flight as a function of latitude, and (c) the CIO mixing ratio as a function of potential temperature. Note that the vertical profile of CIO shown in Figure 9c corresponds to the southernmost point of the flight trajectory, typically 72°S latitude.

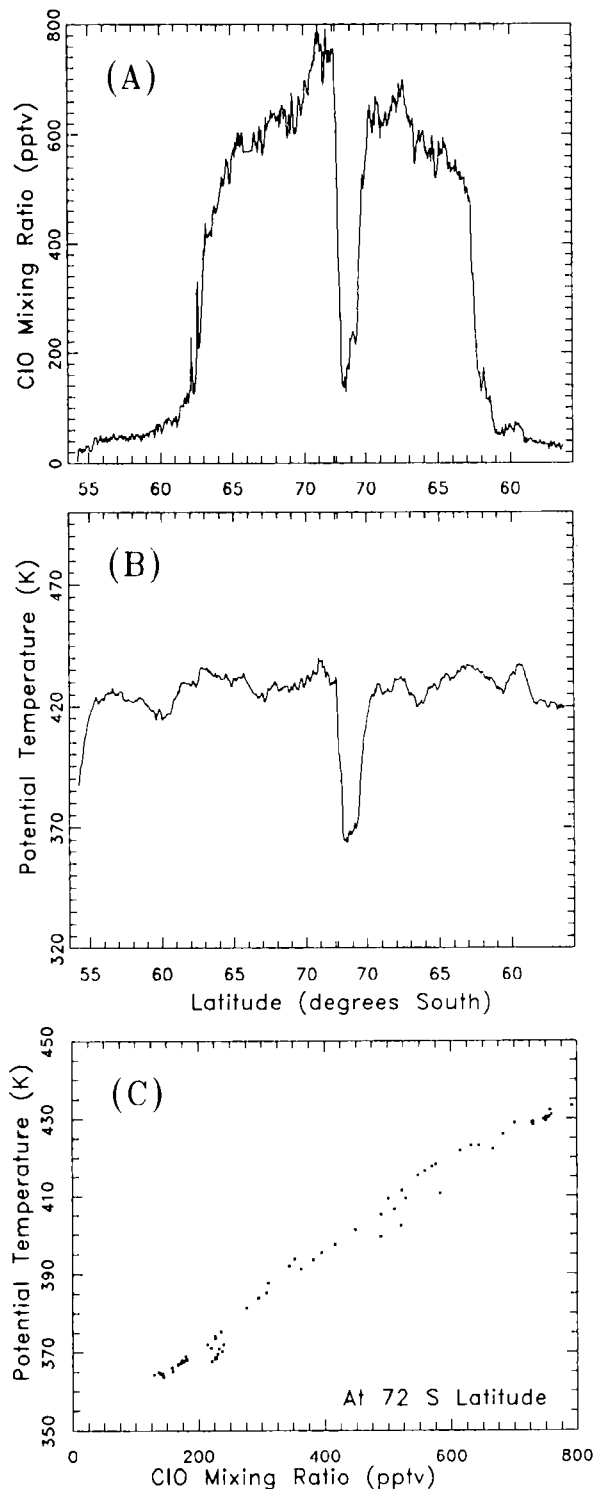


Fig. 10. (a) A survey of the observed CIO mixing ratio as a function of latitude for the September 2 flight, (b) the potential temperature for the flight as a function of latitude, and (c) the CIO mixing ratio as a function of potential temperature. Note that the vertical profile of CIO shown in Figure 10c corresponds to the southernmost point of the flight trajectory, typically 72°S latitude.

Figures 10a–10c define this variation and its consequences on the observed CIO mixing ratio.

The first-order behavior of CIO is consistent with that of previous flights: A step gradient defines the wall of the CPR, and CIO increases somewhat more slowly poleward of the CPR “wall” with a clear vertical gradient such that the

CIO mixing ratio increases with height. At aircraft altitude (18 km or 430 K) the vertical gradient remains large, as it was on August 30. This can be seen clearly in the highest potential temperature segment, Figure 10c.

The character of the vertical profile at 72°S shows a great deal in common with that of all previous flights. CIO mixing

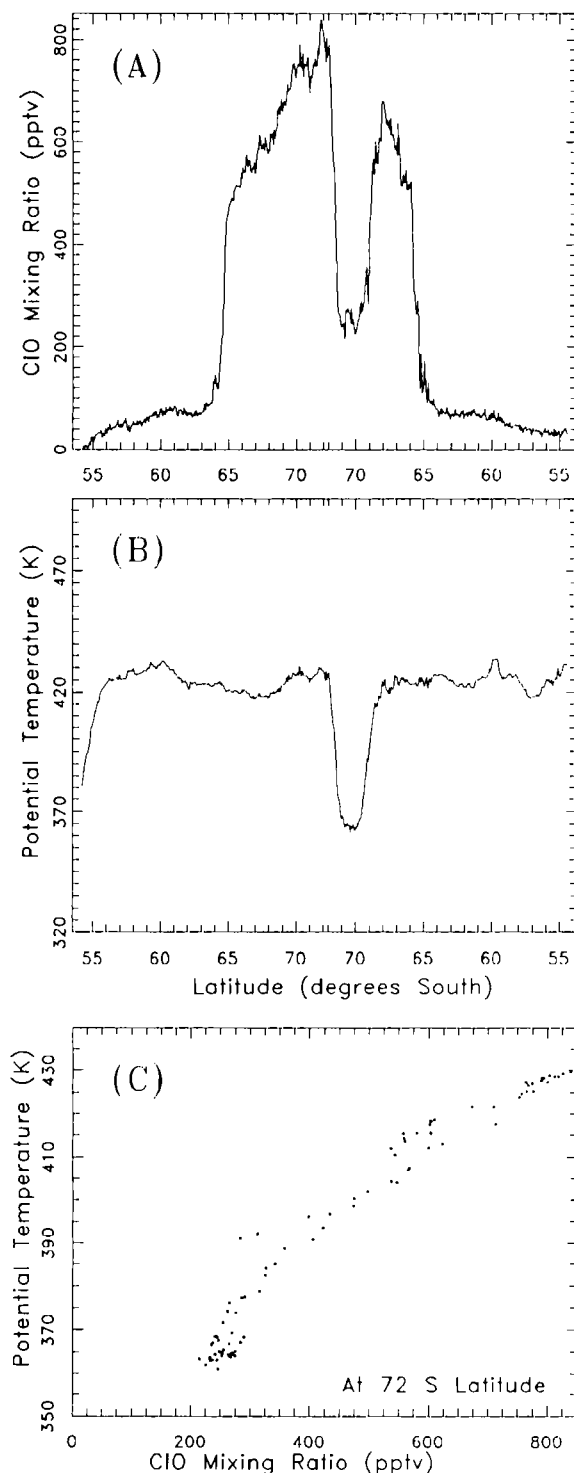


Fig. 11. (a) A survey of the observed ClO mixing ratio as a function of latitude for the September 4 flight, (b) the potential temperature for the flight as a function of latitude, and (c) the ClO mixing ratio as a function of potential temperature. Note that the vertical profile of ClO shown in Figure 11c corresponds to the southernmost point of the flight trajectory, typically 72°S latitude.

ratios drop by an order of magnitude between 430 and 360 K. Flights of considerable penetration ($> 5^\circ$ latitude) begin to fall into a pattern through the end of August and into early September. The ClO mixing ratio falls in the range of 800 pptv at 72°S, and there is a clear tendency for ClO to climb consistently as the aircraft penetrates further into

the vortex. The vertical distribution of ClO exhibits little scatter about a mean that in turn exhibits monotonically decreasing mixing ratios with decreasing potential temperature.

September 4, 1987

Significant deviation from the 424 K potential temperature surface was recorded on the southbound leg for this flight, as summarized in Figure 11. This effectively flattens the gradient of ClO poleward of the edge of the CPR. If the flight surface had been isentropic, considerably more curvature would have been apparent in the ClO mixing ratio between 65° and 72°S. This effect can be viewed explicitly in Anderson *et al.* [1989b], which places the ClO data on a fixed potential temperature surface using the observed vertical gradient shown in Figure 11c.

A clear vertical gradient exists in the ClO mixing ratio in the vicinity of the aircraft cruise altitude, particularly at 72°S. This is evident in the final peak between 71° and 72°S latitude, which correlates with the 4 K increase in potential temperature.

Consideration of the dependence of ClO concentration on potential temperature, which is perhaps more appropriate for a discussion of ozone destruction rates resulting from chlorine catalysis, reveals that the ClO concentration (not the mixing ratio) increases with potential temperature in early September such that ClO doubles between 380 and 440 K. This gradient is consistent for flights on August 23, 28, and 30, and September 2 and 4. Maximum ClO mixing ratios of 840 pptv were observed on September 4, not significantly different from those first observed on August 23.

September 9, 1987

The flight of September 9 was marked by a strict adherence to the 450 K potential temperature surface on the southbound leg and a deeper dive segment, to 340 K rather than 360 K potential temperature, at 68°S. A 420 K isentropic surface was flown on the northbound leg.

While the basic pattern in the ClO mixing ratio was repeated, as displayed in Figure 12a, there were some significant points of departure. The CPR boundary was observed at its greatest equatorward extension, 60°S, and the peak mixing ratio observed was the largest to date, 1100 pptv at the southernmost point. Also, with the dive segment reaching 340 K (~ 12 km altitude), the ClO mixing ratio of 40 pptv represents the deepest minimum reached thus far in the flight sequence. The dynamic range covered in the dive segment approached two orders of magnitude.

A feature that remains is the strong correlation between potential temperature and ClO mixing ratio at peak aircraft altitudes. Another feature of the ClO profile shown in Figure 12a is the consistently broad wings equatorward of the CPR boundary. ClO mixing ratios on the order of 75 pptv extend northward to 55°S on virtually all flights after August 28.

Consideration of the gradient in ClO concentration with potential temperature (which is critical for ozone destruction rates) adheres to the pattern established in the flights through September 4: the ClO concentration doubles between the 380 and 440 K potential temperature surface.

September 16, 1987

Nearly a week of bad weather gave way on September 16 to a high pressure area over southern Chile, which nudged

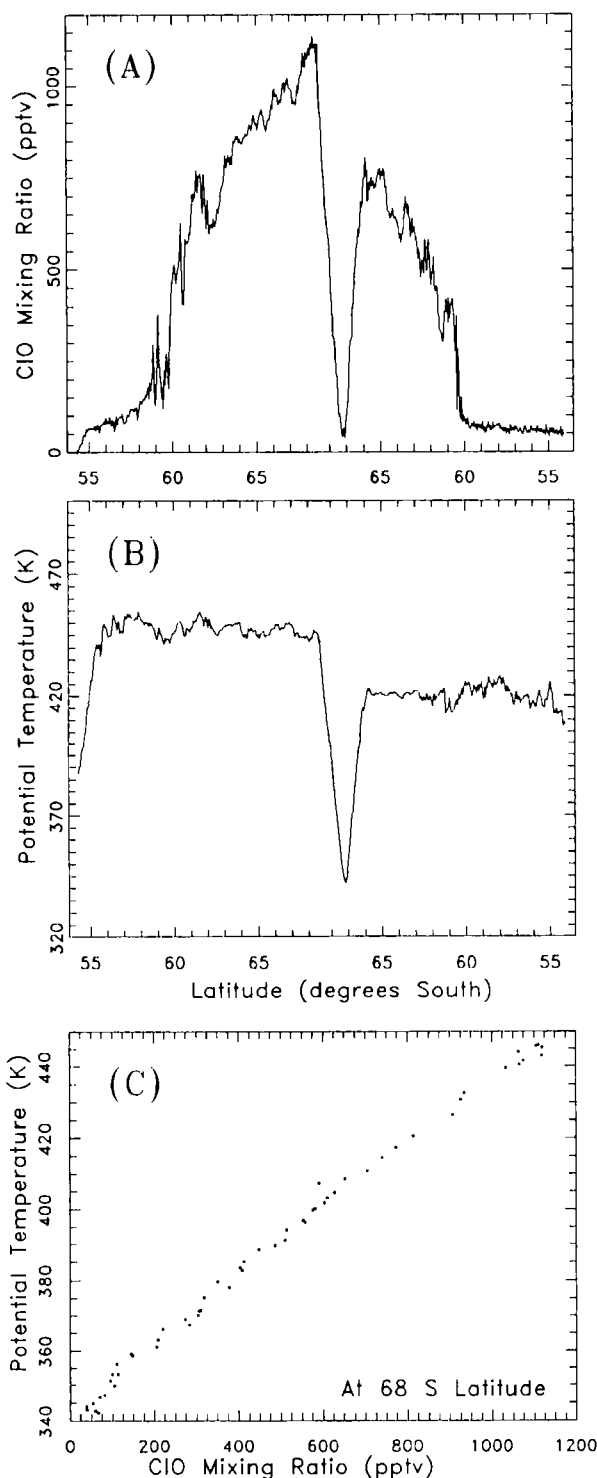


Fig. 12. (a) A survey of the observed ClO mixing ratio as a function of latitude for the September 9 flight, (b) the potential temperature for the flight as a function of latitude, and (c) the ClO mixing ratio as a function of potential temperature. Note that the vertical profile of ClO shown in Figure 12c corresponds to the southernmost point of the flight trajectory, 68°S latitude.

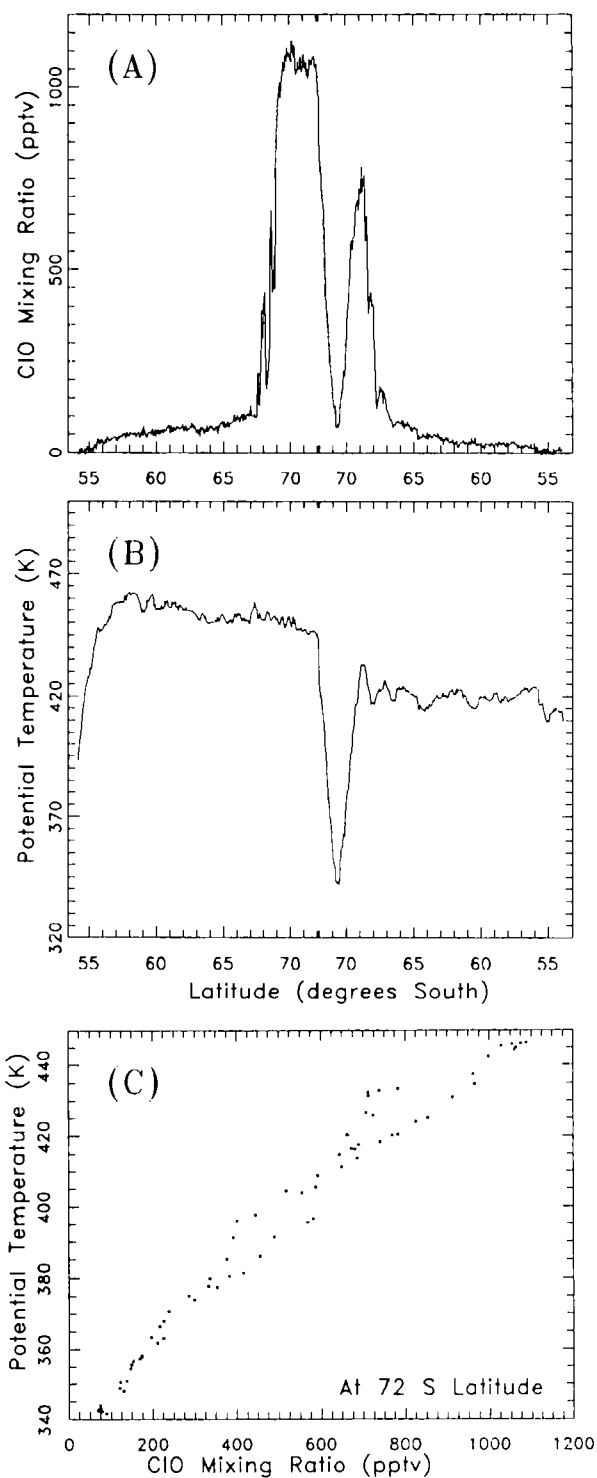


Fig. 13. (a) A survey of the observed ClO mixing ratio as a function of latitude for the September 16 flight, (b) the potential temperature for the flight as a function of latitude, and (c) the ClO mixing ratio as a function of potential temperature. Note that the vertical profile of ClO shown in Figure 13c corresponds to the southernmost point of the flight trajectory, typically 72°S latitude.

the boundary of the CPR poleward. Figure 13 reviews the ClO distribution and points up three crucial observations. First, the maximum observed mixing ratio reached 1100 pptv, equal to the highest values observed in the mission to date. Second, the integrity of the edge of the CPR remained intact and achieved its largest gradient to date. This was

particularly important at the time because the mode of vortex collapse was unknown; we had no precedent upon which to predict the vitality of the circumpolar jet or degree of containment that resulted therefrom. Third, the gradient with latitude poleward of the edge of the CPR did not exhibit its classic domed configuration. There is little if any increase in

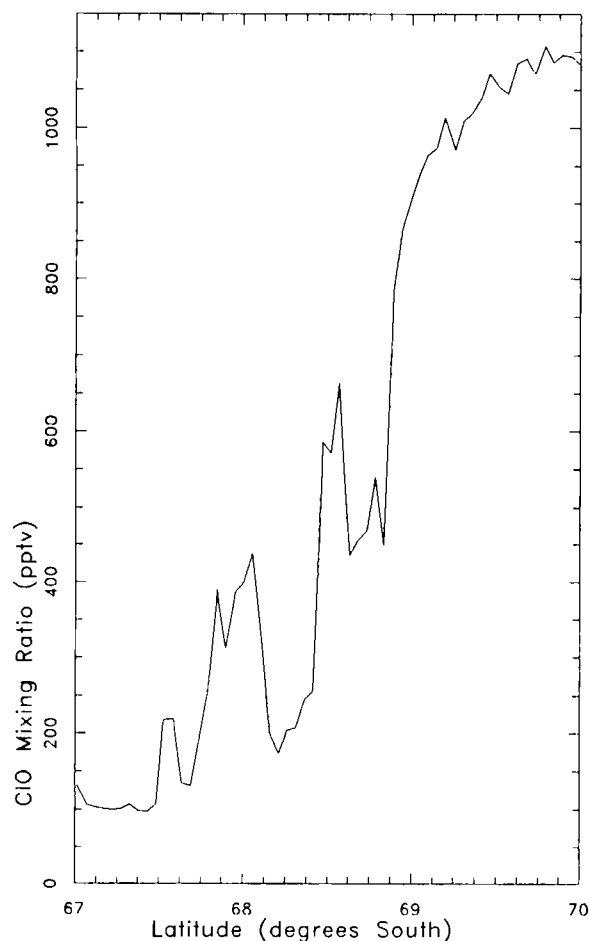


Fig. 14. High-resolution display of ClO through the wall of the chemically perturbed region (CPR) obtained on the flight of September 16.

ClO mixing ratio with penetration. Consideration of the potential temperature surface in Figure 13b demonstrates that the aircraft started its southern leg at 460 K but "sank" uniformly to 450 K at the southern end. On the northbound leg a rather erratic 420 K was achieved. Note the effect of the potential temperature surface on the ClO mixing ratio in the wings of the distribution equatorward of the edge of the CPR. At 460 K, ClO mixing ratios are the typical 75 pptv, at 420 K they are 40 pptv.

As the aircraft penetrates the CPR wall, there are subtle features in the ClO distribution that will prove crucial when a detailed comparison of ClO and O_3 is done [see Anderson *et al.*, 1989a, b]. Observed ClO mixing ratios execute several small scale, large amplitude fluctuations as the mixing ratio rises from < 100 pptv to 1000 pptv in approximately one degree of latitude.

Figure 14 reveals this structure at the CPR wall with considerably greater spatial resolution, demonstrating the instrument's ability to clearly resolve these features. This issue will become important when we consider correlation with other species.

September 20, 1987

The flight profile on September 20 was designed to both adhere to the 460 K isentropic surfaces during the south and northbound legs and to achieve maximum altitude immediately before the dive at 72°S. What is unique about the

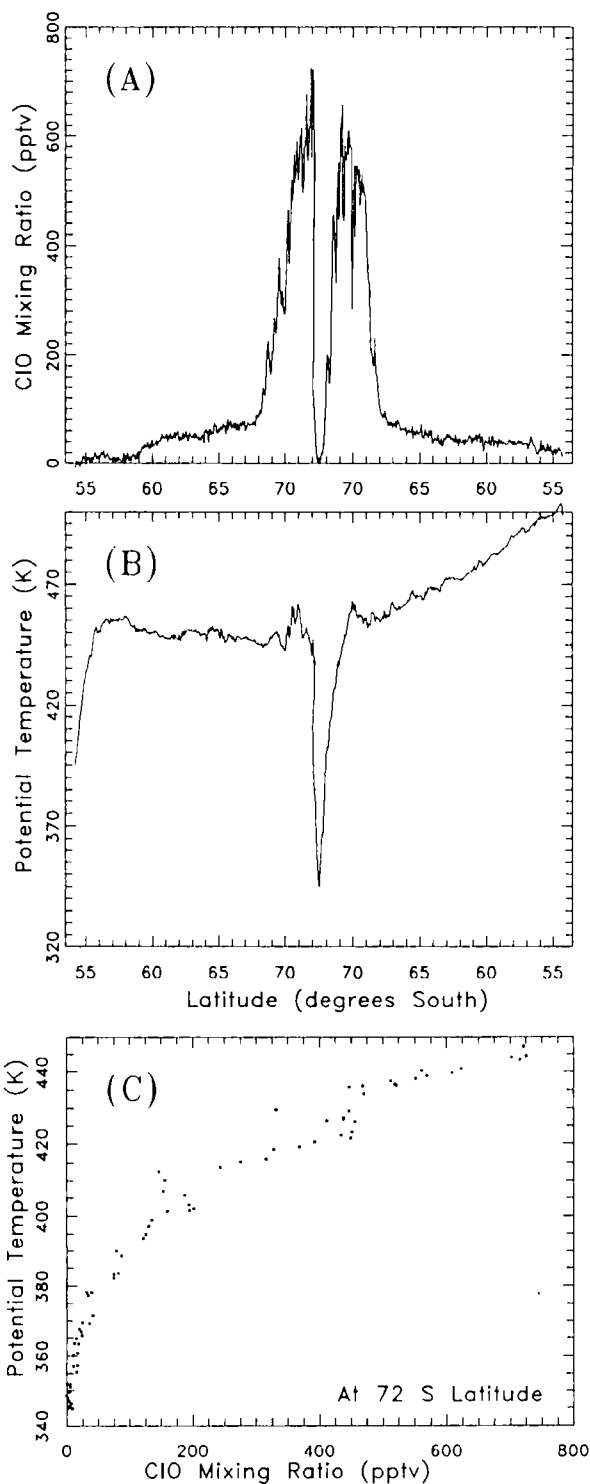


Fig. 15. (a) A survey of the observed ClO mixing ratio as a function of latitude for the September 20 flight, (b) the potential temperature for the flight as a function of latitude, and (c) the ClO mixing ratio as a function of potential temperature. Note that the vertical profile of ClO shown in Figure 15c corresponds to the southernmost point of the flight trajectory, 72°S latitude.

region poleward of the edge of the CPR on this flight is the small-scale structure prevalent all the way to 72°S latitude. This character is displayed in Figure 15. Also displayed is the small degree of penetration into the CPR on September 20.

Consideration of the meteorological atlas [see Newman *et*

al., 1988] for September 20 reveals the unique placement of a potential vorticity fold at the longitude of the flight trajectory. This means that the aircraft penetrated the edge of the CPR on a nearly tangential path, yielding very little effective penetration at the southernmost point. This behavior is also reflected in the highly erratic character of the spatial distribution of CIO shown in Figure 15a. Figure 15b reflects the "cruise climb" taken by the aircraft on the northern leg reaching a potential temperature, just south of Punta Arenas, of 500 K.

Figure 15c displays the dependence of CIO mixing ratio on potential temperature. The extremely low values observed below the 380 K surface reflect the fact that the aircraft probably passed through the boundary of the CPR (to the equatorward side) during the descent. Also, the erratic character of the CIO versus potential temperature surface obtained on September 20 eliminates this flight as a valid contribution to the trend analysis of intravortex CIO mixing ratios.

September 21, 1987

The CPR boundary reached its southernmost observed position in the mission on the September 21. Note, however, in Figure 16, that the gradient in CIO at the wall is as steep as we ever observed and that there is little evidence for breakup in the region poleward of the CPR edge. Peak mixing ratios of 880 pptv were observed within 1° of latitude inside the CPR.

It is also clear from an inspection of Figure 16a that the gradient in CIO with latitude is exceedingly steep and that typical CIO mixing ratios within the CPR have not been reached. Thus the flight of September 21 provides critical information about the position and clarity of the vessel wall, but not about secular trends within the CPR. An analysis of CIO concentration gradients with potential temperature, extracted from the mixing ratio gradient in Figure 16c, reveals for the first time in the flight series that the aircraft may have reached peak CIO concentrations with altitude. There is a clear indication of a flattening of the CIO versus potential temperature gradient above 428 K. However, because of the minimal penetration distance into the CPR, it is dangerous to draw clear conclusions.

September 22, 1987

The peak CIO mixing ratio was 1100 pptv for this last flight in the expedition. Figure 17 displays the now traditional CPR boundary and "domed" distribution first revealed on August 23. At this point the CIO mixing ratio is approximately 30% higher than it was a month earlier, but the striking demarcation at the CPR wall is virtually as precise as it was on the first flight. Except for the absolute magnitude of the CIO mixing ratio, the vertical distribution of CIO at 72°S is very similar to what it was at the beginning of the mission.

Figure 17b displays the degree of adherence to the 460 and 420 K isentropic surfaces on the southbound and northbound legs, respectively. When the CIO mixing ratio dependence on potential temperature is analyzed in terms of concentration, the data clearly indicate that the aircraft reached peak concentration with altitude below the highest point achieved by the aircraft just before the dive at 72°S. This substantiates the suggestion noted for the date of September 21: By late September, the CIO concentration no longer in-

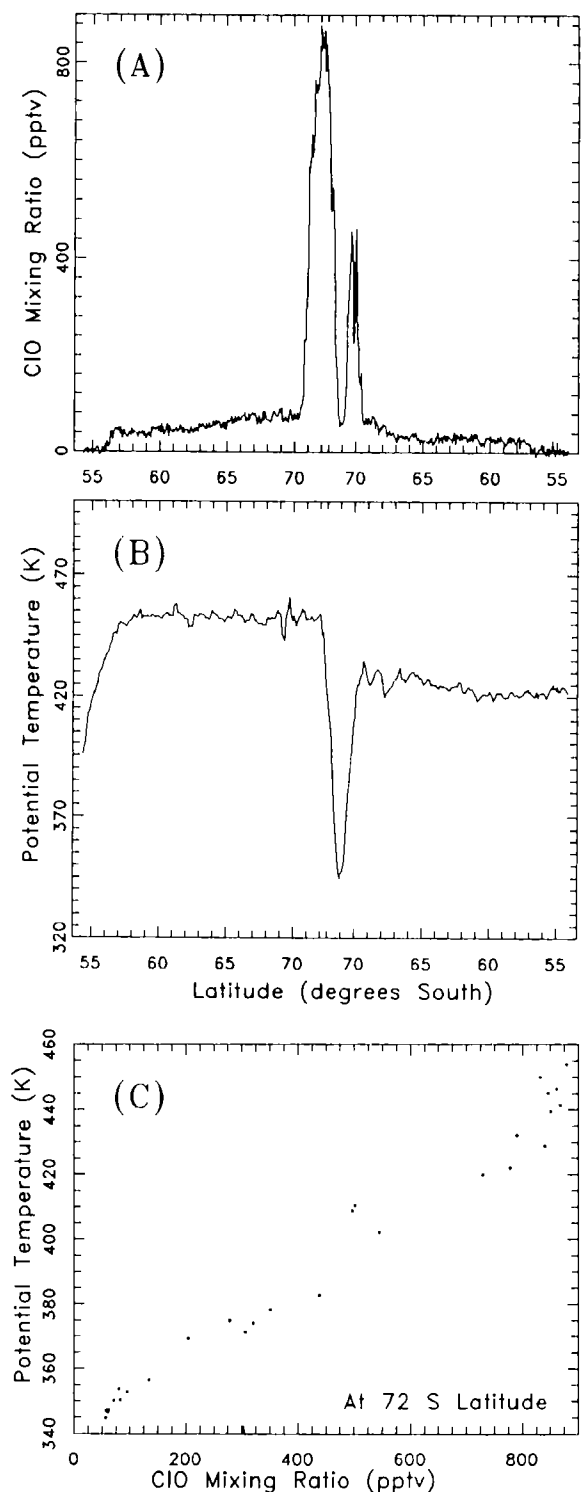


Fig. 16. (a) A survey of the observed CIO mixing ratio as a function of latitude for the September 21 flight, (b) the potential temperature for the flight as a function of latitude, and (c) the CIO mixing ratio as a function of potential temperature. Note that the vertical profile of CIO shown in Figure 16c corresponds to the southernmost point of the flight trajectory, 72°S latitude.

creases with increasing potential temperature at the highest altitudes reached by the ER-2. On September 22, the aircraft penetrated nearly 10° in latitude into the CPR and there is good probability that the observed morphology of intravortex CIO is reasonably represented.

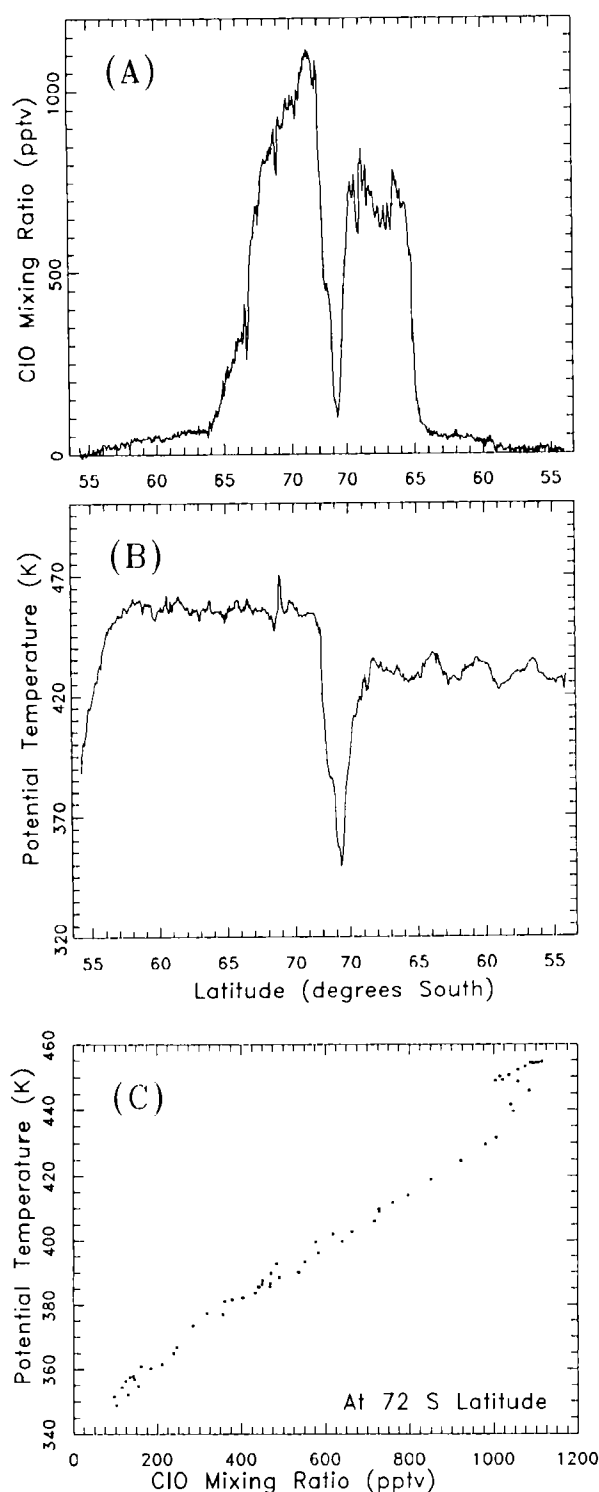


Fig. 17. (a) A survey of the observed CIO mixing ratio as a function of latitude for the September 22 flight, (b) the potential temperature for the flight as a function of latitude, and (c) the CIO mixing ratio as a function of potential temperature. Note that the vertical profile of CIO shown in Figure 17c corresponds to the southernmost point of the flight trajectory, 72°S latitude.

CONCLUSIONS

In situ measurements of the CIO mixing ratio obtained from the ER-2 aircraft in a series of 12 flights extending from August 17 through September 22, 1987, defined the CIO distribution during the latter stages of the austral winter in the latitude belt from 54°S to 72°S.

1. The CIO distribution defines the existence of a "chemically perturbed region" (CPR) with a boundary just poleward of the velocity maximum of the circumpolar jet. Existence of the CPR edge is revealed by a change in CIO mixing ratio by more than an order of magnitude on a fixed potential temperature surface, usually within 3° of latitude, but occasionally within 1° of latitude.

2. Within this CPR at peak aircraft altitudes (~18.5 km) the CIO mixing ratio increased from 800 pptv on August 23, to 1100 pptv on September 22. This corresponds to enhancements of 500 times typical mid-latitude values. Outside (equatorward) of the CPR edge, CIO drops precipitously to ~100 pptv and then slowly decreases with decreasing latitude, often reaching 5–10 pptv at 54°S.

3. The gradient in mixing ratio with altitude (or potential temperature) is very steep inside the CPR. Typically, CIO mixing ratios drop by a factor of 20 between 18 km (450 K potential temperature) and 13 km (350 K potential temperature).

4. While the CPR boundary is very clearly defined by the CIO mixing ratio, there are small-scale events which are resolved by the instrument along the inner edge of the CPR.

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Ozone Destruction by Chlorine Radicals Within the Antarctic Vortex: The Spatial and Temporal Evolution of ClO–O₃ Anticorrelation Based on in Situ ER-2 Data

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In situ O₃ and ClO data obtained from the ER-2 aircraft are used to define the chemical evolution of the Antarctic vortex region from August 23 to September 22, 1987. Initial conditions are characterized at aircraft flight altitude (18 km) by highly amplified ClO mixing ratios (800 parts per trillion by volume (pptv)) within a well-defined "chemically perturbed region" (CPR) poleward of the circumpolar jet, within which ozone exhibits limited erosion (~15%) in middle to late August. Within this CPR, ozone decays consistently throughout the course of a 10-flight series, such that by late September, 75% of the O₃ has disappeared within the region of highly amplified ClO concentrations (which reached 500 times normal levels at ER-2 cruise altitude). As this ozone depletion develops, O₃ and ClO exhibit dramatic negative correlation on isentropic surfaces, obtained as the aircraft passed through the edge of the CPR. Taken in conjunction with an analysis of the mechanisms defining the rate of catalytic O₃ destruction, it is concluded that ClO is an essential constituent in the catalytic destruction of ozone within the vortex. Therefore it is concluded that the observed disappearance of ozone within the Antarctic vortex would not have occurred in the absence of global chlorofluorocarbon release.

INTRODUCTION

One of the most elusive aspects of experimental atmospheric chemistry is that a unique determination of cause and effect is often very difficult. This impasse stems either from a smearing of dynamical and chemical time constants, or from the fact that the chemical system under investigation is controlled by a large network of coupled reactions with convoluted positive and negative feedbacks. At the same time, a quantitative prediction of how the atmosphere will respond to increasing fluxes of foreign compounds entering the troposphere demands knowledge of those rate-limiting catalytic processes that control chemical transformation rates throughout the atmosphere.

Development of modern in situ methods which have sufficient sensitivity and time response to resolve small-scale structure presents the possibility for testing specific mechanisms by correlation studies between (1) reactants in rate-limiting steps of proposed catalytic cycles and (2) the concentration of compounds chemically transformed by those catalytic cycles. This objective suggested the use of in situ methods deployed into the Antarctic vortex at the altitude of the polar ozone maximum to diagnose the mechanism for ozone removal during the austral spring. High-resolution vertical soundings of ozone, temperature, and particle den-

sities by *Hofmann et al.* [1986], using balloons, had previously demonstrated the wealth of mechanistic information that could be obtained by this approach.

Two other papers provide important complementary material for the work reported here. The first defines both the experimental technique used for the ClO radical measurements presented here and the spatial distribution of ClO obtained from the ER-2 flights [*Brune et al.*, 1989]. The experimental techniques used to obtain the results discussed here appear in that paper. All data were obtained approximately symmetrically about local noon, all under daylight conditions. A general pattern in the ClO distribution is reported by *Brune et al.* [1989]; mixing ratios of approximately 10 parts per trillion by volume (pptv) are found at aircraft altitude (~18 km) in the vicinity of 55°S, increasing to 50 pptv at 60°S. In the vicinity of 65°S a steep gradient in ClO mixing ratio is observed, leading to levels of 800–1200 pptv poleward of the jet defining the vortex. This dramatic gradient in ClO defines the edge of a "chemically perturbed region" (CPR), which occupies the spatial regime poleward of the ClO gradient at all altitudes covered by the aircraft (~13–18.5 km).

The second paper addresses the kinetics of ozone destruction within the CPR in the region of 72°S, based on observed concentrations of halogen radicals [*Anderson et al.*, this issue].

In this paper we focus on the evolution of ClO–O₃ anticorrelation from the first flight on August 23, 1987, which penetrated well into the vortex, through the course of 10 flights culminating on September 22, 1987. All flights followed essentially identical trajectories: departing Punta Arenas, Chile at 54°S latitude and climbing immediately to a predetermined potential temperature surface (typically

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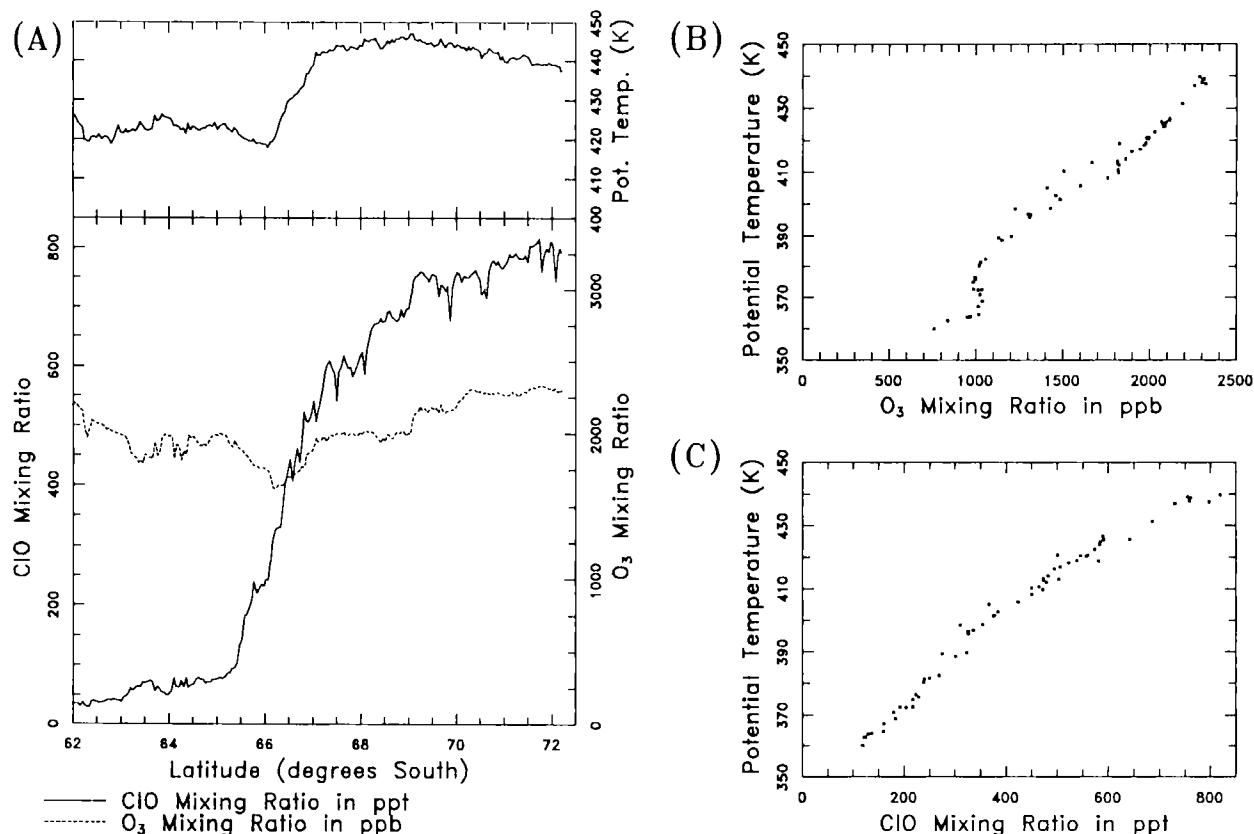


Fig. 1. Summary of the ClO and O₃ data obtained between 62°–72°S latitude by the ER-2 aircraft on August 23, 1987. (a) The simultaneous ClO–O₃ data and the potential temperature followed by the aircraft. (b) The vertical distribution of O₃ at the southernmost point of the flight trajectory, obtained when the aircraft dove from ~18.5 km to ~13 km altitude. (c) The vertical distribution of ClO obtained on the same flight track at 72°S.

between 425–450 K). This isentropic surface was maintained across Cooke Strait and down the west coast of the Palmer Peninsula on the southbound leg to 72°S latitude. A rapid dive-ascent protocol was executed at the southern extremity, covering the 450–350–450 K surfaces. The northward leg to Punta Arenas mimicked the southbound leg. All data within the vortex were obtained close to local noon.

OZONE–CHLORINE MONOXIDE CORRELATION STUDIES

The existence of positive or negative correlation between any two variables does not in itself establish cause and effect. A far more revealing approach is to trace the transition of a system from its initial condition to a subsequent state in which the same two variables are clearly correlated, either negatively or positively. In our case we are concerned with establishing the loss mechanism for ozone resulting from gas-phase homogeneous catalytic cycles, rate-limited by halogen radicals. Thus we will focus on the behavior of ozone in the presence of varying levels of the ClO radical, which is a reactant in the rate-limiting step of virtually every proposed catalytic cycle [see Anderson *et al.*, this issue].

Before we consider each of the 10 flights in detail, some general comments extracted from the observed distribution of ClO [see Brune *et al.*, 1989] are in order. First, the exceedingly steep gradient in ClO mixing ratios as a function of horizontal position on surfaces of constant potential temperature established unequivocally a sharp transition region separating air masses inside of and external to the CPR.

While the choice of a surface at (or in the vicinity of) the ClO “wall” may represent a semipermeable membrane through which material may pass at some imperfectly defined rate, we are concerned here only with an interface which maintains concentration gradients in ClO and O₃ large compared with changes in other variables that could affect the concentration of ozone (i.e., solar flux, temperature, pressure). The situation at the boundary of the CPR is not dissimilar to that which exists in the laboratory under controlled conditions in both flash photolysis and discharge flow systems, in which quantitative kinetic data are extracted within volume elements imperfectly isolated by diffusive and advective processes.

We focus our attention on the relationship between ClO and O₃ for the purpose of exposing the chemical mechanism responsible for ozone destruction within the Antarctic vortex as a whole, using the somewhat limited penetration of the ER-2 (which tends to amplify the importance of the transition region at the edge of the CPR) to establish typical intravortex conditions.

Ten flights of the ER-2 penetrated poleward of the circumpolar jet. These flights, taken as a set, clearly reveal conditions within the CPR, including a dive segment at the southern extremity of the penetration, typically at 72°S latitude. We will use these 10 flights, which spanned the period from August 23 to September 22, to define the temporal evolution of O₃ in the presence of ClO.

Given that both ClO and O₃ are rapidly varying functions

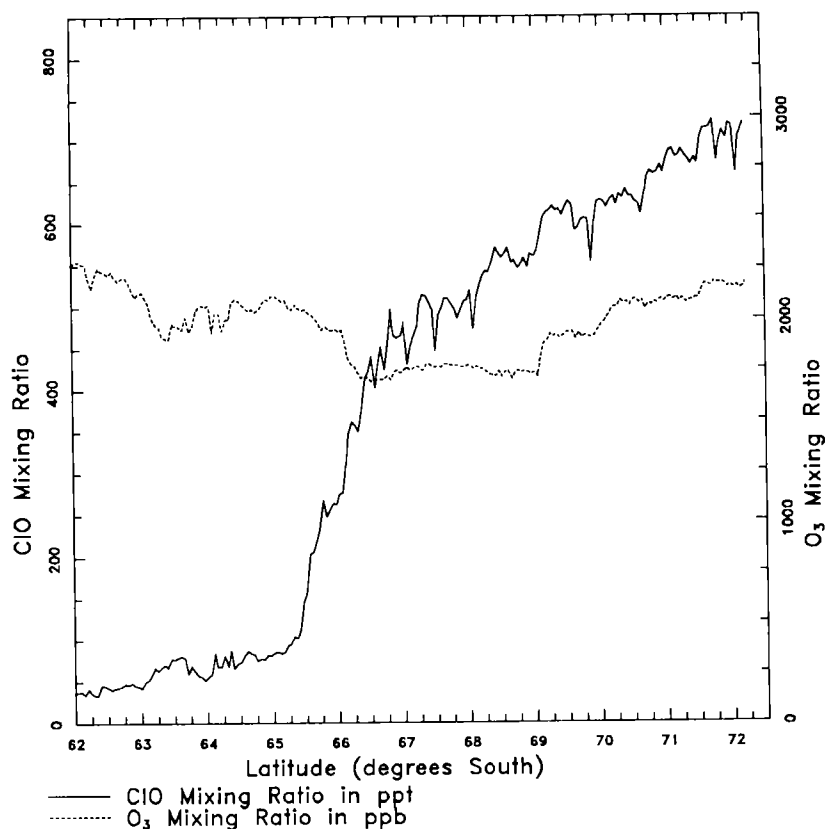


Fig. 2. Simultaneously observed ClO and O₃ obtained on August 23, 1987, by the ER-2, with corrections made for variations in potential temperature. Results shown here correspond to what the aircraft would have observed on a 430 K isentropic surface.

of latitude, altitude (potential temperature), and (calendar) time, we adopt the same approach for each flight: First, the distribution of ClO and O₃ with latitude on an approximately constant potential temperature surface is defined for the segment of the flight which includes the region equatorward of the CPR, the transection of the CPR boundary, and the segment extending to the southernmost point of the flight (usually 72°S latitude). Companion profiles of ClO and O₃ in the dive segment of the trajectory are included to reveal the vertical distribution of both species inside the CPR (i.e., poleward of the CPR boundary). Second, knowledge of the vertical distribution of ClO and O₃ within the CPR is used to remove fluctuations in ClO and O₃ resulting from variations in potential temperature executed by the aircraft. This first-order correction for changes in aircraft altitude (potential temperature) reduces confusion caused by the mixing of horizontal and vertical gradients in species concentration. This simple analysis leaves us with latitude transections that would closely approximate data obtained by the aircraft flying on a precise isentropic surface.

RESULTS OF ER-2 FLIGHTS

Figure 1a summarizes the ClO and O₃ data obtained by the ER-2 on August 23 over 8° in latitude, centered at the edge of the CPR. Also shown in Figure 1a is an insert, which traces the potential temperature of the air within which the ER-2 obtained the results displayed in this figure. Note the step function in Θ from 420–440 K at 67°S latitude; the impact of this precipitous change in altitude (Θ) on reported

ClO and O₃ mixing ratios can be accounted for because the dive segment at 72°S latitude provides data on the vertical gradient of ClO and O₃ within the CPR. Figures 1b and 1c summarize those results. Note that while the vertical gradient was obtained at 72°S latitude, we are correcting for a change in Θ at 67°S. This is acceptable for two reasons. First, experience with other flights, which penetrated only 1° in latitude into the CPR (see data from September 21, for example), reveals a consistency in the vertical gradients of ClO and O₃ over a wide range of penetration distances. Second, we are correcting for changes in Θ over a limited vertical range. We thus have the data necessary to eliminate, to first order, the excursion in Θ executed by the aircraft. That is, we can reconstruct what the aircraft would have observed had it adhered strictly to an isentropic surface. Figure 2 presents these results for the identical latitude range spanned by Figure 1a, corrected to a 430 K isentropic surface.

A number of important issues are addressed in Figure 2. First, while there is clear evidence for ozone erosion on the poleward side of the CPR edge, ozone has emerged from the polar night largely unchanged. That is, on August 23, ClO has reached levels approaching 1 ppb, some 500 times normal levels at this altitude, while ozone exhibits a decrease of perhaps 15% just poleward of the CPR boundary. This establishes the initial conditions for the subsequent development of the covariant behavior of [ClO] and [O₃]. It also reveals that whatever the mechanism is linking ClO and O₃, the amount of O₃ which has been lost (~15%) is a key di-

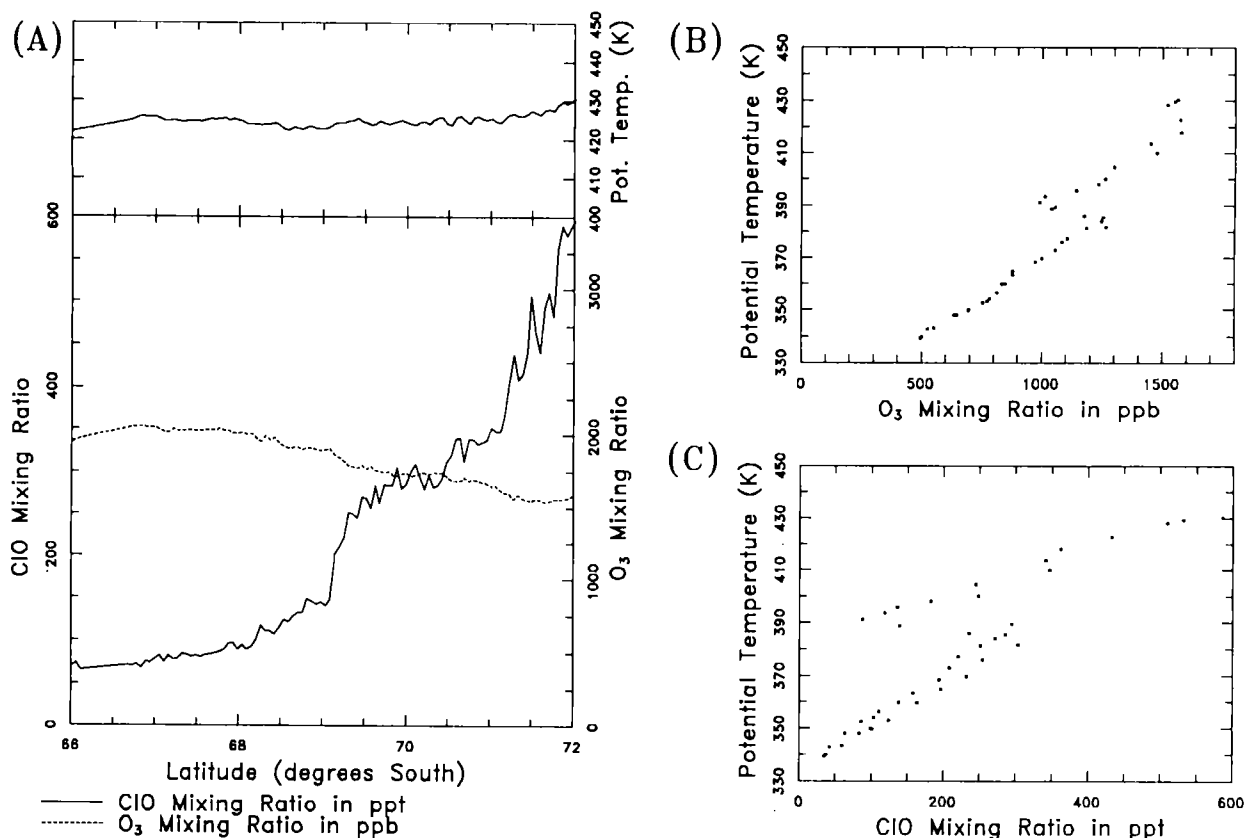


Fig. 3. Summary of the ClO and O₃ data obtained between 62°–72°S latitude by the ER-2 aircraft on August 28, 1987. (a) The simultaneous ClO–O₃ data and the potential temperature followed by the aircraft. (b) The vertical distribution of O₃ at the southernmost point of the flight trajectory, obtained when the aircraft dove from ~18.5 km to ~13 km altitude. (c) The vertical distribution of ClO obtained on the same flight track at 72°S.

agnostic. This issue is noted in the paper by Anderson *et al.* [this issue] on ClO–BrO–O₃ kinetics.

On August 28, 5 days after the ER-2 clearly penetrated the CPR boundary for the first time, a second mission was executed that achieved marginal penetration. Figure 3 summarizes those results, using the same format discussed for Figure 1. On this flight the adherence to the 425 K Θ surface was considerably more precise on the southbound leg. The discontinuity in the ClO mixing ratio in the dive segment is almost certainly a manifestation of the aircraft recrossing the edge of the CPR.

Although we used the observed vertical gradient in [ClO] and [O₃] for this flight to eliminate variations in ClO and O₃ resulting from fluctuations in Θ , the corrections were extremely small. Figure 4 tracks the simultaneously obtained ClO and O₃ mixing ratios between 66°–72°S for a potential temperature of 425 K. While it is clear that the penetration distance is limited on this flight, it is also clear that a pattern is beginning to develop in the relationship between ClO and O₃, namely, that as the ClO mixing ratio increases when the aircraft crosses into the CPR, the ozone mixing ratio clearly decreases in response. On August 28 ozone has dropped by some 23% in the region of maximum [ClO]/[M] at 72°S latitude. This represents very significant ozone loss, although it pales in comparison with what is to come.

On August 30, 2 days later, the circumpolar jet had shifted significantly northward and the aircraft penetrated deeply into the vortex, as Figure 5 reveals. This provides

critical insight because the 425 K isentropic surface was adhered to fairly rigorously, yet the latitudinal gradient in ClO showed clear evidence of flattening as the aircraft reached its southernmost point. This behavior suggests that a ClO mixing ratio characteristic of the interior of the CPR was approached on this flight. Figures 5b and 5c demonstrate the well-behaved vertical gradient in both O₃ and ClO. This provides the data needed to eliminate fluctuations induced by excursions of the aircraft from an isentropic surface.

Figure 6 traces the developing relationship between ClO and O₃ for a fixed potential temperature surface of 425 K through the edge of the CPR. By this third flight, 7 days after the first flight, significant erosion of ozone was apparent. In addition, there is clear evidence in Figure 6 for a developing anticorrelation between ClO and O₃ as the aircraft traverses the boundary of the CPR. Another signature of the ClO–O₃ anticorrelation apparent in Figure 6 is that the most dramatic removal of O₃ appears in the vicinity of the maximum gradient in the ClO mixing ratio. This would appear to be counterintuitive, given the quadratic dependence of O₃ loss rate on the ClO concentration that the ClO-dimer mechanism suggests [see Molina and Molina, 1987; Anderson *et al.*, this issue]. What we believe causes this accentuated O₃ loss close to the wall is the temporal evolution of the ClO concentration prior to this flight series. Specifically, in the early to middle part of August, ClO concentrations were highest just poleward of the jet that defines and confines the CPR, because that is the region initially illuminated by UV

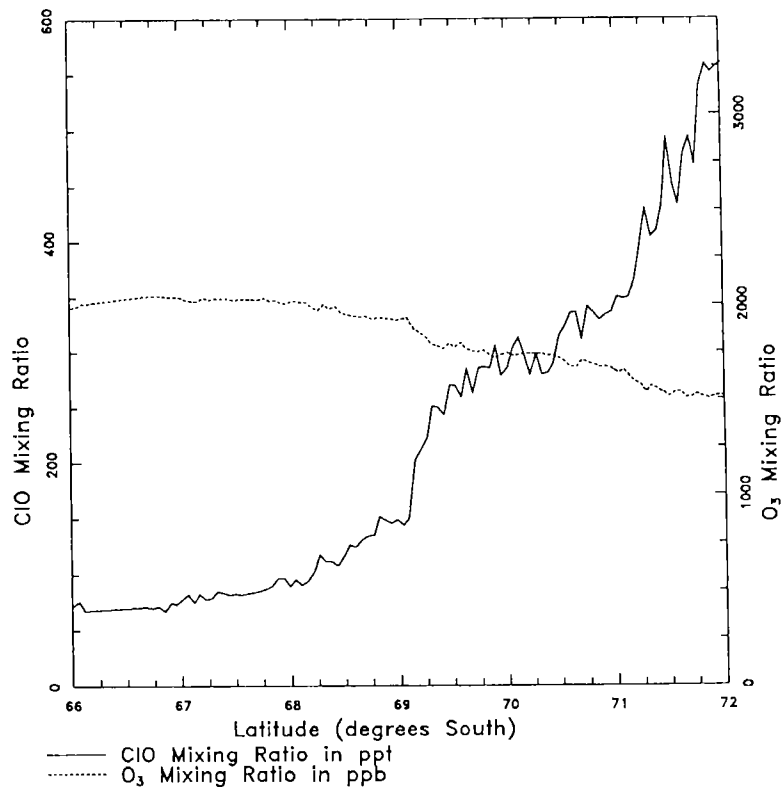


Fig. 4. Simultaneously observed ClO and O₃ obtained on August 28, 1987, by the ER-2, with corrections made for variations in potential temperature. Results shown here correspond to what the aircraft would have observed on a 425 K isentropic surface.

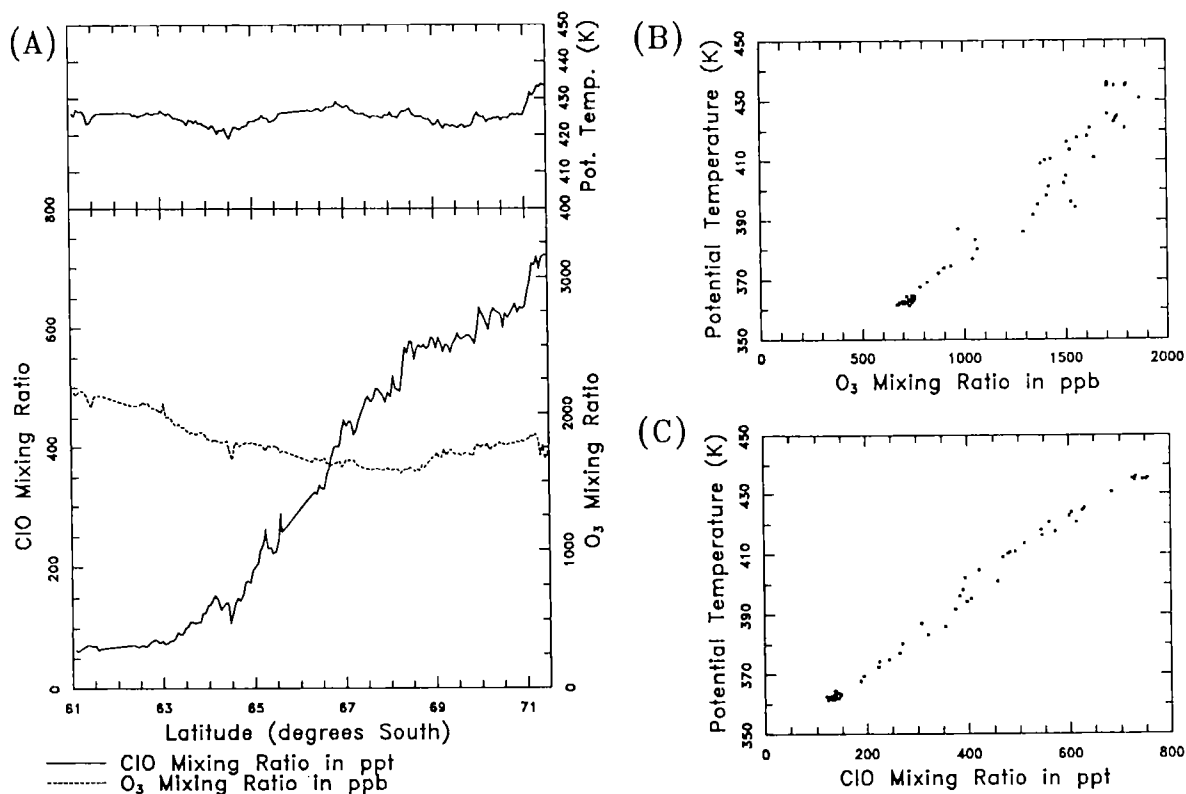


Fig. 5. Summary of the ClO and O₃ data obtained between 62°–72°S latitude by the ER-2 aircraft on August 30, 1987. (a) The simultaneous ClO–O₃ data and the potential temperature followed by the aircraft. (b) The vertical distribution of O₃ at the southernmost point of the flight trajectory, obtained when the aircraft dove from ~18.5 km to ~13 km altitude. (c) The vertical distribution of ClO obtained on the same flight track at 72°S.

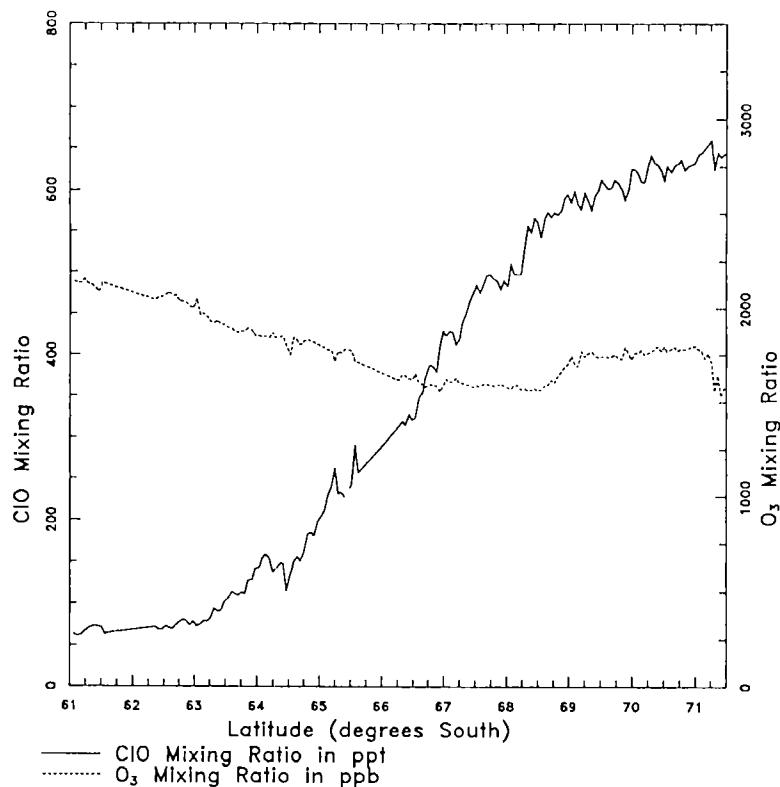


Fig. 6. Simultaneously observed ClO and O₃ obtained on August 30, 1987, by the ER-2, with corrections made for variations in potential temperature. Results shown here correspond to what the aircraft would have observed on a 425 K isentropic surface.

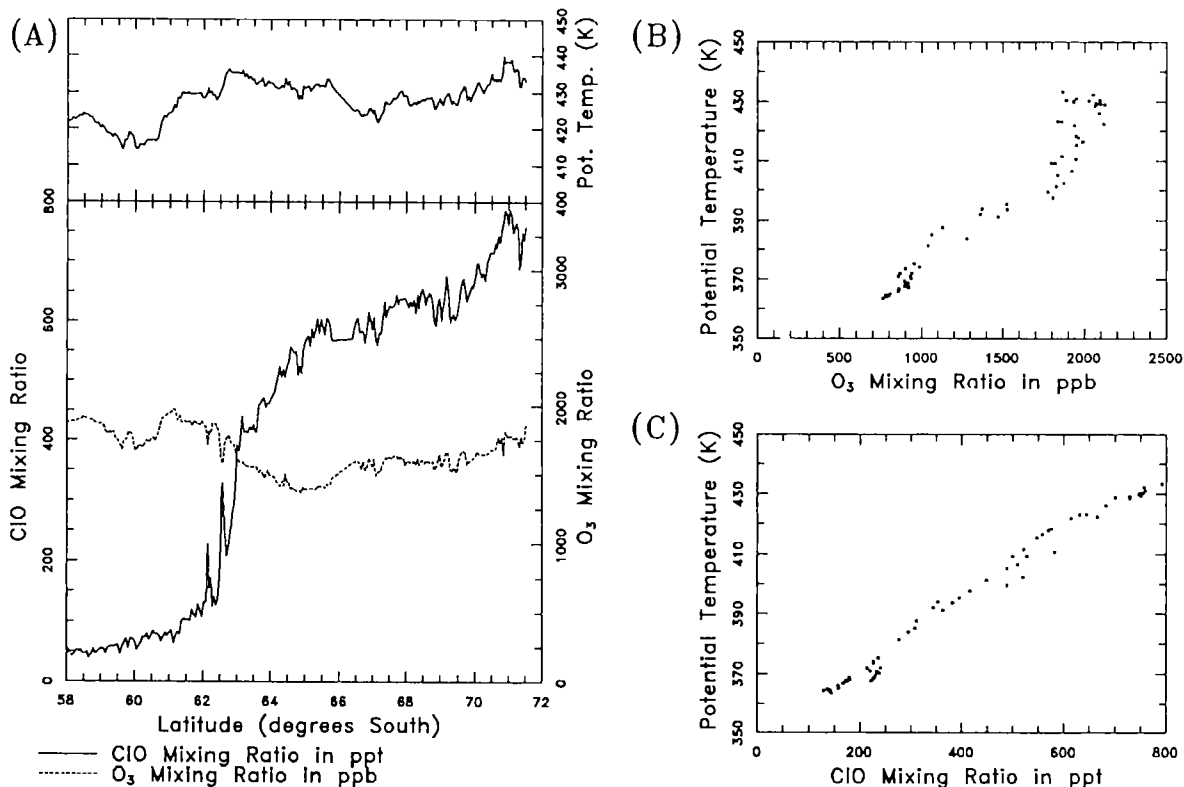


Fig. 7. Summary of the ClO and O₃ data obtained between 62°–72°S latitude by the ER-2 aircraft on September 2, 1987. (a) The simultaneous ClO–O₃ data and the potential temperature followed by the aircraft. (b) The vertical distribution of O₃ at the southernmost point of the flight trajectory, obtained when the aircraft dove from ~18.5 km to ~13 km altitude. (c) The vertical distribution of ClO obtained on the same flight track at 72°S.

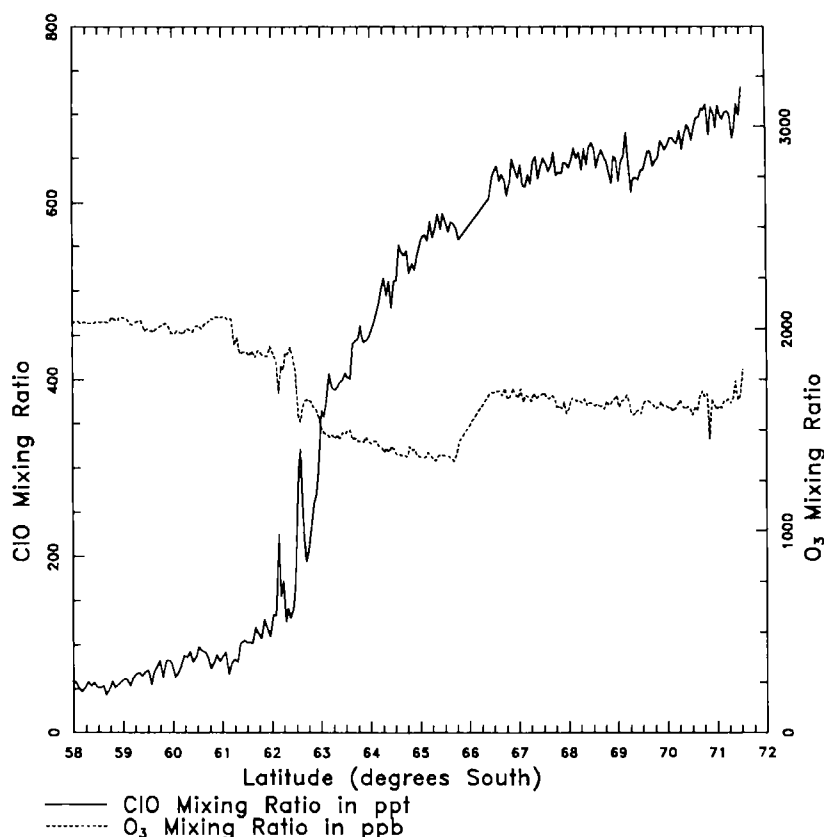


Fig. 8. Simultaneously observed ClO and O₃ obtained on September 2, 1987, by the ER-2, with corrections made for variations in potential temperature. Results shown here correspond to what the aircraft would have observed on a 430 K isentropic surface.

radiation during austral winter. Thus ozone began to erode first at the equatorward extremity of the CPR; the catalytic destruction then migrates poleward as the solar declination angle increases.

Three days later, on September 2, the aircraft again penetrated a significant distance into the vortex, as the circumpolar jet remained well north of its mean position. Figure 7a reveals the edge of the CPR at $\sim 63^\circ\text{S}$ latitude, providing a full 9° of intravortex data. On this particular flight the isentropic surface was not adhered to with great precision, but the results were not significantly compromised. Figures 7b and 7c demonstrate once again the well-behaved vertical gradients in ClO and O₃, which can then be used to largely eliminate fluctuations resulting from Θ surface departures. Figure 8 summarizes the relationship between ClO and O₃ on an isentropic surface corresponding to a potential temperature of 430 K. Three characteristics bear notice. First, the gradient in ClO which clarifies the edge of the ozone depletion region is clearly defined in Figure 8, revealing the characteristic "gouge" in O₃ just poleward of the CPR edge. Second, the percentage of ozone depletion is approaching 30% at this Θ level (which corresponds in altitude approximately to the ozone maximum at these latitudes). Finally, strong evidence for microstructure is appearing along the wall of the CPR. In the vicinity of 62°S there are at least two clearly defined spikes in the ClO mixing ratio, which correspond precisely in space to local minima in the O₃ concentration. This behavior provided a hint of what was to come.

Two days later, on September 4, 1987, a repeat performance was recorded. As Figure 9 demonstrates, the vortex edge was favorably positioned to allow nearly 8° of penetration into the CPR through a clearly defined edge in the ClO mixing ratio. Although adherence to a fixed isentropic surface was not precise, the well-behaved vertical distribution of ClO and O₃ rendered these Θ variations inconsequential. What Figure 10 reveals is a clearly developing ozone depletion region, which would stand as strong evidence implicating chlorine in the destruction of Antarctic ozone (when supported by a quantitatively defensible mechanism for catalytic destruction of O₃ by chlorine), even if this had been the last flight of the series. Figure 10 demonstrates that ozone levels had dropped by 40% within the CPR by the middle of the first week of September. In any other region of the stratosphere this would be dramatic indeed, for the clarity of the pattern in ClO-O₃ variance is unmistakable. A remarkable feature of the results obtained on September 4 was the absence of significant density fluctuations on the microscopic scale. Figure 10 shows a very simple two-regime pattern in ClO: a single, sharp transition connecting the CPR, characterized by ClO mixing ratios approaching 1 ppb, with the equatorward segment, characterized by ClO mixing ratios less than 100 pptv.

Five days later, on September 9, the aircraft adhered nearly perfectly to an isentropic surface, achieving 8° of penetration even though flight requirements restricted the trajectory to 68°S latitude. Figure 11 summarizes these results, which require virtually no correction for fluctuations

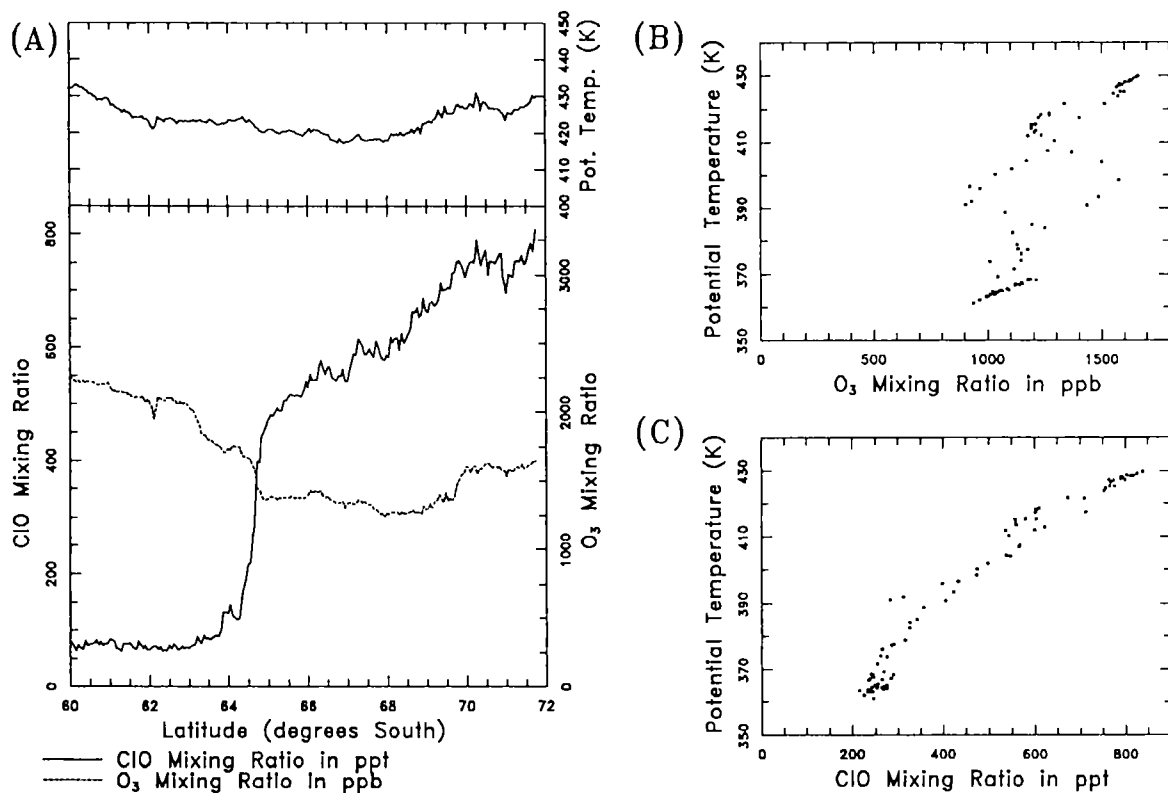


Fig. 9. Summary of the ClO and O₃ data obtained between 62°–72°S latitude by the ER-2 aircraft on September 4, 1987. (a) The simultaneous ClO–O₃ data and the potential temperature followed by the aircraft. (b) The vertical distribution of O₃ at the southernmost point of the flight trajectory, obtained when the aircraft dove from ~18.5 km to ~13 km altitude. (c) The vertical distribution of ClO obtained on the same flight track at 72°S.

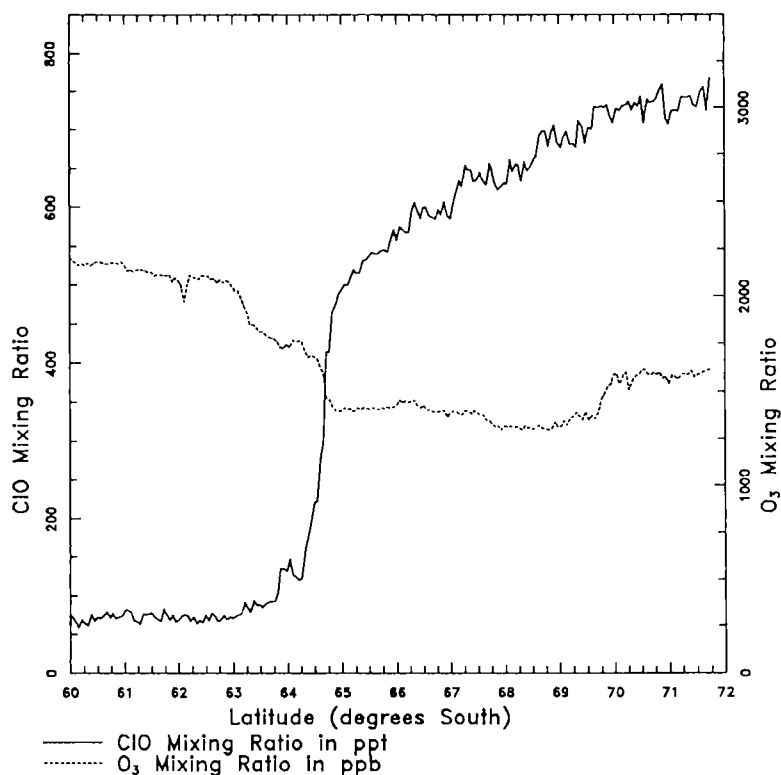


Fig. 10. Simultaneously observed ClO and O₃ obtained on September 4, 1987, by the ER-2, with corrections made for variations in potential temperature. Results shown here correspond to what the aircraft would have observed on a 425 K isentropic surface.

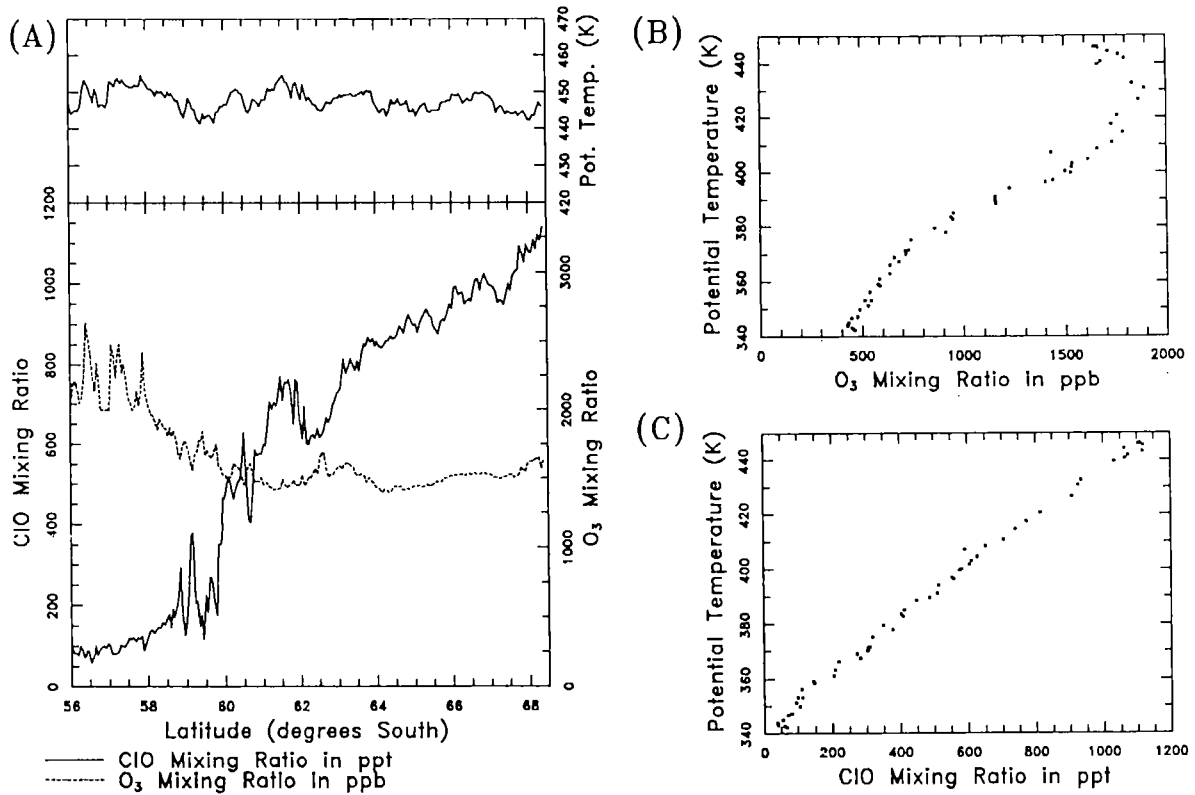


Fig. 11. Summary of the ClO and O₃ data obtained between 62°–72°S latitude by the ER-2 aircraft on September 9, 1987. (a) The simultaneous ClO–O₃ data and the potential temperature followed by the aircraft. (b) The vertical distribution of O₃ at the southernmost point of the flight trajectory, obtained when the aircraft dove from ~18.5 km to ~13 km altitude. (c) The vertical distribution of ClO obtained on the same flight track at 72°S.

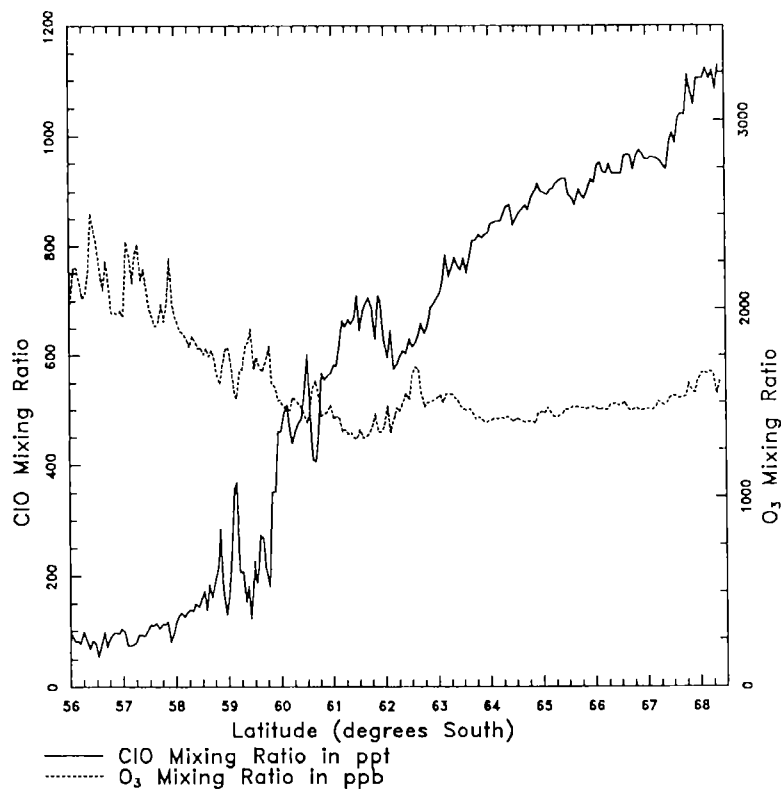


Fig. 12. Simultaneously observed ClO and O₃ obtained on September 9, 1987, by the ER-2, with corrections made for variations in potential temperature. Results shown here correspond to what the aircraft would have observed on a 445 K isentropic surface.

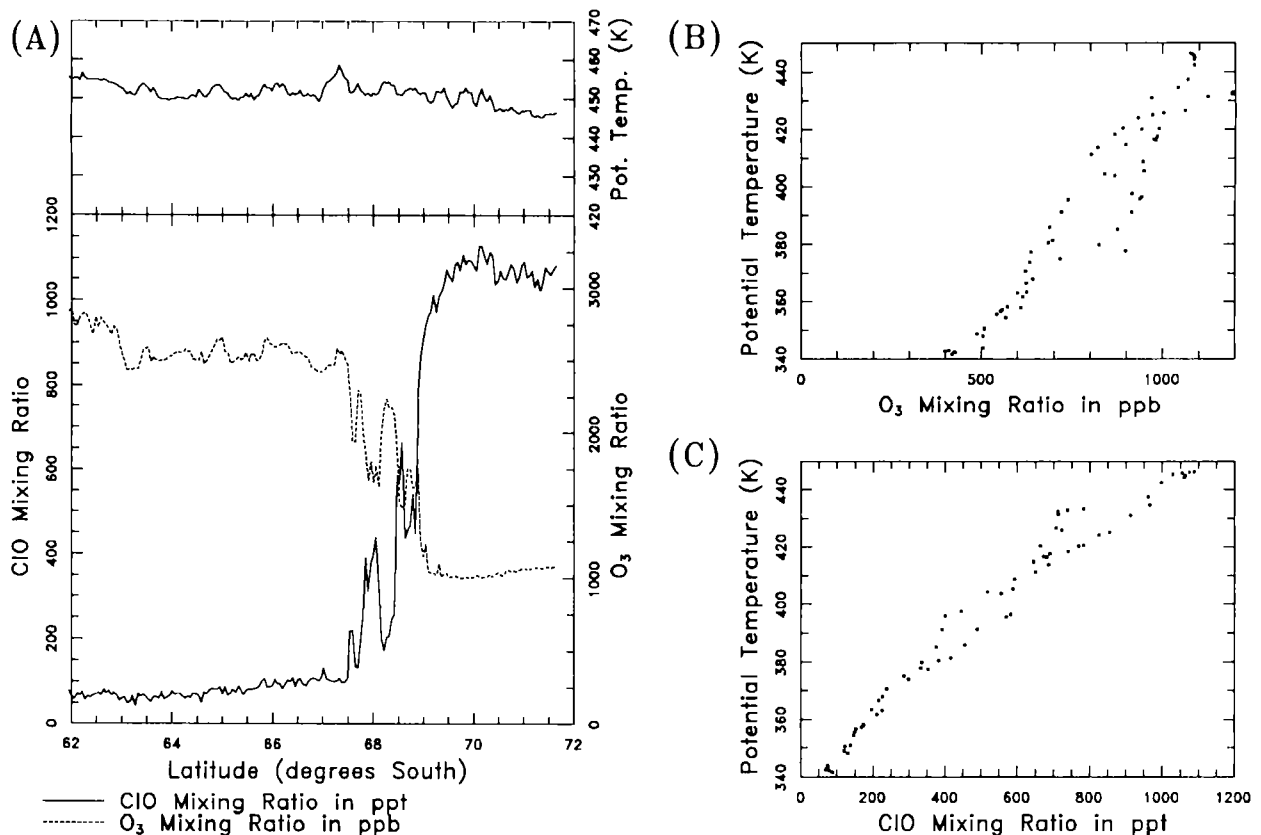


Fig. 13. Summary of the ClO and O₃ data obtained between 62°–72°S latitude by the ER-2 aircraft on September 16, 1987. (a) The simultaneous ClO–O₃ data and the potential temperature followed by the aircraft. (b) The vertical distribution of O₃ at the southernmost point of the flight trajectory, obtained when the aircraft dove from ~18.5 km to ~13 km altitude. (c) The vertical distribution of ClO obtained on the same flight track at 72°S.

in Θ . For consistency, however, we use the observed vertical gradient in ClO and O₃ to establish the behavior of ClO and O₃ on a fixed Θ surface. Those results are shown in Figure 12.

While the general pattern displayed in Figure 12 reflects to first order what has evolved through the course of five previous flights, the details are distinct in their character. First, there is a great deal of fine structure in [ClO] and [O₃] in the region of the ClO gradient (59°–62°S). Second, the ClO gradient has flattened considerably, weakening the clear delineation of the CPR wall, which characterized, for the most part, the previous data sets. There is also strong evidence for anticorrelation between ClO and O₃ within this small-scale structure. A simple analysis of ozone loss, estimated by comparing the ozone mixing ratio outside of and within the CPR on the 445 K isentropic surface, indicates that by September 9, O₃ has dropped by approximately 40% within the CPR. It should also be noted that little evidence remains in the data of Figure 12 for a “step” in the ozone abundance at greater penetration distances into the vortex. As noted in the previous discussion, the cause for the accentuated O₃ removal at the poleward edge of the CPR results from the fact that in the early stages of the “ozone hole” formation, the ClO concentration is strongly peaked in that region. By the end of the first week of September, the system has been exposed to UV radiation for a sufficient period and over a wide enough latitude range to wash out this initial signature.

Poor weather conditions in Punta Arenas prevented deployment of the aircraft for a full week following the flight of September 9. On September 16 the aircraft adhered with considerable precision to the 450 K isentropic surface and achieved 5° latitude penetration into the CPR. Those results are summarized in Figure 13. The development of [ClO]–[O₃] anticorrelation exhibits a demarcation at the edge of the CPR, which is for the first time nearly as dramatic for O₃ as it has been for ClO on previous flights. The transition region in the vicinity of 69°S is narrower than any previous data set. The ribbons of high ClO stripped from the poleward edge of the vortex wall retain their chemical identity over extremely small horizontal spatial scales. Virtually every volume element down to the resolution of the instrument (<1 km) that contains enhanced ClO is characterized by suppressed O₃ concentrations.

Figure 14 places both the ClO and O₃ data on a 450 K isentropic surface, but the corrections are negligible. An inspection of Figure 14 does, however, reveal an array of interesting detail. First, note the absence of a latitudinal gradient in both ClO and O₃ poleward of the CPR edge. As we noted in earlier data sets, this has been a developing characteristic of O₃, but not so distinctly of ClO. Second, the width of the transition zone defining the edge of the CPR and the achievement of true intravortex values of [ClO] are more sensitively dependent on the details of dynamical fields (for example, velocity, potential vorticity) poleward of the jet than of time throughout the course of the ER-2

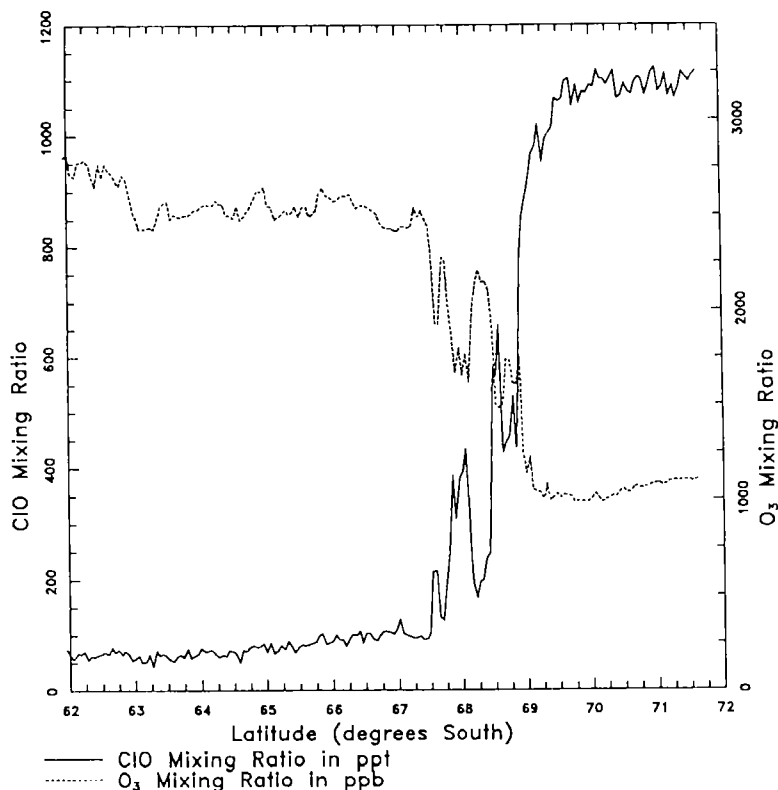


Fig. 14. Simultaneously observed ClO and O₃ obtained on September 16, 1987, by the ER-2, with corrections made for variations in potential temperature. Results shown here correspond to what the aircraft would have observed on a 450 K isentropic surface.

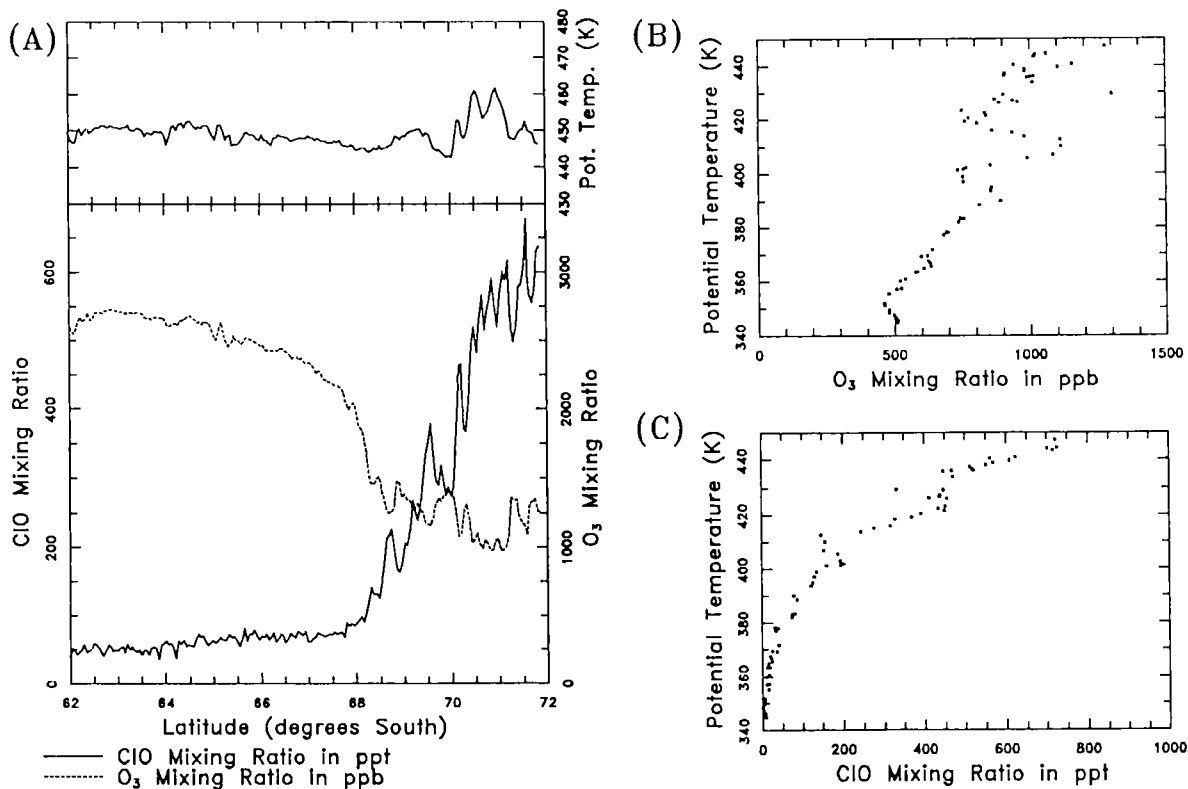


Fig. 15. Summary of the ClO and O₃ data obtained between 62°–72°S latitude by the ER-2 aircraft on September 20, 1987. (a) The simultaneous ClO–O₃ data and the potential temperature followed by the aircraft. (b) The vertical distribution of O₃ at the southernmost point of the flight trajectory, obtained when the aircraft dove from ~18.5 km to ~13 km altitude. (c) The vertical distribution of ClO obtained on the same flight track at 72°S.

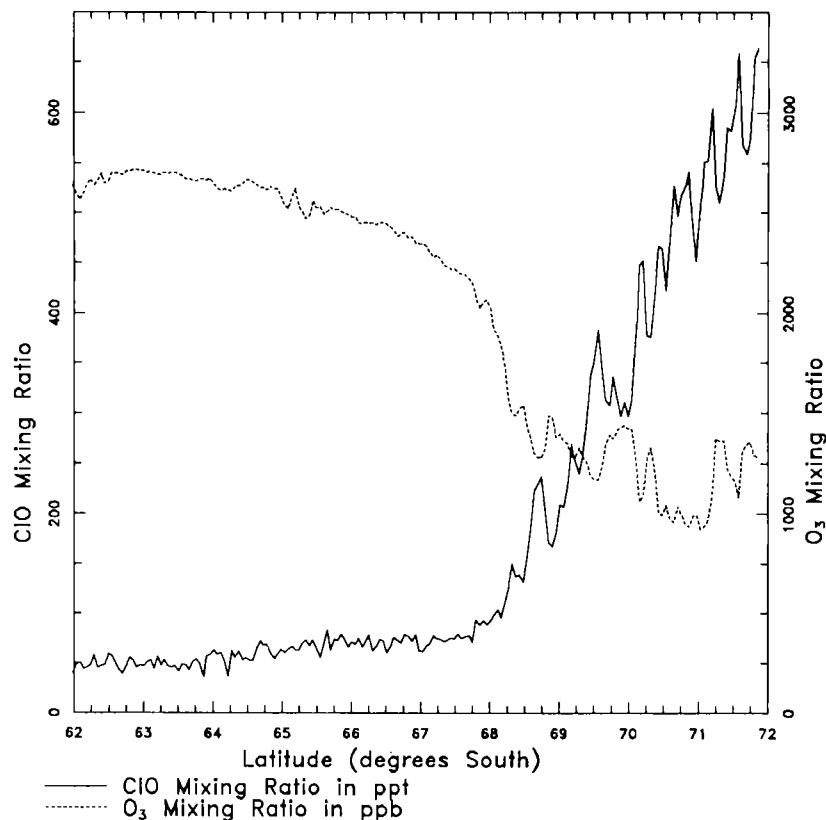


Fig. 16. Simultaneously observed ClO and O₃ obtained on September 20, 1987, by the ER-2, with corrections made for variations in potential temperature. Results shown here correspond to what the aircraft would have observed on a 450 K isentropic surface.

flight series. If anything, the [ClO] gradient steepened in the data sets obtained in late September. Considerable insight into this question can be obtained by inspection of potential vorticity maps in the vicinity of the region penetrated by the ER-2 on each of these flights. Finally, we can estimate the percentage loss of O₃ within the CPR on the 450 K surface quite easily by inspection of Figure 14. By September 16, ozone has decreased within the CPR from approximately 2.6 ppm to 1.0 ppm, a drop of just over 60%.

The next flight took place on September 20, 1987. The results are summarized in Figure 15. Analysis of potential vorticity contours at flight altitude reveal that this flight was unusual in that the aircraft trajectory penetrated a fold in the isentropic potential vorticity (IPV) surface [see *Newman et al.*, 1988]. This meant that the flight trajectory nearly paralleled the edge of the CPR and did not penetrate deeply into the vortex. Nevertheless, the results are revealing. Equatorward of the edge of the CPR, O₃ has a mixing ratio of ~ 2.5 parts per million by volume (ppmv) and ClO is present at ~ 80 pptv. As the aircraft begins to penetrate the CPR on a trajectory nearly parallel to the edge, the data reflect a series of vortex wall entry-exit events. In each case those volume elements characterized by high ClO levels exhibit suppressed ozone concentrations. As the envelope of the ClO mixing ratio grows, the envelope of ozone mixing ratios decreases. The large scatter in the ozone mixing ratio at higher potential temperatures is a graphic display of both the entry-exit pattern along the IPV fold and the significant impact that the catalytic loss of O₃ has on the ozone distribution in late September.

Further evidence of the turbulence associated with the inner wall of the vortex in the region where the ER-2 penetrated is the unique vertical profiles of O₃ and ClO displayed in Figures 15b and 15c. The ozone profile shows tremendous scatter in the dive segment, with an upper envelope approaching values observed outside the CPR. ClO, on the other hand, exhibits a very steep vertical gradient, dropping to less than 20 pptv in the vicinity of the 360 K surface. The behavior of both the O₃ and ClO vertical distribution strongly implies that the aircraft recrossed the edge of the CPR during the descent phase of the flight trajectory at 72°S latitude.

Variations resulting from changes in the Θ surface followed by the aircraft are removed in Figure 16, which displays the ClO-O₃ data on a 450 K isentropic surface. Again, the anticorrelation between ClO and O₃ is apparent south of 68°S latitude on all spatial scales resolved by the instrument.

The following day, September 21, the aircraft clearly traversed the CPR wall, but it only penetrated 2° inside the region. These results are summarized in Figure 17. Again, the transition is very sharp, indicating the perpendicular penetration of the aircraft through the vortex wall within which the ozone concentration has dropped to 30% of its original level of ~ 2.5 ppmv, a mixing ratio maintained outside the CPR.

There was a clear correlation between the latitude of the vortex wall and the weather conditions in the vicinity of Punta Arenas. Under ideal flying conditions, characterized by a high-pressure region over the southern tip of South

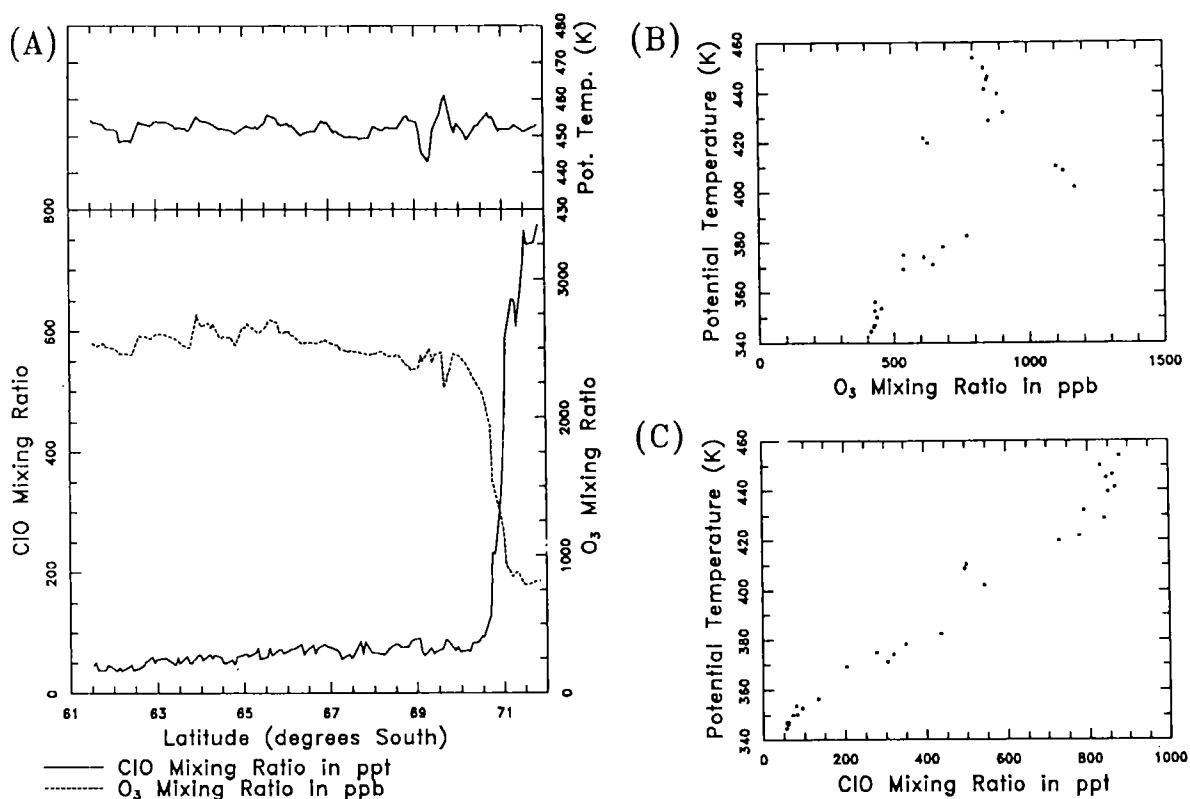


Fig. 17. Summary of the ClO and O₃ data obtained between 62°–72°S latitude by the ER-2 aircraft on September 21, 1987. (a) The simultaneous ClO–O₃ data and the potential temperature followed by the aircraft. (b) The vertical distribution of O₃ at the southernmost point of the flight trajectory, obtained when the aircraft dove from ~18.5 km to ~13 km altitude. (c) The vertical distribution of ClO obtained on the same flight track at 72°S.

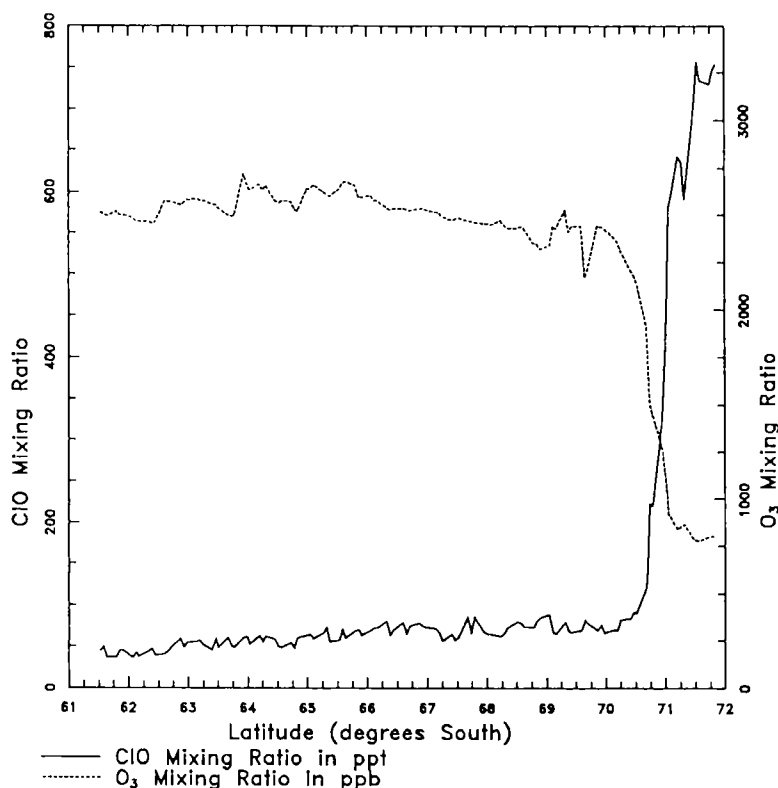


Fig. 18. Simultaneously observed ClO and O₃ obtained on September 21, 1987, by the ER-2, with corrections made for variations in potential temperature. Results shown here correspond to what the aircraft would have observed on a 450 K isentropic surface.

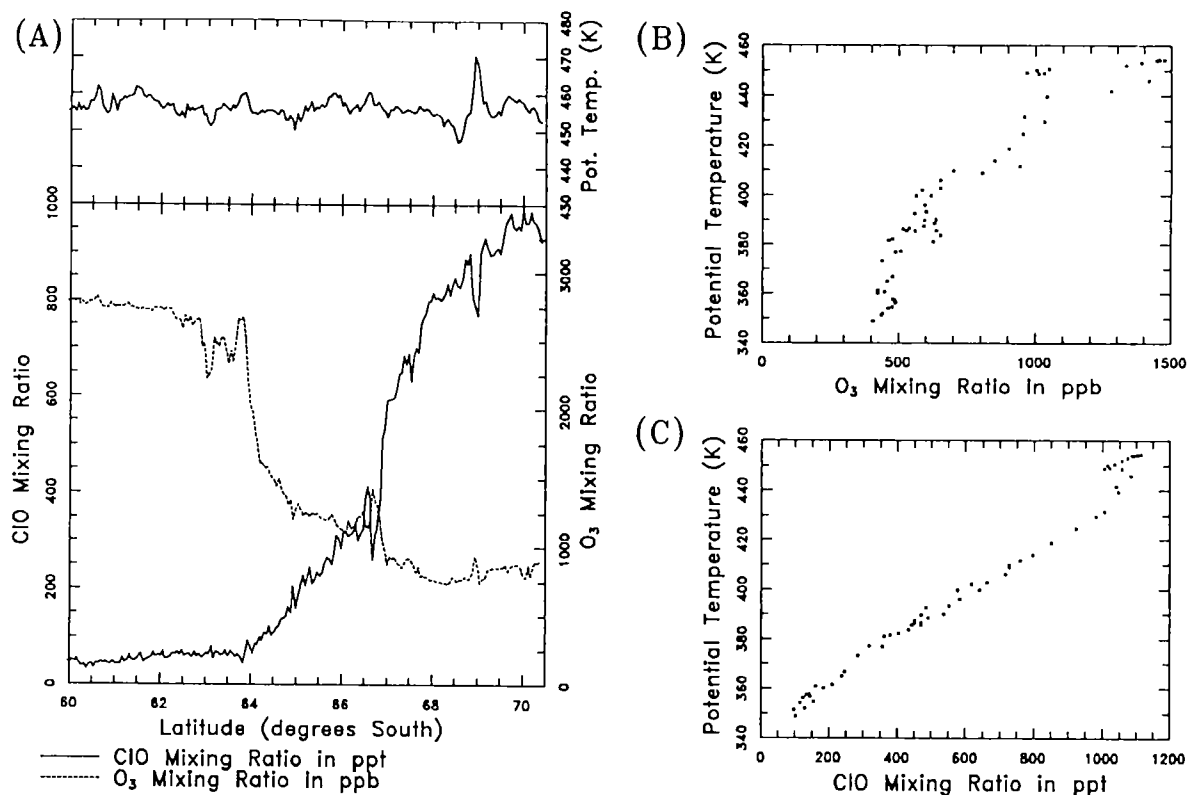


Fig. 19. Summary of the ClO and O₃ data obtained between 62°–72°S latitude by the ER-2 aircraft on September 22, 1987. (a) The simultaneous ClO–O₃ data and the potential temperature followed by the aircraft. (b) The vertical distribution of O₃ at the southernmost point of the flight trajectory, obtained when the aircraft dove from ~18.5 km to ~13 km altitude. (c) The vertical distribution of ClO obtained on the same flight track at 72°S.

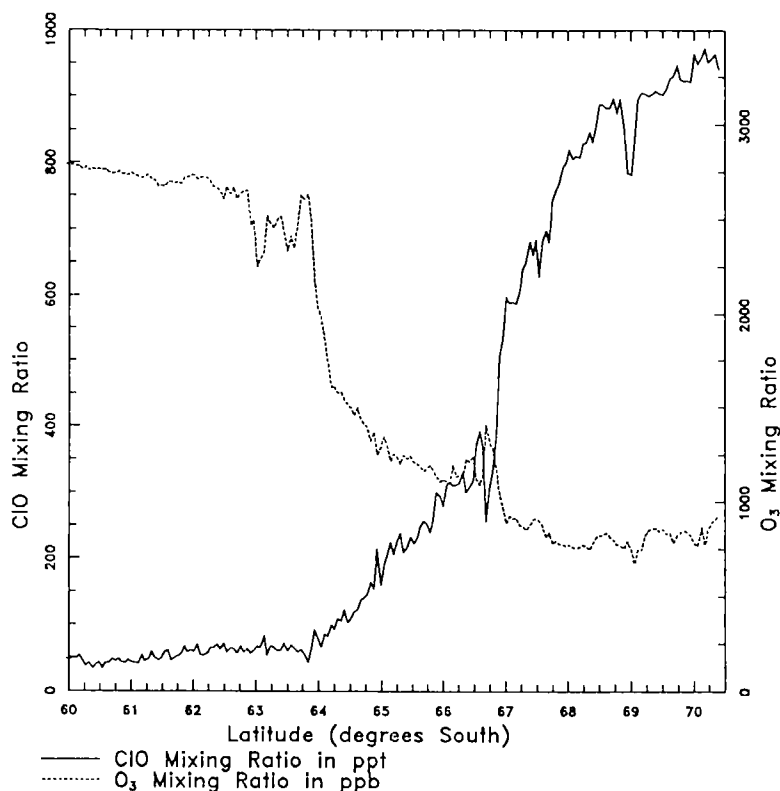


Fig. 20. Simultaneously observed ClO and O₃ obtained on September 22, 1987, by the ER-2, with corrections made for variations in potential temperature. Results shown here correspond to what the aircraft would have observed on a 455 K isentropic surface.

America, the vortex wall was pushed significantly to the south. This was, in fact, the case on September 21, 1987. However, the exceedingly steep gradient in ClO resulted in observed mixing ratios of nearly 1000 pptv; the response of ozone to those densities is clear.

Vertical profiles of O₃ and ClO are displayed in Figures 17b and 17c. There is evidence that the aircraft recrossed the CPR wall in the vicinity of the 400 K surface. There is also a clearly developing signature in the ozone vertical distribution, characterized by a distinct flattening of the O₃ vertical gradient above the 360 K surface. Contrast, for example, the data in Figure 17b with Figure 1b.

Figure 18 eliminates variations resulting from imperfect adherence of the aircraft to the 450 K isentropic surface. What is perhaps most dramatic about these data, apart from what has been treated in the preceding discussion, is the clarity of the transition into the CPR. The ClO mixing ratio increases by a factor of 20 within 0.2° latitude, which corresponds to a horizontal displacement of less than 10 km. Maintaining gradients of this magnitude represents a critical test of horizontal mixing lengths.

September 22, 1987 marked the third day in a row that a mission was completed, and it marked the last flight into the Antarctic for this expedition. Figure 19 summarizes both the horizontal and the vertical distribution of ClO and O₃ obtained on September 22. A penetration of 7° latitude into the CPR was obtained, as the vortex wall had shifted its position well north up the Palmer Peninsula. What is particularly unique about these data is the relationship between ClO and O₃ at the CPR wall, that is, in the vicinity of 64°–66°S latitude. There is a clear spatial separation between the maximum in the [O₃] gradient, which occurs at 64°S latitude, and the [ClO] gradient, which occurs at 67°S latitude. This may be the first sign of chemical "aging" along the vortex wall. Specifically, the chemical time constant for ClO removal is much shorter than that of ozone, particularly if NO₂ is reintroduced by mixing across the CPR wall. Thus the absence of ClO in the latitude slice between 64°–67°S in the region of significantly depleted ozone may simply reflect the rapid conversion of ClO to ClONO₂ by nitrogen oxides, with the accumulated destruction of O₃ still retained in the ozone record.

As in all previous flights, we display the ClO-O₃ data for a flight at fixed potential temperature in Figure 20, in this case 455 K. These data reveal that by the end of the third week of September, nearly 75% of the ozone has been eliminated at the 18.5-km altitude level.

SUMMARY AND CONCLUSION

While the existence of anticorrelation between two variables does not in itself prove a causal relation, we present a case here for the observed evolution of a system from (1) an initial condition exhibiting dramatically enhanced (X500) ClO mixing ratios, which define a chemically perturbed region within which ozone is marginally depleted (~15%) in middle to late August, to (2) a situation in which the dramatic increase in ClO recorded on surfaces of fixed potential temperature was spatially coincident with a precipitous

decrease in ozone mixing ratio. This development of negative correlation between O₃ and ClO, which occurs at a rate predicted by a kinetic analysis of catalytic destruction by halogen radicals, constitutes the basis for our conclusion that the disappearance of ozone within the Antarctic vortex results from halogen-catalyzed recombination of O₃ to molecular oxygen. When taken with an analysis of the kinetics of ozone destruction by halogen radicals [see Anderson *et al.*, this issue], this constitutes the case linking chlorine compounds, and thus the release of chlorofluorocarbons at the surface, to the destruction of ozone within the Antarctic polar vortex.

Acknowledgments. A very large number of individuals were directly responsible for the success of this mission. Within the Harvard community the most notable are Nate Hazen, Joe Demusz, Norton Allen, Maria Mueller, Lenny Solomon, Elliot Weinstock, Rick Stimpfle, Jim Schwab, Ed Thompson, Joe Freitas, Ed Dobbey, Terry Schiller, Bob Heroux, and Gregory Freytsis. Paul Soderman, of the Ames Large-Scale Aerodynamics Group, played a critical role in the design of the double-ducting system used in the experiment. Art Schmeltekopf gave invaluable advice and was largely responsible for teaching us the lore of aircraft-borne experimentation. Bill Ferguson of Lockheed was the critical element in our interface with the ER-2 aircraft. Within the Ames High-Altitude Branch we were given superb cooperation and guidance by John Arvesen and Jim Barrilleaux. Estelle Condon provided considerable help, with extraordinary patience. Finally, the mission rested with the pilots, whose commitment and courage defined this mission: Ron Williams, Jerry Hoyt, Jim Barrilleaux, Doyle Krumrey, and Jim Barnes. Jim Cherbonneaux and Marty Knutson provided essential leadership and perspective. This research was supported by NASA contracts NASW 3960 and NAG 2-443, under Robert T. Watson.

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Kinetics of O₃ Destruction by ClO and BrO Within the Antarctic Vortex: An Analysis Based on in Situ ER-2 Data

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Simultaneous, in situ observations of ClO, BrO, O₃, N₂O, pressure, and temperature are used to examine the kinetics of ozone destruction within the Antarctic polar vortex. The high azimuthal symmetry of the vortex is used to simplify the problem such that the time rate of change of ozone on isentropic surfaces between 450 and 360 K (18.3- to 13.5-km geometric altitude) can be calculated based on proposed catalytic cycles involving ClO, BrO, HO₂ and O(³P). The availability of simultaneous, spatially resolved data on N₂O, pressure, and temperature is used to reduce scatter in observed O₃; this clarifies the quantitative analysis of ozone loss rates on isentropic surfaces. The kinetics of ozone destruction is thus cast in an N₂O-potential temperature coordinate system to suppress atmospheric variability. We conclude, based upon observed radical concentrations and the most recent laboratory kinetics data, that the chlorine dimer mechanism (Molina and Molina, 1987) rate limited by $\text{ClO} + \text{ClO} + M \rightarrow \text{ClOOC}l + M$, referred to herein as mechanism I, constitutes the largest single contribution to the integrated rate of ozone destruction within the vortex on isentropic surfaces between altitudes of 14 and 18.3 km. We find that approximately 40% of the observed ozone loss rate in this altitude interval results from this mechanism, using the recently established pressure and temperature dependence for the rate of dimer formation reported by Sander et al. (1989). The coupled bromine-chlorine catalytic cycle (McElroy et al., 1986) rate limited by $\text{ClO} + \text{BrO} \rightarrow \text{Cl} + \text{Br} + \text{O}_2$ (herein mechanism II) constitutes approximately 20% of the ozone loss rate integrated over the course of the mission, August 23 to September 22, 1987. Mechanism III, suggested by Solomon et al. (1986), which is rate limited by $\text{ClO} + \text{HO}_2 \rightarrow \text{HOCl} + \text{O}_2$ (in close competition with $\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$), constitutes 4% of the observed ozone loss rate based on observed ClO, but calculated HO₂ concentrations. We find that the time-honored catalytic coupled $\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2$ followed by $\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$, identified by Molina and Rowland (1974) as the key reaction linking chlorofluorocarbon release to middle- and low-latitude stratospheric ozone depletion, constitutes 3% of the observed loss in the Antarctic vortex. The sum of all four mechanisms thus constitutes 65% of the observed O₃ loss with an experimental uncertainty of $\pm 30\%$. An array of other halogen-oxygen radical catalytic cycles are considered. The manifold of possible catalytic cycles is large, particularly when the temperature and pressure regime characteristic of the Antarctic lower stratosphere is considered. Quantitative analysis is impeded primarily by the absence of laboratory data on key reaction rates. For example, a potentially critical alternative channel, designated herein as mechanism V, is the termolecular process $\text{ClO} + \text{O}_3 + M \rightarrow \text{ClO} \cdot \text{O}_3 + M$, followed by photolysis, for which no kinetic data exist. Explicit note is also taken, in the quantitative conclusions, of the ozone flux divergence within the chemically perturbed region reported by Hartmann (1989). This constitutes an additional $20 \pm 10\%$ requirement on the rate of chemical removal.

INTRODUCTION

It is rare in the study of atmospheric chemistry that we have the luxury of mechanistic analyses based on simultaneous, in situ observations of chemical reactants. However, given spatially resolved observations of ClO, BrO, and O₃, obtained from the ER-2 aircraft [Brune et al., 1989a, b; Starr et al., this issue; Proffitt et al., 1989], we are in a

position to test quantitatively several proposed mechanisms that seek to define the fundamental processes linking the existence of halogen radicals to ozone destruction rates in the Antarctic vortex region.

The Airborne Antarctic Ozone Experiment (AAOE) case linking chlorofluorocarbon (CFC) release to halogen radical destruction of ozone within the Antarctic polar vortex is comprised of three elements. The first is knowledge of the absolute ClO and BrO concentrations obtained by the aircraft within the vortex region, referred to hereafter as the chemically perturbed region (CPR). That subject is dealt with by Brune et al. [1989a, b]. The second is an analysis of the evolution of the ClO-O₃ system in time and space from an initial condition, characterized by marginally perturbed O₃ concentrations within the CPR in middle to late

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August, to the condition in late September, characterized by dramatic negative correlation between O_3 and ClO as the aircraft passed from the equatorward side of the CPR to the poleward side [see Anderson *et al.*, this issue]. The third element is mechanistic in nature: an analysis of the kinetics of ozone loss on isentropic (constant potential temperature) surfaces based on (1) observed concentrations of ClO, BrO, and O_3 and (2) proposed catalytic processes controlling the destruction rate of ozone. This third element in the CFC-ozone case is the subject of this paper.

Our objective is straightforward: We wish to calculate the rate of ozone destruction on each of the potential temperature surfaces, from 360 to 450 K, that move on a circumpolar trajectory at a latitude of 72°S (the southernmost extension of the aircraft flight path), using simultaneous, in situ observations of ClO, BrO, and O_3 obtained from the ER-2. A striking characteristic of the Antarctic vortex region during the course of the aircraft mission (August 23 to September 22, 1987) was the stability of the circumpolar jet. A graphic demonstration of this is provided by the Total Ozone Mapping Spectrometer (TOMS) maps of the ozone depletion region throughout the August–October time period [see Newman *et al.*, 1988; Krueger *et al.*, 1987]. Stability in the position of the circumpolar jet is reflected in the in situ chlorine radical observations reported by Brune *et al.* [1989a]. The steep gradient in ClO mixing ratio on surfaces of constant potential temperature provides a dramatic fiducial defining the edge of the CPR.

In addition to the relative stability in the position of the chemically perturbed region, tracer data obtained from the ER-2 exhibit a remarkably predictable and reproducible spatial distribution of N_2O and the chlorofluorocarbons [see Loewenstein *et al.*, this issue; Heidt *et al.*, this issue] at 72°S latitude. This stability suggests a simple approach for the analysis of the kinetics of ozone destruction by halogen radicals throughout the course of the mission. Specifically, we will calculate the time rate of change of ozone in a volume element that circumscribes a trajectory on a fixed potential temperature surface at a fixed latitude (72°S). The appropriate continuity equation for the time rate of change of ozone is

$$d[O_3]/dt = P_{O_3} - L_{O_3} - \vec{\nabla} \cdot \vec{\phi}$$

where P_{O_3} is the photochemical production rate of ozone, L_{O_3} is the photochemical loss rate of ozone, and $\vec{\nabla} \cdot \vec{\phi}$ is the ozone flux divergence term determined for the volume element.

As can be demonstrated easily, the loss rate of ozone based on the observed concentration of ClO greatly exceeds the production rate of ozone from O_2 photolysis in August and September, so $L_{O_3} \gg P_{O_3}$, and we can write

$$-d[O_3]/dt = L_{O_3} + \vec{\nabla} \cdot \vec{\phi}_{O_3}$$

In fact, the rate of ozone loss by halogen catalysis in late August and September exceeds the rate of O_3 production by O_2 photolysis, even at the summer solstice.

Our objective is to use the in situ free radical observations in combination with each of the proposed catalytic mechanisms and with associated laboratory rate data to establish the fractional contribution each of these mechanisms makes to the experimentally observed O_3 loss rate. Given the tem-

poral development of the fractional loss rate for each mechanism as a function of altitude (potential temperature), we can then address the question of whether the observed decay rate of ozone is fully accounted for by our understanding of the rate-limiting steps in the available array of catalytic cycles. An important issue in this quantitative analysis is, of course, the magnitude of the flux divergence term, $\vec{\nabla} \cdot \vec{\phi}$ in the continuity equation for ozone. Here we accept the analysis by Hartmann *et al.* [1989] that $\vec{\nabla} \cdot \vec{\phi}$ increases the requirement for an O_3 photochemical sink by $20 \pm 10\%$, as a result of the influx of ozone into the CPR from higher altitudes and lower latitudes.

Our approach is straightforward. We wish to calculate the amount of ozone destroyed each day within a volume element located on a given isentropic surface at 72°S latitude by each of the proposed mechanisms. Thus for day i , mechanism j :

$$(\Delta O_3)_i^j = \int_{24 \text{ hours}} L_i^j dt$$

The total amount of ozone destroyed over a given period of n days is thus

$$(\Delta O_3)^j = \sum_{i=1}^n (\Delta O_3)_i^j$$

This will be true on each potential temperature (Θ) surface. Thus we must establish the time evolution of ClO on each Θ surface, based on the flight data at 72°S , and relate the observed midday concentration to the diurnal variation of ClO for each day. Finally, we must subtract the amount of ozone lost in each 24-hour period by ClO-catalyzed reactions from the remaining amount to establish the time dependence of the ozone removal rate for comparison with the simultaneously observed ozone concentrations.

We begin with a summary of proposed mechanisms for catalytic destruction of ozone by halogen radicals. The discussion is cast in terms of the appropriate rate-limiting steps and the observed ClO and BrO concentrations. Next, we present a synthesis of the temporal development of ClO on isentropic surfaces from the first flight into the vortex, which included a vertical scan at the southern extremity (August 23) to the last flight of the series (September 22).

A discussion of the method by which midday, in situ ClO and BrO observations are used to calculate the amount of O_3 removed each day is presented. This involves approximate knowledge of the shape of the diurnal variation of ClO, BrO, HO_2 , and $O(^3P)$ through each 24-hour period. We then calculate the amount of ozone removed each day, based on observed ClO and BrO on each of 10 isentropic surfaces, 450–360 K inclusive. These decay rates are then compared with the observed ozone concentration obtained simultaneously with the free radical concentrations.

TRENDS IN ClO ON ISENTROPIC SURFACES

The first step in the comparison of calculated and observed rates of ozone loss is to establish the time development of ClO on isentropic surfaces in the “dive” region of the flight trajectories (that is, at 72°S latitude). These data are presented in Figure 1, a 10-panel display representing a linear least squares fit to the observed ClO mixing ratios. The

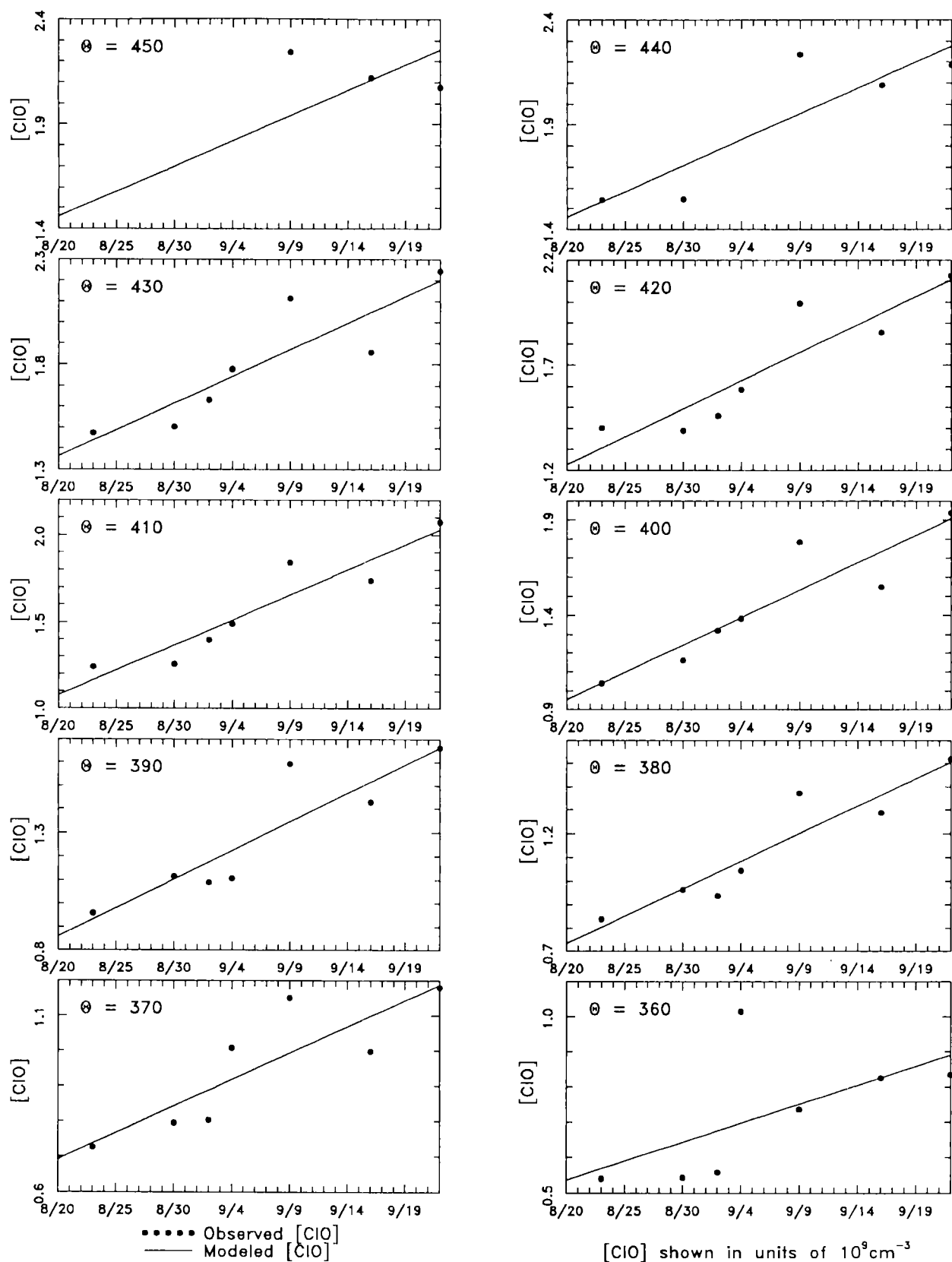


Fig. 1. Summary of the linear least squares fit to the temporal evolution of ClO on isentropic surfaces throughout the course of the mission.

data display covers the period from August 20 to September 23; the temporal development is presented on potential temperature surfaces of 450–360 K. All experimental points fall reasonably close to the least squares fit except the data of August 28, September 20, and September 21. On these days, however, there was insufficient penetration into the CPR by the ER-2 to reach representative intravortex values of ClO. In fact, on September 20, the aircraft entered the vortex in the vicinity of a potential vorticity surface fold and virtually paralleled the wall of the CPR. Given that our objective in this section is to define the temporal evolution of ClO within the CPR as a whole, rather than focusing on the region immediately poleward of the jet, we will adhere to the envelope for each isentropic surface shown in Figure 1.

DISTRIBUTION OF BrO WITH RESPECT TO POTENTIAL TEMPERATURE

The midday distribution of BrO in the CPR is a far weaker function of altitude and of time throughout the course of the mission because it constitutes a major fraction (> 70% at local noon) of the total inorganic reactive bromine budget at all altitudes. In addition, the 5 part per trillion by volume (pptv) average mixing ratio of BrO approaches the 1-pptv detection threshold of the instrument and thus limited altitude data exist [see Brune *et al.*, 1989b]. Therefore we condense our altitude-dependent BrO results into an average, which we believe is valid throughout the course of the mission; we find little evidence for any temporal trends. An altitude-independent value of 5 pptv represents our best judgment of the daytime BrO mixing ratio; we will use it in all subsequent calculations.

DEFINING THE OBSERVED RATE OF OZONE LOSS

Before presenting a graphical series comparing the observed rate of O₃ loss with rates of ozone loss based on various catalytic mechanisms, we address the question of ozone variability on isentropic surfaces resulting from variations in aircraft penetration distance into the vortex. As an example, Figure 2 presents the raw ozone data points obtained on the 420 ± 3 K potential temperature surfaces on flights between August 23 and September 22. We ignore the

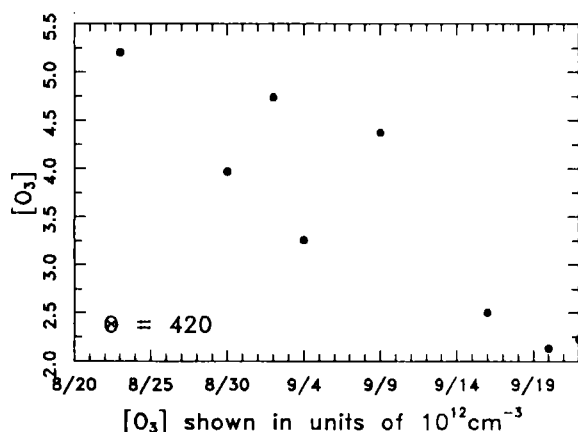


Fig. 2. The time evolution of ozone obtained from the ER-2 on the 420 ± 5 K potential temperature surface. While there is a clear downward trend, the scatter in the data significantly degrades any detailed quantitative analysis of O₃ loss rates.

flights of August 28 and September 20 because the aircraft barely penetrated the CPR wall even at maximum altitude: we are concerned here with establishing typical conditions within the CPR.

Inspection of Figure 2 reveals a pattern that is characteristic of the ozone observations on virtually all isentropic surfaces: there exists a clear downward trend in ozone concentration, but there is also considerable scatter. In order to analyze this scatter with an eye both toward understanding it and eliminating it, we begin by noting that two conserved quantities are available to us based on direct onboard measurements from the ER-2: potential temperature (Θ) and N₂O. We have made use of the former by executing our calculations on isentropic surfaces. We now make use of the latter by regressing O₃ mixing ratios against N₂O mixing ratios in the dive segment of each flight trajectory.

The reasoning is as follows: Prior to significant in situ removal by chlorine catalysis, ozone may be viewed as a dependent function of the independent variables Θ and N₂O. A surface of O₃ as a function of the orthogonal variables Θ and N₂O is well-behaved, such that specification of Θ and [N₂O] for a given volume element will yield a unique value for [O₃]. Analysis of the large gradient in N₂O across the CPR wall demonstrates that this tracer serves as a fiducial to calibrate the depth of penetration into the vortex. An elegant analysis demonstrating the stability of the N₂O, potential vorticity and Θ surfaces throughout the mission is given by Schoeberl *et al.* [1989].

We consider six examples of O₃-N₂O dependence in Figure 3, which displays the relationship between O₃ and N₂O for the dive segment of flights on August 23, 28, and 30 and September 2, 4, and 9. The remarkable consistency of these O₃ versus N₂O surfaces stands, first, as a unique and surprising signature of this mission [see Loewenstein *et al.*, this issue] and, second, as the basis for removing scatter present in the O₃ data resulting from different penetration distances into the vortex.

In order to demonstrate this, we represent the relationship between O₃ and N₂O on surfaces of (approximately) equal potential temperature. Figure 4 demonstrates a least squares fit to the O₃ versus N₂O surface at the 420 K surface. The family of curves extracted from an identical analysis for each isentropic surface from 360 to 440 K is displayed in Figure 5.

This provides the information required to reference each ozone concentration obtained in the dive segment at 72°S latitude to a standard N₂O concentration valid prior to significant chemical loss on each of the 10 isentropic surfaces. If we define a reference N₂O mixing ratio, $f_{\text{ref}}^{\text{N}_2\text{O}}$, for each surface, then a simple Taylor series correction to the observed O₃ concentration at any other N₂O mixing ratio, $f_{\text{obs}}^{\text{N}_2\text{O}}$, is given by

$$[\text{O}_3] = [\text{O}_3]_{\text{obs}} + \Delta\text{O}_3/\Delta\text{N}_2\text{O} \left(f_{\text{obs}}^{\text{N}_2\text{O}} - f_{\text{ref}}^{\text{N}_2\text{O}} \right)$$

This is demonstrated for a series of Θ surfaces by comparing the dispersion of ozone values uncorrected for penetration distance (that is, for N₂O) in Figure 6a with those for which O₃ has been corrected for N₂O through August 9 (prior to large chemical depletion) in Figure 6b. While some scatter remains, the temporal development of ozone is significantly clarified.

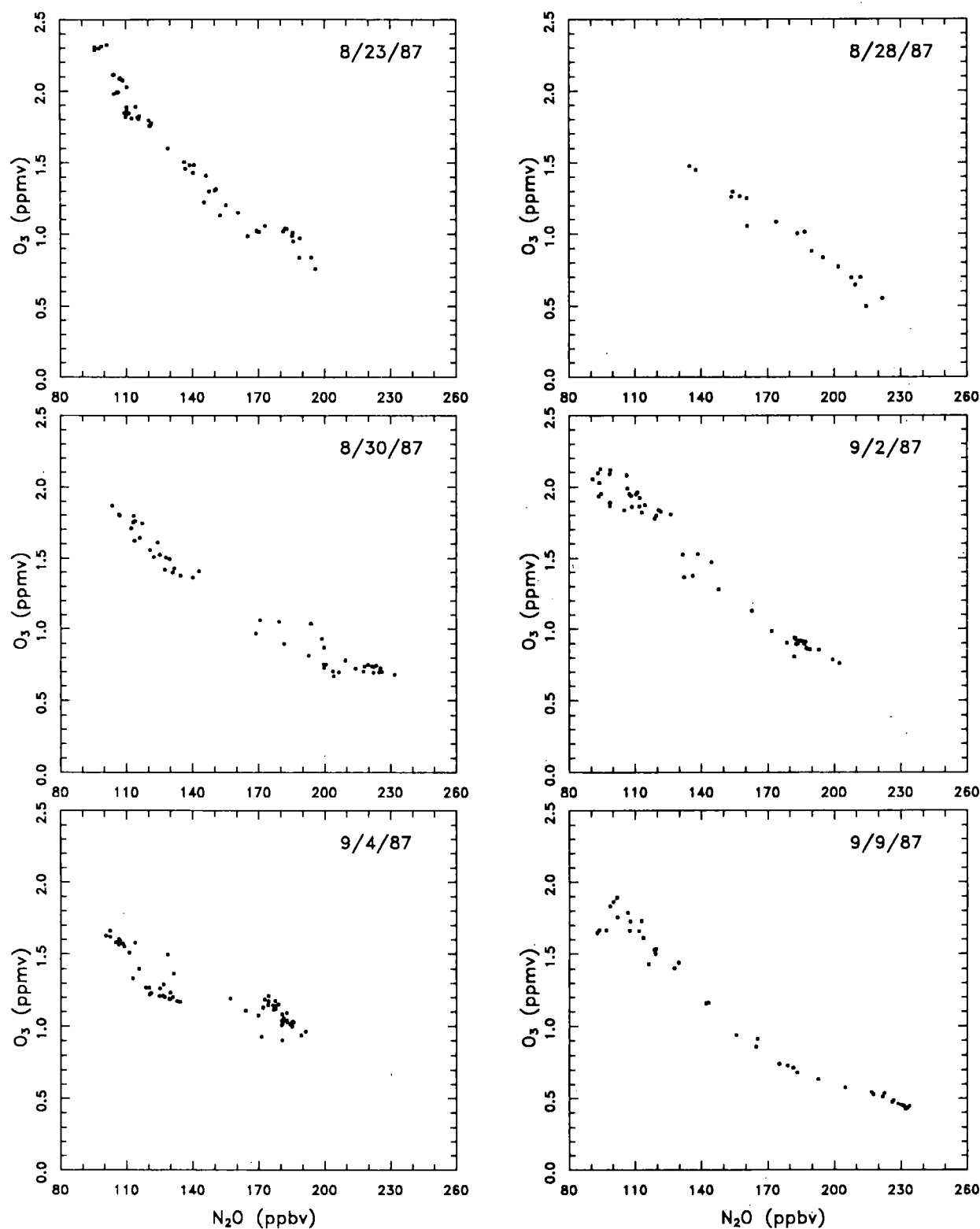


Fig. 3. Relationship between O_3 and N_2O for the flights of August 23, 28, and 30, and September 2, 4, and 9.

ANALYSIS OF CATALYTIC LOSS PROCESSES

For purposes of form we divide the manifold of plausible catalytic cycles into two classes. The first set is comprised of those reactions that have been explicitly suggested as an explanation for ozone destruction in the prior literature. The

second set includes mechanisms that are potentially important, but for which little kinetic data are available.

Several proposals have been made for the catalytic mechanism linking halogen radicals to the chemical destruction of ozone. Within this class we consider the ClO dimer mechanism suggested by *Molina and Molina* [1987], the ClO-BrO

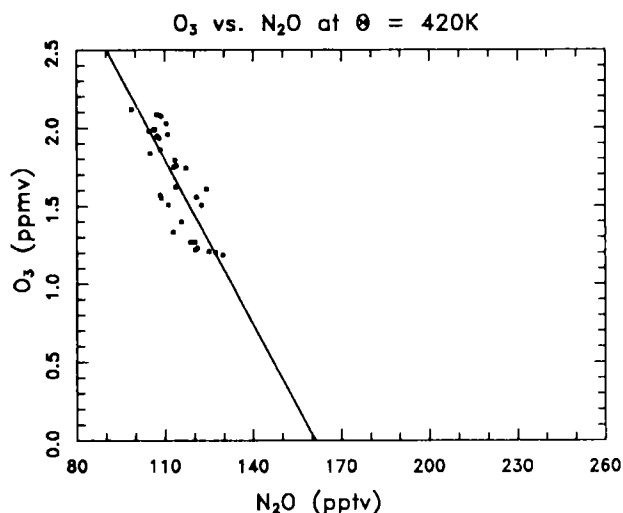


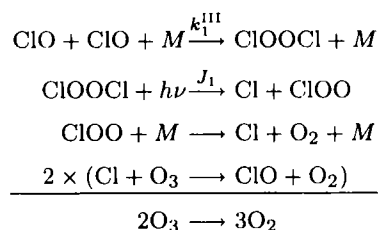
Fig. 4. Relationship between O_3 and N_2O on the 420 ± 5 K potential temperature surface. Both the raw data and the least squares fit to these data are shown.

mechanism suggested by *McElroy et al.* [1986], the ClO-HO₂ mechanism suggested by *Solomon et al.* [1986], and the classical catalytic couplet originally suggested by *Molina and Rowland* [1974] to explain mid-latitude ozone destruction: $Cl + O_3 \rightarrow ClO + O_2$ followed (and rate limited) by $ClO + O \rightarrow Cl + O_2$.

Mechanism I

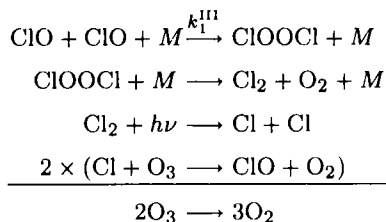
Molina and Molina [1987] introduced the concept of ClO dimer formation at low temperatures followed by photolysis and thermal decomposition:

Mechanism Ia

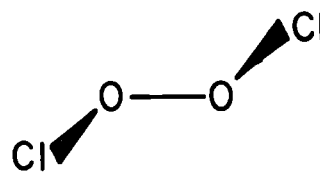


A variation on this theme, but with ClOOC l photolysis replaced by thermal decomposition, was recently proposed by *Molina et al.* [1988]:

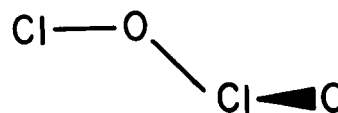
Mechanism Ib



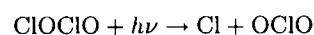
It is critical to realize that the product of the first reaction is not limited to the channel indicated here. We implicate the symmetric form of the ClO dimer in the first reaction of mechanism I:



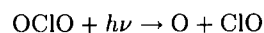
However, the asymmetric structure of the dimer:



is also possible. If the asymmetric form is the product of ClO self-reaction, the subsequent photolysis step may well form Cl and OCIO



The OCIO product will photolyze to form O and ClO



which will terminate the catalytic cycle by regenerating ozone via $O + O_2 + M \rightarrow O_3 + M$. Photolysis of the symmetric dimer to two ClO radicals would render the sequence null. Thus there is critical concern regarding the structure of the dimer and the photolytic channels at wavelengths greater than 300 nm.

In the calculations that follow we will assume that the step forming the dimer from ClO,

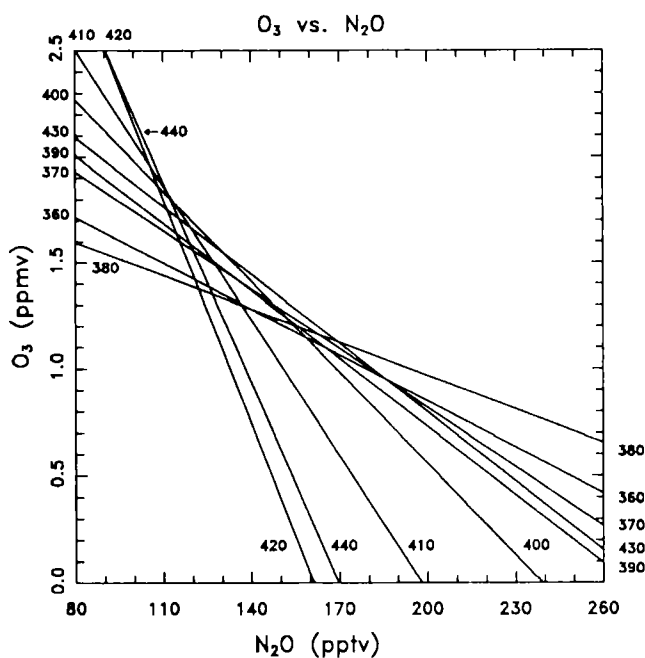
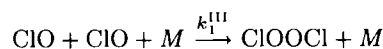


Fig. 5. Family of curves representing the relationship between O_3 and N_2O in potential temperature surfaces 350–440 K.

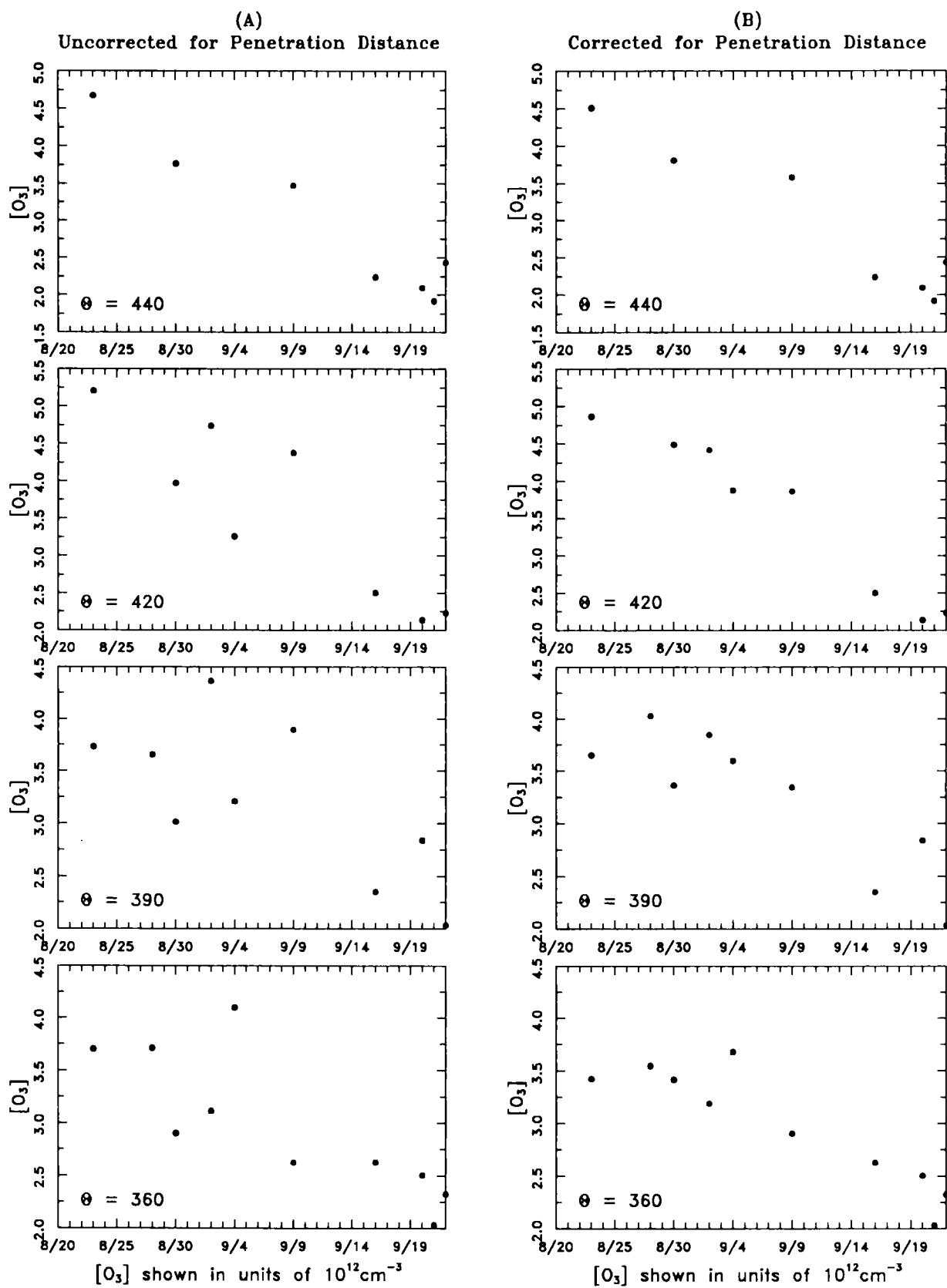
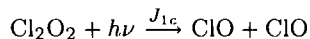
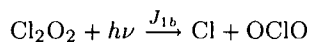
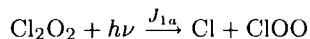


Fig. 6. (a) Comparison between raw ozone data obtained from the ER-2 on the 440, 420, 390, and 360 K surfaces and (b) the same data corrected for aircraft penetration distance into the CPR, using simultaneously obtained N_2O data.

is rate limiting during the daytime, when dimer photolysis is rapid. The absence of detailed knowledge of the photolysis products is also a significant issue. However, given the product branching ratio



from laboratory measurements any time in the future, the post hoc correction to these calculations is simple; it is only necessary to multiply the loss rate of ozone,

$$(-d[\text{O}_3]/dt)_{\text{mech. I}} = L_{\text{O}_3} = 2k_1^{\text{III}}[\text{M}][\text{ClO}]^2$$

by the factor

$$\left(\frac{J_{1a}}{J_{1a} + J_{1b} + J_{1c}} \right)$$

Thus we wish to calculate the incremental amount of ozone, ΔO_3 , removed each day, based on the in situ ClO observations, such that

$$(\Delta\text{O}_3)_{\text{mech. I}} = 2k_1^{\text{III}}[\text{M}][\text{ClO}]^2\Delta t$$

for each diurnal cycle. This raises three issues. First, we must consider the diurnal dependence of $[\text{ClO}]$ (or more precisely $[\text{ClO}]^2$) over each 24-hour period. Second, we must establish the effective exposure time, Δt , for the catalytic cycle. Third, we must normalize that diurnally varying ClO to the observed midday concentration obtained from the flight data.

Figure 7 represents the diurnal behavior of $[\text{ClO}]$ and $[\text{ClO}]^2$ calculated using a model consisting of two components: a radiative transfer code developed at the Naval Research Laboratory (NRL) [see Meier *et al.*, 1982; Anderson, 1983] and a photochemical kinetic model developed both at NRL and Harvard University (D. E. Anderson and S. A. Lloyd, Polar twilight UV-visible radiation field: Effects due to multiple scattering, ozone depletion, clouds, and surface albedo, submitted to the *Journal of Geophysical Research*, 1989). The radiative transfer code was developed by a careful comparison of a spherical geometry, multiple scattering model with a plane-parallel treatment, which demonstrated the quantitative precision of the latter, computationally simpler approach. Special emphasis was placed on the accurate calculation of the actinic flux at twilight (solar zenith angles up to 95°). The radiation field calculation includes both single and multiple scattering, as well as atmospheric refraction. The input ozone profile was a composite Antarctic O_3 profile for late August, 1986 (derived from Hofmann [1988]). The radiative transfer code incorporates photochemical cross sections [DeMore *et al.*, 1987] to generate photochemical rate constants (J -values), which are then used as first-order reaction rate constants in a zero-dimensional kinetics code encompassing 130 thermal and photolytic reactions relevant to the lower stratosphere. Recently measured ClO dimer absorption cross sections (J. B. Burkholder *et al.*, private communication, 1988) were used in these calculations. Heterogeneous reactions were simulated by the inclusion of effective bimolecular rate constants for these processes [Rodriguez *et al.*, 1986]. The

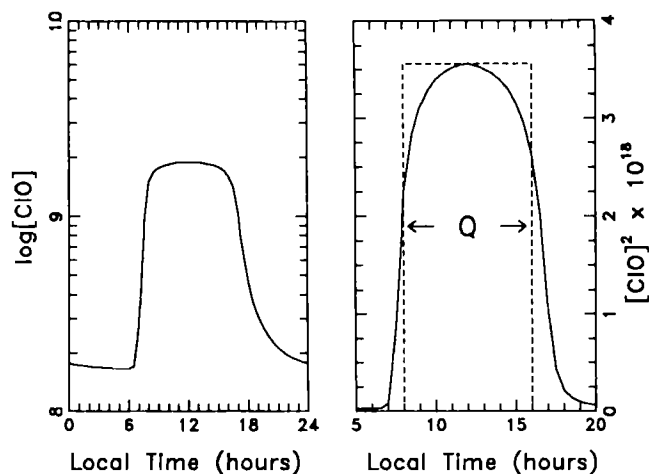


Fig. 7. Diurnal behavior of ClO and $[\text{ClO}]^2$ on the 440 K (18 km) surface, used for the determination of the effective exposure time of ozone to the catalytic action of mechanism I. This effective exposure time, $Q^{\text{ClO}-\text{ClO}}$, increases with time through the course of the mission as the solar declination angle increases.

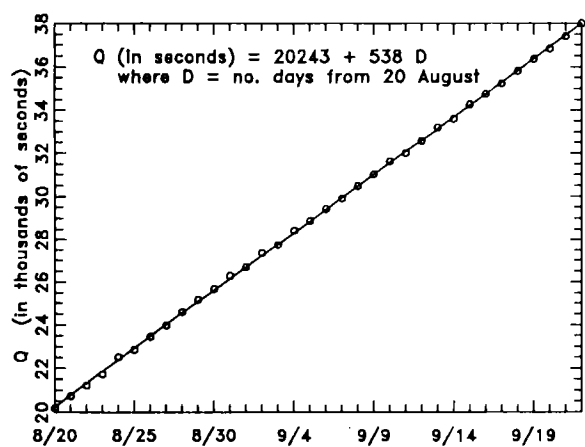
model calculations accurately reproduce the observed ClO and BrO to within the experimental uncertainties. Figure 7 presents sample waveforms generated by these calculations, appropriate to the conditions inside the vortex where the inorganic chlorine budget is dominated by ClO and the ClO dimer, rather than by HCl, ClONO_2 and HOCl, as is the case outside (equatorward) of the CPR. In the denitrified Antarctic stratosphere, inorganic bromine cycles between the daytime reservoir BrO and nighttime BrCl.

Next, we make the assumption that the observed ClO and BrO were also the maximum ClO and BrO during each diurnal cycle. Inspection of Figure 7 indicates that this assumption is valid for ClO if our observations were made within an hour of local noon, which was indeed the case for all observations at 72°S latitude [Brune *et al.*, 1989a]. The modeled ClO diurnal waveform is then used to determine the equivalent width, Q , corresponding to the effective exposure time of ozone to the rate-limiting step of the catalytic cycle. That is, for mechanism I, we wish to solve for a factor Q such that

$$\int_{24 \text{ hours}} [\text{ClO}]^2 dt = [\text{ClO}]_{\text{max}}^2 (Q^{\text{ClO}-\text{ClO}})$$

where $[\text{ClO}]_{\text{max}}^2$ is the modeled maximum $[\text{ClO}]^2$ for any diurnal cycle, which corresponds to the experimentally determined $[\text{ClO}]_{\text{obs}}^2$. Thus in our calculation of ozone depletion, the product $[\text{ClO}]_{\text{obs}}^2 (Q^{\text{ClO}-\text{ClO}})$ will be equivalent to the integral $\int [\text{ClO}]^2 dt$ over a given day.

Since Q can be thought of as an "effective exposure time" of O_3 to photochemical catalysis, we expect that Q will increase throughout the austral spring as the length of the day increases (see Figure 8). Since the number of hours of daylight increases linearly with the date in the polar regions near the equinoxes, Q also increases linearly with the date throughout the experiment. The effective exposure time, Q , is assumed to be independent of altitude. In our calculations, Q was normalized to account for the fact that



Q values inside the chemically perturbed region

Fig. 8. Temporal evolution of $Q^{\text{ClO-ClO}}$ inside the chemically perturbed region from mid-August through the end of September, 1987.

dimer photolysis becomes rate limiting (shutting down the catalytic cycle) when the Sun is near or below the horizon.

It is also important to note that the details of the (large solar zenith angle) "wings" of the ClO waveform are suppressed in the diurnal integral because of the quadratic dependence of the rate-limiting step on ClO. This has important implications for this simplified approach: the Q values are not sensitive to the details of the amount of NO_x (and thus of ClONO_2) assumed in the model. To demonstrate this, we calculated Q for NO_x values of 10^{-6} parts per billion by volume (ppbv) to 3.2 ppbv ($\text{NO}_x = \text{NO} + \text{NO}_2 + \text{NO}_3 + 2 \times \text{N}_2\text{O}_5 + \text{ClONO}_2$) and found that Q varies by less than 2% across this range on any given date.

Results from ground-based millimeter wave emission techniques [deZafra *et al.*, this issue] report that ClO in the vicinity of 20 km drops below the detection limit at night. The diurnal waveform we present here does not conflict with the millimeter wave results.

Thus on each potential temperature surface the amount of ozone removal on day i will be (for example, $\Theta = 440$ K)

$$(\Delta\text{O}_3)_i^{440\text{ K}} = 2k_1^{\text{III}}[\text{M}][\text{ClO}]_{440\text{ K}}^2 Q_i^{\text{ClO-ClO}}$$

for mechanism I. While it is most efficient to present these results in graphical form by subtracting the amount of ozone removed each day from the amount of ozone present at the end of the previous day (and then superimposing that decay profile on the in situ ozone concentration observed simultaneously with ClO), we will digress briefly to tabulate the same calculation on the 440, 420, 390, and 360 K isentropic surfaces. This will both clarify our approach and facilitate comparison with other methods. Table 1 summarizes the temporal evolution of the values used for the determination of ozone loss rates from mechanism I for the 440, 420, 390, and 360 K surfaces, based on observed values of ClO.

In order to quantify the comparison between observed ozone loss and that predicted by each mechanism, we digress briefly to consider the question of fitting the functional form of the temporal development of O_3 on each Θ surface. This is not fundamental to the analysis; it merely provides a way to quantify observed ozone loss. Two approaches will be taken to establish a "best" fit to the temporal trend in observed ozone. The first is a simple linear, least squares regression of O_3 versus time through the course of the flight series; the second is a quadratic function, which assumes that the loss rate of O_3 with time is proportional to the square of the observed ClO concentration. The latter case would be most appropriate if mechanism I were the dominant loss; the former would be true if the rate-limiting step in O_3 destruction were proportional to the first power of ClO and Q were not a function that increased with time. Note that even with a loss linearly proportional to $[\text{ClO}]$, there would be a natural steepening of the O_3 loss rate through September, all other things being equal, because of the longer exposure time to sunlight. This would tend to mimic the quadratic form, even if the rate-limiting step were linear with respect to ClO.

TABLE 1. Summary of Ozone Loss Rate as a Function of Calendar Day Resulting From Mechanism I, $\text{ClO} + \text{ClO} + \text{M} \rightarrow \text{ClOOC} + \text{M}$, Suggested by Molina and Molina [1985], on Potential Temperature Surfaces of 440, 420, 390, and 360 K

Day	$[\text{ClO}]$, mol cm^{-3}	$[\text{M}]$, $\times 10^{18} \text{cm}^{-3}$	T , $^{\circ}\text{K}$	k_1^{III} , $\text{cm}^3 \text{s}^{-1}$	Q , $\times 10^4 \text{s}$	$-\Delta\text{O}_3$, $\text{mol cm}^{-3} \text{d}^{-1}$
<i>440 ± 5 K Surface</i>						
Aug. 20	1.46×10^9	2.16	191.3	1.62×10^{-13}	2.02	1.39×10^{10}
Aug. 21	1.48×10^9	2.16	191.4	1.62×10^{-13}	2.07	1.48×10^{10}
Aug. 22	1.51×10^9	2.16	191.5	1.61×10^{-13}	2.12	1.56×10^{10}
Aug. 23	1.53×10^9	2.15	191.5	1.61×10^{-13}	2.17	1.65×10^{10}
Aug. 24	1.56×10^9	2.15	191.6	1.61×10^{-13}	2.25	1.76×10^{10}
Aug. 25	1.58×10^9	2.15	191.7	1.61×10^{-13}	2.29	1.84×10^{10}
Aug. 26	1.61×10^9	2.15	191.8	1.60×10^{-13}	2.35	1.94×10^{10}
Aug. 27	1.63×10^9	2.15	191.9	1.60×10^{-13}	2.40	2.04×10^{10}
Aug. 28	1.66×10^9	2.15	191.9	1.60×10^{-13}	2.46	2.16×10^{10}
Aug. 29	1.68×10^9	2.15	192.0	1.59×10^{-13}	2.52	2.27×10^{10}
Aug. 30	1.71×10^9	2.14	192.1	1.59×10^{-13}	2.57	2.38×10^{10}
Aug. 31	1.73×10^9	2.14	192.2	1.59×10^{-13}	2.63	2.50×10^{10}
Sept. 1	1.76×10^9	2.14	192.2	1.58×10^{-13}	2.67	2.61×10^{10}
Sept. 2	1.78×10^9	2.14	192.3	1.58×10^{-13}	2.74	2.74×10^{10}
Sept. 3	1.81×10^9	2.14	192.4	1.58×10^{-13}	2.77	2.86×10^{10}

TABLE 1. (continued)

Day	[ClO], mol cm ⁻³	[M], ×10 ¹⁸ cm ⁻³	T, °K	k ^{II} , cm ³ s ⁻¹	Q, ×10 ⁴ s	-ΔO ₃ , mol cm ⁻³ d ⁻¹
<i>440 ± 5 K Surface (continued)</i>						
Sept. 4	1.83 × 10 ⁹	2.14	192.5	1.57 × 10 ⁻¹³	2.84	3.00 × 10 ¹⁰
Sept. 5	1.86 × 10 ⁹	2.13	192.5	1.57 × 10 ⁻¹³	2.89	3.12 × 10 ¹⁰
Sept. 6	1.88 × 10 ⁹	2.13	192.6	1.57 × 10 ⁻¹³	2.94	3.26 × 10 ¹⁰
Sept. 7	1.91 × 10 ⁹	2.13	192.7	1.56 × 10 ⁻¹³	2.99	3.40 × 10 ¹⁰
Sept. 8	1.93 × 10 ⁹	2.13	192.8	1.56 × 10 ⁻¹³	3.05	3.55 × 10 ¹⁰
Sept. 9	1.95 × 10 ⁹	2.13	192.9	1.56 × 10 ⁻¹³	3.10	3.69 × 10 ¹⁰
Sept. 10	1.98 × 10 ⁹	2.13	192.9	1.56 × 10 ⁻¹³	3.16	3.85 × 10 ¹⁰
Sept. 11	2.00 × 10 ⁹	2.12	193.0	1.55 × 10 ⁻¹³	3.20	3.99 × 10 ¹⁰
Sept. 12	2.03 × 10 ⁹	2.12	193.1	1.55 × 10 ⁻¹³	3.26	4.16 × 10 ¹⁰
Sept. 13	2.05 × 10 ⁹	2.12	193.2	1.55 × 10 ⁻¹³	3.32	4.33 × 10 ¹⁰
Sept. 14	2.08 × 10 ⁹	2.12	193.2	1.54 × 10 ⁻¹³	3.36	4.48 × 10 ¹⁰
Sept. 15	2.10 × 10 ⁹	2.12	193.3	1.54 × 10 ⁻¹³	3.43	4.67 × 10 ¹⁰
Sept. 16	2.13 × 10 ⁹	2.12	193.4	1.54 × 10 ⁻¹³	3.48	4.84 × 10 ¹⁰
Sept. 17	2.15 × 10 ⁹	2.12	193.5	1.53 × 10 ⁻¹³	3.52	5.01 × 10 ¹⁰
Sept. 18	2.18 × 10 ⁹	2.11	193.5	1.53 × 10 ⁻¹³	3.58	5.20 × 10 ¹⁰
Sept. 19	2.20 × 10 ⁹	2.11	193.6	1.53 × 10 ⁻¹³	3.64	5.39 × 10 ¹⁰
Sept. 20	2.23 × 10 ⁹	2.11	193.7	1.52 × 10 ⁻¹³	3.68	5.57 × 10 ¹⁰
Sept. 21	2.25 × 10 ⁹	2.11	193.8	1.52 × 10 ⁻¹³	3.74	5.77 × 10 ¹⁰
Sept. 22	2.28 × 10 ⁹	2.11	193.9	1.52 × 10 ⁻¹³	3.80	5.98 × 10 ¹⁰
<i>420 ± 5 K Surface</i>						
Aug. 20	1.23 × 10 ⁹	2.45	190.3	1.85 × 10 ⁻¹³	2.02	1.12 × 10 ¹⁰
Aug. 21	1.25 × 10 ⁹	2.45	190.4	1.84 × 10 ⁻¹³	2.07	1.20 × 10 ¹⁰
Aug. 22	1.28 × 10 ⁹	2.45	190.5	1.84 × 10 ⁻¹³	2.12	1.28 × 10 ¹⁰
Aug. 23	1.31 × 10 ⁹	2.45	190.6	1.84 × 10 ⁻¹³	2.17	1.36 × 10 ¹⁰
Aug. 24	1.33 × 10 ⁹	2.45	190.7	1.84 × 10 ⁻¹³	2.25	1.47 × 10 ¹⁰
Aug. 25	1.36 × 10 ⁹	2.46	190.9	1.83 × 10 ⁻¹³	2.29	1.55 × 10 ¹⁰
Aug. 26	1.39 × 10 ⁹	2.46	191.0	1.83 × 10 ⁻¹³	2.35	1.65 × 10 ¹⁰
Aug. 27	1.41 × 10 ⁹	2.46	191.1	1.83 × 10 ⁻¹³	2.40	1.75 × 10 ¹⁰
Aug. 28	1.44 × 10 ⁹	2.46	191.2	1.83 × 10 ⁻¹³	2.46	1.86 × 10 ¹⁰
Aug. 29	1.47 × 10 ⁹	2.46	191.4	1.82 × 10 ⁻¹³	2.52	1.97 × 10 ¹⁰
Aug. 30	1.49 × 10 ⁹	2.47	191.5	1.82 × 10 ⁻¹³	2.57	2.09 × 10 ¹⁰
Aug. 31	1.52 × 10 ⁹	2.47	191.6	1.82 × 10 ⁻¹³	2.63	2.21 × 10 ¹⁰
Sept. 1	1.55 × 10 ⁹	2.47	191.7	1.82 × 10 ⁻¹³	2.67	2.32 × 10 ¹⁰
Sept. 2	1.57 × 10 ⁹	2.47	191.9	1.81 × 10 ⁻¹³	2.74	2.46 × 10 ¹⁰
Sept. 3	1.60 × 10 ⁹	2.47	192.0	1.81 × 10 ⁻¹³	2.77	2.57 × 10 ¹⁰
Sept. 4	1.63 × 10 ⁹	2.47	192.1	1.81 × 10 ⁻¹³	2.84	2.72 × 10 ¹⁰
Sept. 5	1.65 × 10 ⁹	2.48	192.2	1.81 × 10 ⁻¹³	2.89	2.85 × 10 ¹⁰
Sept. 6	1.68 × 10 ⁹	2.48	192.3	1.80 × 10 ⁻¹³	2.94	2.99 × 10 ¹⁰
Sept. 7	1.71 × 10 ⁹	2.48	192.5	1.80 × 10 ⁻¹³	2.99	3.14 × 10 ¹⁰
Sept. 8	1.73 × 10 ⁹	2.48	192.6	1.80 × 10 ⁻¹³	3.05	3.29 × 10 ¹⁰
Sept. 9	1.76 × 10 ⁹	2.48	192.7	1.80 × 10 ⁻¹³	3.10	3.45 × 10 ¹⁰
Sept. 10	1.79 × 10 ⁹	2.49	192.8	1.79 × 10 ⁻¹³	3.16	3.62 × 10 ¹⁰
Sept. 11	1.81 × 10 ⁹	2.49	193.0	1.79 × 10 ⁻¹³	3.20	3.77 × 10 ¹⁰
Sept. 12	1.84 × 10 ⁹	2.49	193.1	1.79 × 10 ⁻¹³	3.26	3.95 × 10 ¹⁰
Sept. 13	1.87 × 10 ⁹	2.49	193.2	1.79 × 10 ⁻¹³	3.32	4.13 × 10 ¹⁰
Sept. 14	1.89 × 10 ⁹	2.49	193.3	1.78 × 10 ⁻¹³	3.36	4.30 × 10 ¹⁰
Sept. 15	1.92 × 10 ⁹	2.49	193.5	1.78 × 10 ⁻¹³	3.43	4.50 × 10 ¹⁰
Sept. 16	1.95 × 10 ⁹	2.50	193.6	1.78 × 10 ⁻¹³	3.48	4.68 × 10 ¹⁰
Sept. 17	1.97 × 10 ⁹	2.50	193.7	1.78 × 10 ⁻¹³	3.52	4.88 × 10 ¹⁰
Sept. 18	2.00 × 10 ⁹	2.50	193.8	1.77 × 10 ⁻¹³	3.58	5.08 × 10 ¹⁰
Sept. 19	2.03 × 10 ⁹	2.50	194.0	1.77 × 10 ⁻¹³	3.64	5.29 × 10 ¹⁰
Sept. 20	2.05 × 10 ⁹	2.50	194.1	1.77 × 10 ⁻¹³	3.68	5.49 × 10 ¹⁰
Sept. 21	2.08 × 10 ⁹	2.50	194.2	1.77 × 10 ⁻¹³	3.74	5.72 × 10 ¹⁰
Sept. 22	2.11 × 10 ⁹	2.51	194.3	1.76 × 10 ⁻¹³	3.80	5.95 × 10 ¹⁰
<i>390 ± 5 K Surface</i>						
Aug. 20	8.60 × 10 ⁸	3.13	190.6	2.28 × 10 ⁻¹³	2.02	6.82 × 10 ⁹
Aug. 21	8.85 × 10 ⁸	3.14	190.8	2.28 × 10 ⁻¹³	2.07	7.40 × 10 ⁹
Aug. 22	9.09 × 10 ⁸	3.15	191.0	2.28 × 10 ⁻¹³	2.12	7.99 × 10 ⁹
Aug. 23	9.33 × 10 ⁸	3.15	191.2	2.28 × 10 ⁻¹³	2.17	8.61 × 10 ⁹
Aug. 24	9.57 × 10 ⁸	3.16	191.3	2.28 × 10 ⁻¹³	2.25	9.39 × 10 ⁹
Aug. 25	9.82 × 10 ⁸	3.17	191.5	2.27 × 10 ⁻¹³	2.29	1.00 × 10 ¹⁰
Aug. 26	1.01 × 10 ⁹	3.18	191.7	2.27 × 10 ⁻¹³	2.35	1.08 × 10 ¹⁰
Aug. 27	1.03 × 10 ⁹	3.18	191.9	2.27 × 10 ⁻¹³	2.40	1.15 × 10 ¹⁰
Aug. 28	1.05 × 10 ⁹	3.19	192.1	2.27 × 10 ⁻¹³	2.46	1.24 × 10 ¹⁰

TABLE 1. (continued)

Day	[ClO], mol cm ⁻³	[M], × 10 ¹⁸ cm ⁻³	T, °K	k ^{II} , cm ³ s ⁻¹	Q, × 10 ⁴ s	-ΔO ₃ , mol cm ⁻³ d ⁻¹
390 ± 5 K Surface (continued)						
Aug. 29	1.08 × 10 ⁹	3.20	192.3	2.26 × 10 ⁻¹³	2.52	1.33 × 10 ¹⁰
Aug. 30	1.10 × 10 ⁹	3.21	192.5	2.26 × 10 ⁻¹³	2.57	1.41 × 10 ¹⁰
Aug. 31	1.13 × 10 ⁹	3.21	192.6	2.26 × 10 ⁻¹³	2.63	1.51 × 10 ¹⁰
Sept. 1	1.15 × 10 ⁹	3.22	192.8	2.26 × 10 ⁻¹³	2.67	1.60 × 10 ¹⁰
Sept. 2	1.18 × 10 ⁹	3.23	193.0	2.25 × 10 ⁻¹³	2.74	1.71 × 10 ¹⁰
Sept. 3	1.20 × 10 ⁹	3.24	193.2	2.25 × 10 ⁻¹³	2.77	1.80 × 10 ¹⁰
Sept. 4	1.22 × 10 ⁹	3.24	193.4	2.25 × 10 ⁻¹³	2.84	1.92 × 10 ¹⁰
Sept. 5	1.25 × 10 ⁹	3.25	193.6	2.25 × 10 ⁻¹³	2.89	2.02 × 10 ¹⁰
Sept. 6	1.27 × 10 ⁹	3.26	193.8	2.25 × 10 ⁻¹³	2.94	2.14 × 10 ¹⁰
Sept. 7	1.30 × 10 ⁹	3.27	194.0	2.24 × 10 ⁻¹³	2.99	2.26 × 10 ¹⁰
Sept. 8	1.32 × 10 ⁹	3.27	194.1	2.24 × 10 ⁻¹³	3.05	2.39 × 10 ¹⁰
Sept. 9	1.35 × 10 ⁹	3.28	194.3	2.24 × 10 ⁻¹³	3.10	2.51 × 10 ¹⁰
Sept. 10	1.37 × 10 ⁹	3.29	194.5	2.24 × 10 ⁻¹³	3.16	2.65 × 10 ¹⁰
Sept. 11	1.39 × 10 ⁹	3.30	194.7	2.23 × 10 ⁻¹³	3.20	2.78 × 10 ¹⁰
Sept. 12	1.42 × 10 ⁹	3.30	194.9	2.23 × 10 ⁻¹³	3.26	2.93 × 10 ¹⁰
Sept. 13	1.44 × 10 ⁹	3.31	195.1	2.23 × 10 ⁻¹³	3.32	3.08 × 10 ¹⁰
Sept. 14	1.47 × 10 ⁹	3.32	195.3	2.23 × 10 ⁻¹³	3.36	3.22 × 10 ¹⁰
Sept. 15	1.49 × 10 ⁹	3.33	195.5	2.22 × 10 ⁻¹³	3.43	3.39 × 10 ¹⁰
Sept. 16	1.52 × 10 ⁹	3.33	195.6	2.22 × 10 ⁻¹³	3.48	3.55 × 10 ¹⁰
Sept. 17	1.54 × 10 ⁹	3.34	195.8	2.22 × 10 ⁻¹³	3.52	3.71 × 10 ¹⁰
Sept. 18	1.56 × 10 ⁹	3.35	196.0	2.22 × 10 ⁻¹³	3.58	3.89 × 10 ¹⁰
Sept. 19	1.59 × 10 ⁹	3.36	196.2	2.22 × 10 ⁻¹³	3.64	4.07 × 10 ¹⁰
Sept. 20	1.61 × 10 ⁹	3.36	196.4	2.21 × 10 ⁻¹³	3.68	4.24 × 10 ¹⁰
Sept. 21	1.64 × 10 ⁹	3.37	196.6	2.21 × 10 ⁻¹³	3.74	4.43 × 10 ¹⁰
Sept. 22	1.66 × 10 ⁹	3.38	196.8	2.21 × 10 ⁻¹³	3.80	4.63 × 10 ¹⁰
360 ± 5 K Surface						
Aug. 20	5.37 × 10 ⁸	3.89	190.5	2.76 × 10 ⁻¹³	2.02	3.22 × 10 ⁹
Aug. 21	5.48 × 10 ⁸	3.92	190.8	2.76 × 10 ⁻¹³	2.07	3.44 × 10 ⁹
Aug. 22	5.59 × 10 ⁸	3.94	191.1	2.77 × 10 ⁻¹³	2.12	3.66 × 10 ⁹
Aug. 23	5.69 × 10 ⁸	3.97	191.4	2.77 × 10 ⁻¹³	2.17	3.89 × 10 ⁹
Aug. 24	5.80 × 10 ⁸	3.99	191.8	2.77 × 10 ⁻¹³	2.25	4.19 × 10 ⁹
Aug. 25	5.91 × 10 ⁸	4.02	192.1	2.77 × 10 ⁻¹³	2.29	4.42 × 10 ⁹
Aug. 26	6.01 × 10 ⁸	4.05	192.4	2.77 × 10 ⁻¹³	2.35	4.70 × 10 ⁹
Aug. 27	6.12 × 10 ⁸	4.07	192.7	2.77 × 10 ⁻¹³	2.40	4.98 × 10 ⁹
Aug. 28	6.23 × 10 ⁸	4.10	193.0	2.77 × 10 ⁻¹³	2.46	5.29 × 10 ⁹
Aug. 29	6.33 × 10 ⁸	4.12	193.3	2.77 × 10 ⁻¹³	2.52	5.60 × 10 ⁹
Aug. 30	6.44 × 10 ⁸	4.15	193.7	2.77 × 10 ⁻¹³	2.57	5.91 × 10 ⁹
Aug. 31	6.55 × 10 ⁸	4.17	194.0	2.77 × 10 ⁻¹³	2.63	6.25 × 10 ⁹
Sept. 1	6.66 × 10 ⁸	4.20	194.3	2.77 × 10 ⁻¹³	2.67	6.56 × 10 ⁹
Sept. 2	6.76 × 10 ⁸	4.23	194.6	2.78 × 10 ⁻¹³	2.74	6.95 × 10 ⁹
Sept. 3	6.87 × 10 ⁸	4.25	194.9	2.78 × 10 ⁻¹³	2.77	7.27 × 10 ⁹
Sept. 4	6.98 × 10 ⁸	4.28	195.3	2.78 × 10 ⁻¹³	2.84	7.68 × 10 ⁹
Sept. 5	7.08 × 10 ⁸	4.30	195.6	2.78 × 10 ⁻¹³	2.89	8.05 × 10 ⁹
Sept. 6	7.19 × 10 ⁸	4.33	195.9	2.78 × 10 ⁻¹³	2.94	8.45 × 10 ⁹
Sept. 7	7.30 × 10 ⁸	4.35	196.2	2.78 × 10 ⁻¹³	2.99	8.84 × 10 ⁹
Sept. 8	7.40 × 10 ⁸	4.38	196.5	2.78 × 10 ⁻¹³	3.05	9.28 × 10 ⁹
Sept. 9	7.51 × 10 ⁸	4.41	196.8	2.78 × 10 ⁻¹³	3.10	9.71 × 10 ⁹
Sept. 10	7.62 × 10 ⁸	4.43	197.2	2.78 × 10 ⁻¹³	3.16	1.02 × 10 ¹⁰
Sept. 11	7.73 × 10 ⁸	4.46	197.5	2.78 × 10 ⁻¹³	3.20	1.06 × 10 ¹⁰
Sept. 12	7.83 × 10 ⁸	4.48	197.8	2.78 × 10 ⁻¹³	3.26	1.11 × 10 ¹⁰
Sept. 13	7.94 × 10 ⁸	4.51	198.1	2.78 × 10 ⁻¹³	3.32	1.16 × 10 ¹⁰
Sept. 14	8.05 × 10 ⁸	4.53	198.4	2.78 × 10 ⁻¹³	3.36	1.21 × 10 ¹⁰
Sept. 15	8.15 × 10 ⁸	4.56	198.7	2.78 × 10 ⁻¹³	3.43	1.26 × 10 ¹⁰
Sept. 16	8.26 × 10 ⁸	4.59	199.1	2.78 × 10 ⁻¹³	3.48	1.32 × 10 ¹⁰
Sept. 17	8.37 × 10 ⁸	4.61	199.4	2.78 × 10 ⁻¹³	3.52	1.37 × 10 ¹⁰
Sept. 18	8.47 × 10 ⁸	4.64	199.7	2.77 × 10 ⁻¹³	3.58	1.43 × 10 ¹⁰
Sept. 19	8.58 × 10 ⁸	4.66	200.0	2.77 × 10 ⁻¹³	3.64	1.49 × 10 ¹⁰
Sept. 20	8.69 × 10 ⁸	4.69	200.3	2.77 × 10 ⁻¹³	3.68	1.54 × 10 ¹⁰
Sept. 21	8.79 × 10 ⁸	4.71	200.7	2.77 × 10 ⁻¹³	3.74	1.60 × 10 ¹⁰
Sept. 22	8.90 × 10 ⁸	4.74	201.0	2.77 × 10 ⁻¹³	3.80	1.67 × 10 ¹⁰

Values of ClO concentration, total atmospheric concentration, and temperature, obtained from the ER-2, are given in the second, third, and fourth columns respectively. The effective bimolecular reaction rate from Sander *et al.* [1989] is given in column five, and the effective exposure time in each 24-hour period appears in column six. The last column displays the amount of O₃ removed in each 24-hour period.

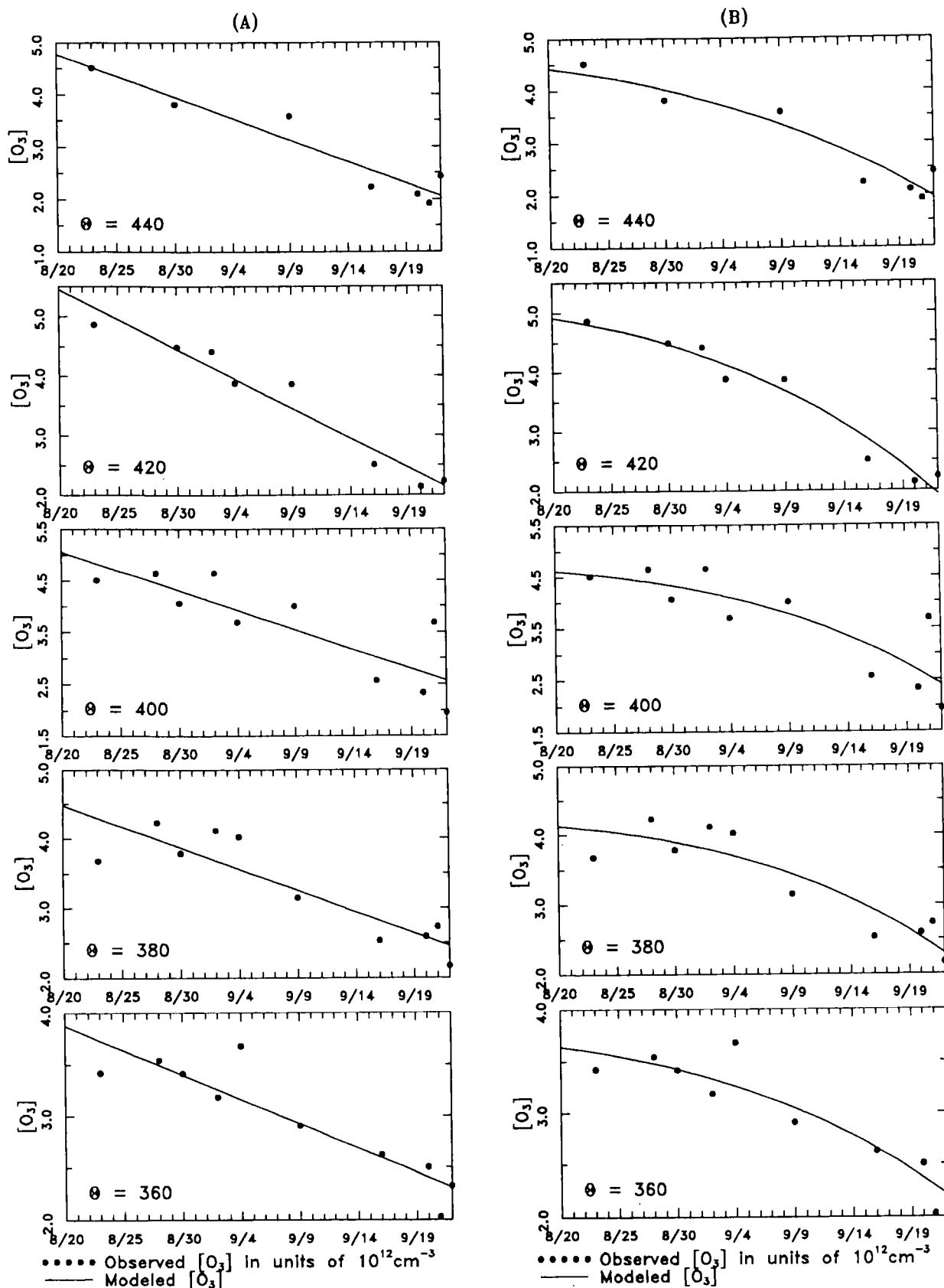


Fig. 9. Comparison between (a) linear least squares fit to the observed O_3 decay and (b) an O_3 loss proportional to the ClO concentration squared. Analysis is shown for the 440, 420, 400, 380, and 360 K surfaces.

Figure 9 summarizes the two approaches and makes it clear that there is little reason to select the quadratic over the linear function simply on the basis of fit to observed O_3 . Obviously, the linear least squares approach yields sig-

nificantly larger loss rates for O_3 in the early phase of the mission, but in both cases the fit is quite acceptable. In all subsequent discussion we will use the quadratic fit, both because Q increases during the course of the mission and

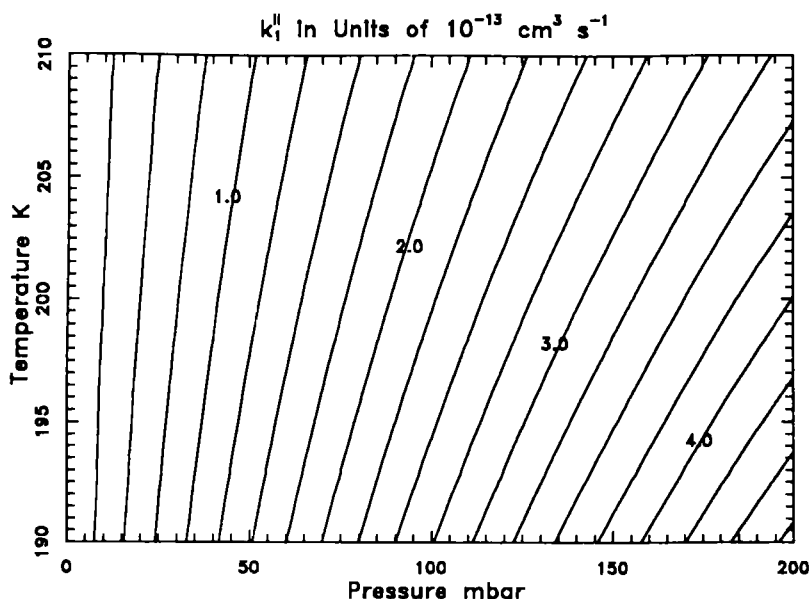


Fig. 10. Contour plot of the second-order rate for ClO dimer formation from ClO, based on the recent laboratory results of Sander *et al.* [1989]. We include the temperature and pressure regime of interest to our analysis of in situ ClO results.

because of the importance of mechanism I to the time rate of change of ozone. We return now to the analysis of mechanism I.

Although considerable effort has gone into laboratory studies of the kinetics and photochemistry of the ClO dimer, there are major quantitative issues which remain. The most significant of these is the disparity between the two available reaction rate constants for the forward rate of dimer formation and the absence of data on the photolysis products for the dimer. Specifically, Hayman *et al.* [1986] report a temperature-dependent termolecular rate for k_1^{III} given by

$$k_1^{\text{III}} = 6.1 \times 10^{-32} (T/300)^{-2.1} \text{ cm}^6 \text{ s}^{-1}$$

This is the rate which has been used for virtually all O₃ loss rate calculations to date (see, for example, earlier versions of this manuscript; Barrett *et al.* [1988]; McElroy and Salawitch [1989]).

In an extensive study of the forward rate k_1^{III} as a function of temperature (195–250 K) and pressure (100–500 torr) Sander *et al.* [1989] report a pressure and temperature-dependent rate in bimolecular form (see the discussion in DeMore *et al.* [1987])

$$k_1^{\text{II}}(M, T) = \frac{k_0(T)[M]0.6\{1 + [\log_{10}(k_0(T)[M]/k_\infty(T))]\}^{-1}}{[1 + (k_0(T)[M]/k_\infty(T))]}$$

where

$$k_0(T) = 1.8 \times 10^{-32} (T/300)^{-3.6} \text{ cm}^6 \text{ s}^{-1}$$

$$k_\infty = 6 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$$

This represents a very significant departure from the Hayman *et al.* [1986] rate. In the temperature and pressure region of the Antarctic vortex, the Sander *et al.* [1989] rate constant is more than a factor of 2 slower than the Hayman *et al.* [1986] result. We summarize both the temperature and pressure dependence of the Sander *et al.* [1989] result

in Figure 10 over the region covered by the in situ ClO results reported here.

In the Sander *et al.* [1989] study the flash photolysis/ultraviolet absorption technique was used to measure k_1 over the temperature range 194–247 K and the concentration range $(1\text{--}30) \times 10^{18} \text{ molecule cm}^{-3}$ in Ar, O₂, and N₂ buffer gases. The ClO + ClO study of Hayman *et al.* [1986] was carried out over the temperature range 268–338 K and the pressure range 2–700 torr, using the technique of molecular modulation with ultraviolet absorption detection.

The primary difference between the two studies had to do with the time scales under which the kinetics of ClO were observed. In the flash photolysis study, rate constants were determined directly from the observed time-resolved decays of ClO radical. The formation of ClO took place on a time scale several orders of magnitude faster than its decay by self-reaction. It was shown that under the reaction conditions employed, ClO reacted irreversibly to form (ClO)₂, and there were no secondary reactions involving ClO and (ClO)₂. In the molecular modulation study, thermal decomposition of the dimer could not be neglected in the temperature range used in the study. In addition, the photolysis period was long compared with the characteristic time for (ClO)₂ thermal decomposition. The ClO temporal profile was therefore a convolution of several processes, including self-reaction, and secondary reactions of (ClO)₂, including thermolysis, photolysis, and reaction with Cl. We believe that the Sander *et al.* [1989] results for k_1^{II} are correct.

Figures 11–14 present the comparison between calculated and observed O₃ loss based on observed ClO using the Hayman *et al.* [1986] value for k_1^{III} (Figures 11a, 12a, 13a, and 14a) and the Sander *et al.* [1989] value for k_1^{II} (Figures 11b, 12b, 13b, and 14b). Results are presented on each potential temperature surface between 360 and 450 K. Our objective in Figures 11–14 is both to define the quantitative behavior of ozone loss on each potential temperature surface using the quadratic fit discussed in conjunction with Figure 9 and

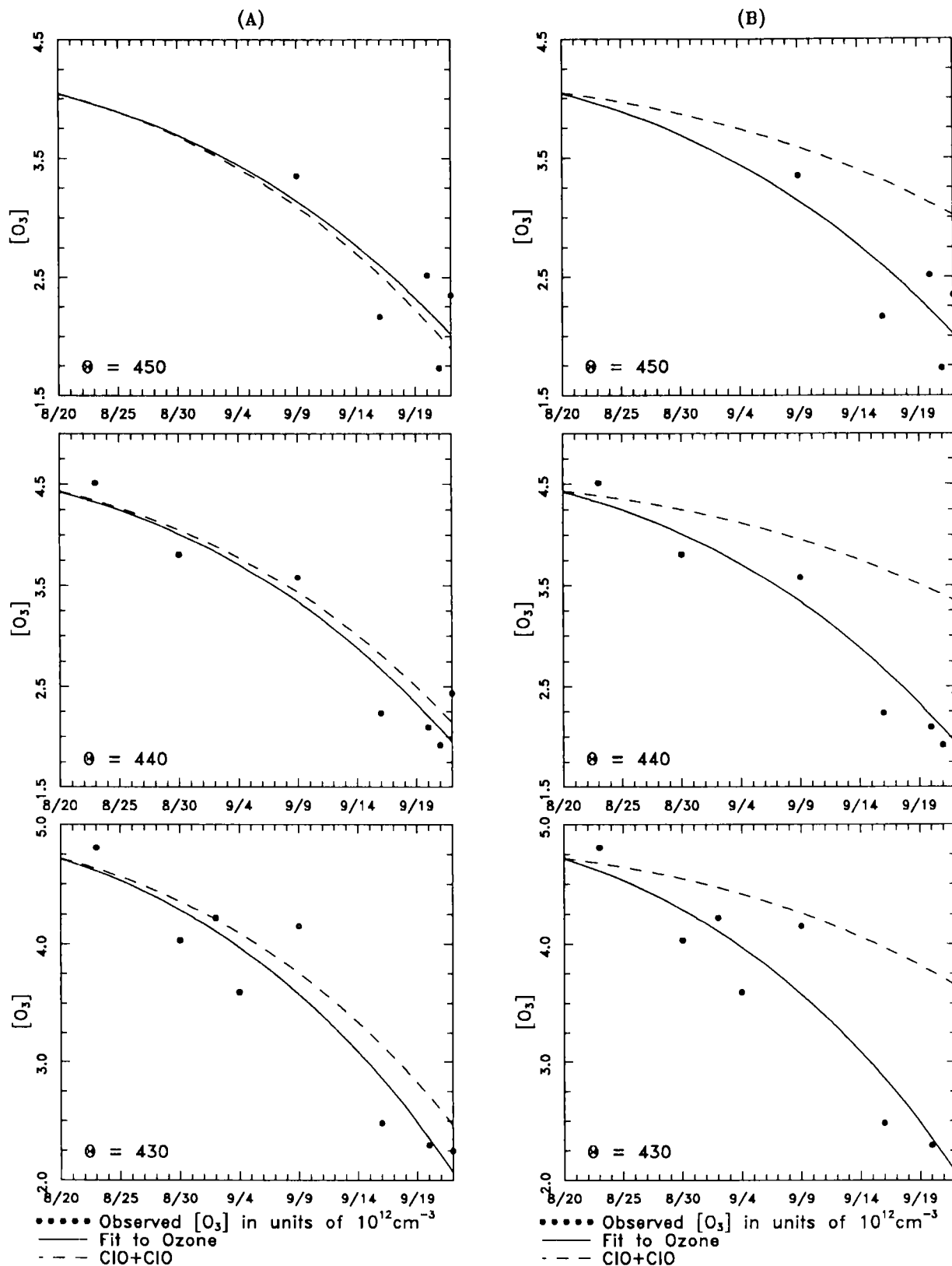


Fig. 11. Comparison between calculated and observed O_3 destruction using two different values for k_1^{III} . (a) The rate of ozone destruction, based on observed ClO and the value for k_1^{III} reported by Hayman *et al.* [1986]. (b) The rate of ozone destruction, based on observed ClO and the value for k_1^{III} reported by Sander *et al.* [1989]. In all cases the solid curve represents a fit to the O_3 data, assuming a slope proportional to $[ClO]^2$. Potential temperature surfaces 450, 440, and 430 K are shown.

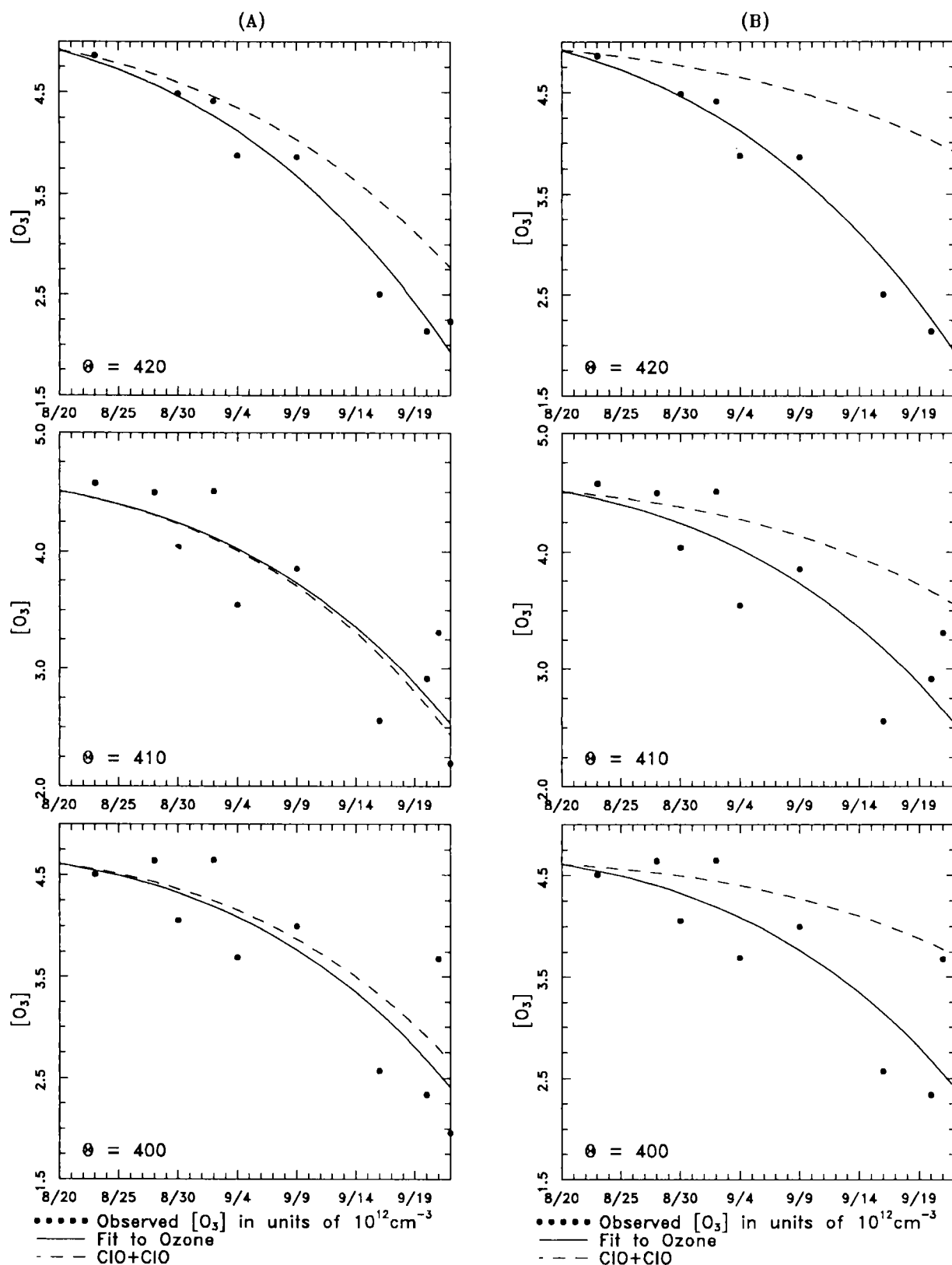


Fig. 12. Comparison between calculated and observed O_3 destruction using two different values for k_1^{III} . (a) The rate of ozone destruction, based on observed ClO and the value for k_1^{III} reported by Hayman *et al.* [1986]. (b) The rate of ozone destruction, based on observed ClO and the value for k_1^{III} reported by Sander *et al.* [1989]. In all cases the solid curve represents a fit to the O_3 data, assuming a slope proportional to $[\text{ClO}]^2$. Potential temperature surfaces 420, 410, and 400 K are shown.

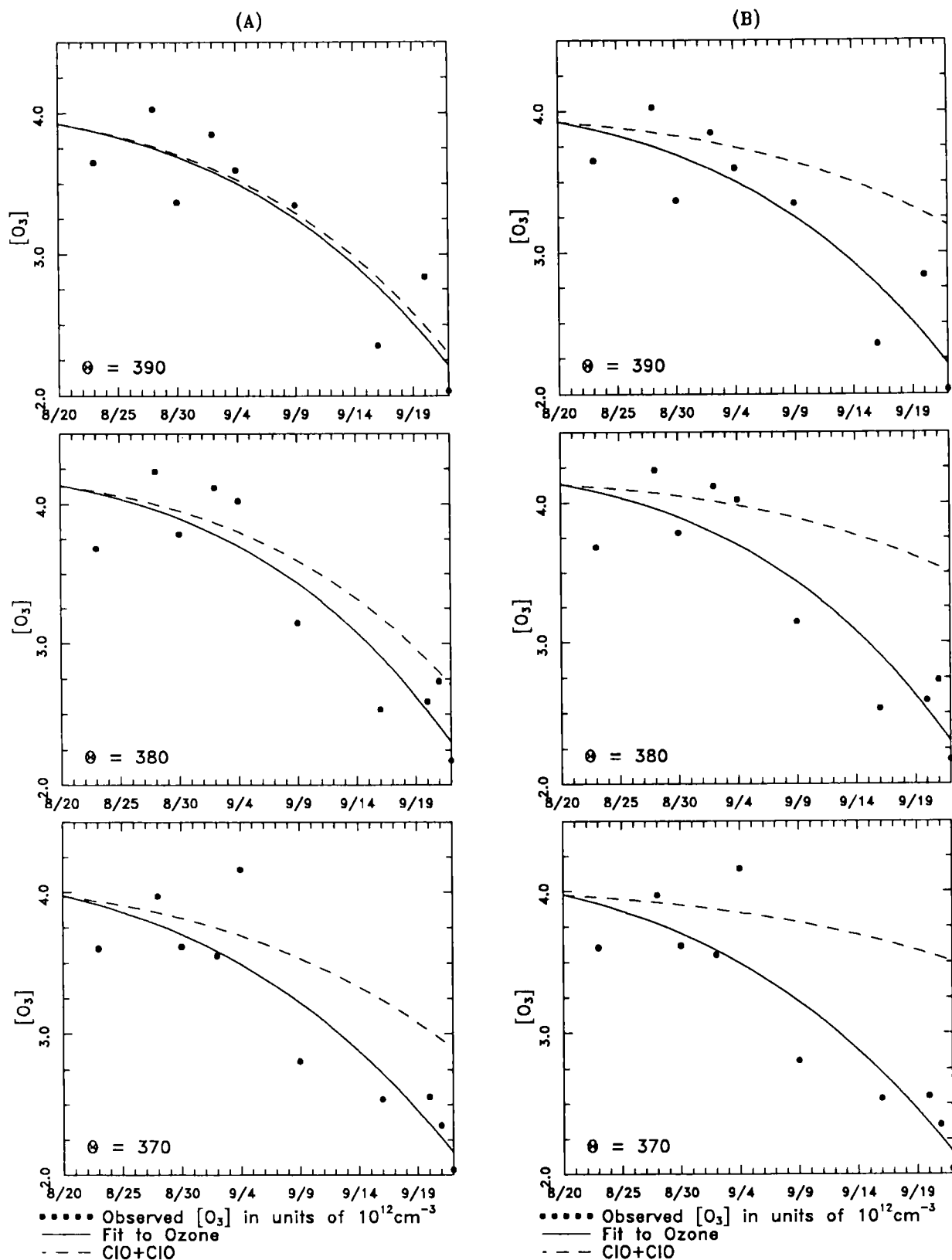


Fig. 13. Comparison between calculated and observed O_3 destruction using two different values for k_1^{III} . (a) The rate of ozone destruction, based on observed ClO and the value for k_1^{III} reported by Hayman *et al.* [1986]. (b) The rate of ozone destruction, based on observed ClO and the value for k_1^{III} reported by Sander *et al.* [1989]. In all cases the solid curve represents a fit to the O_3 data assuming a slope proportional to $[ClO]^2$. Potential temperature surfaces 390, 380, and 370 K are shown.

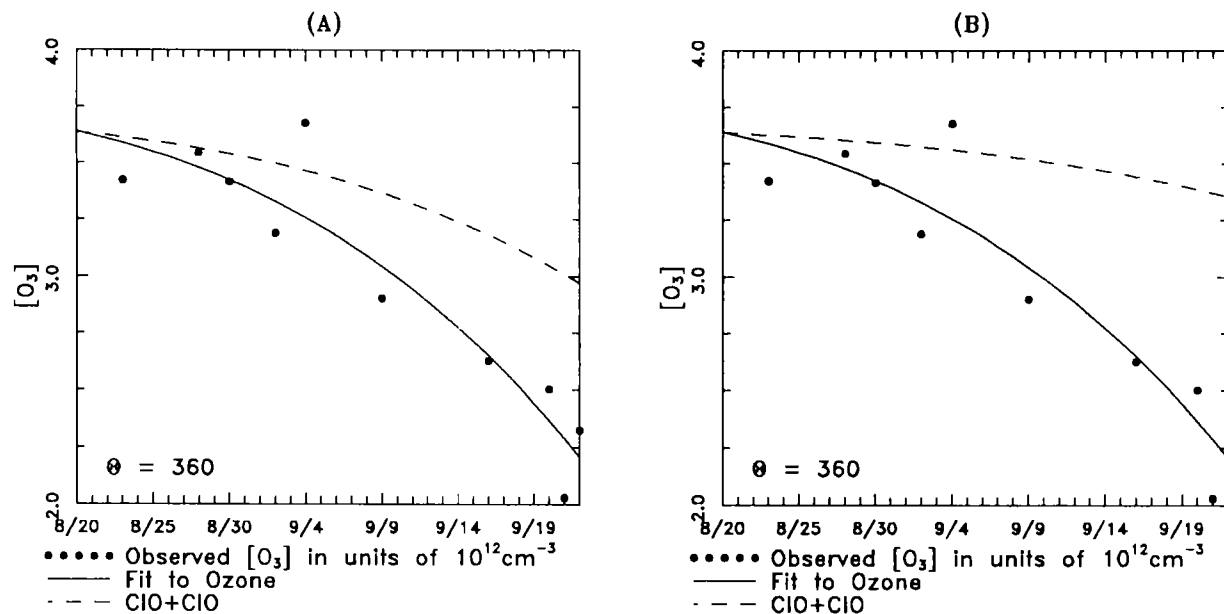


Fig. 14. Comparison between calculated and observed O_3 destruction using two different values for k_1^{III} . (a) The rate of ozone destruction based on observed ClO and the value for k_1^{III} reported by Hayman *et al.* [1986]. (b) The rate of ozone destruction based on observed ClO and the value for k_1^{III} reported by Sander *et al.* [1989]. In all cases the solid curve represents a fit to the O_3 data assuming a slope proportional to $[\text{ClO}]^2$. Potential temperature surface 360 K is shown.

to demonstrate the implications of a factor of 2 change in k_1^{III} within the context of our analysis. With respect to the latter point, the difference is dramatic. For the Hayman *et al.* [1986] rate constant (Figures 11a, 12a, 13a, and 14a), the calculated rate of ozone loss based on mechanism I alone is nearly identical to the observed rate of ozone loss. This conclusion holds for all Θ surfaces from 380 to 450 K. In marked contrast, however, are the rates based on the recent results of Sander *et al.* [1989]. In this case, the reported rate of dimer formation at the temperatures and pressures appropriate to the vortex are more than a factor of 2 lower than the Hayman *et al.* [1986] rate constant. Thus the calculated rate of ozone loss is less than half of that observed.

It is important to note that the results presented in Figures 11–14 assume that the only product of ClO recombination is the symmetric dimer, ClOOC l , and further, that the sole product of dimer photodissociation is Cl and ClO. As we have noted, both of these assumptions need careful study in the laboratory.

We can summarize the fractional removal rates of ozone attributable to mechanism I in three ways. Figure 15 presents the calculated O_3 loss for each potential temperature, superposed on the observed loss using the $[\text{ClO}]^2$ fit to O_3 data. This is done for the Hayman *et al.* [1986] rate constant and the Sander *et al.* [1989] rate constant. This shows at a glance the altitude dependent relationship between calculated O_3 loss based on mechanism I and observed O_3 loss.

An alternative summary of the fraction of observed O_3 loss described by mechanism I is shown in Figure 16. Figure 16a tracks the percent of observed O_3 loss integrated over potential temperature surfaces 360–450 K as a function of

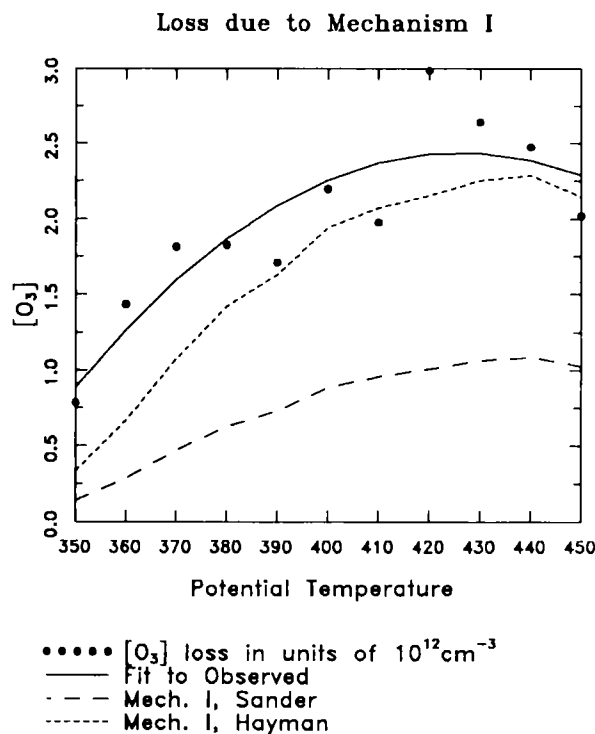


Fig. 15. Comparison between the observed absolute amount of ozone destroyed within the Antarctic vortex, represented by the solid curve fit to the data points, and the amount of ozone removed by mechanism I ($\text{ClO} + \text{ClO} + M \rightarrow \text{ClOOC l} + M$), using the termolecular rate reported by Sander *et al.* [1989] (dashed curve), and the termolecular rate reported by Hayman *et al.* [1986] (dotted curve).

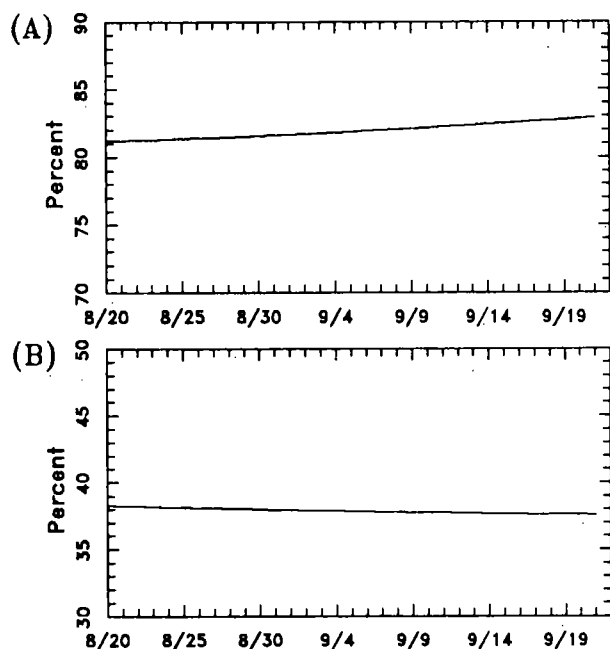


Fig. 16. The time development of the fractional amount of observed ozone loss accounted for by mechanism I using (a) the forward rate of dimer formation reported by Hayman *et al.* [1986], and (b) Sander *et al.* [1989].

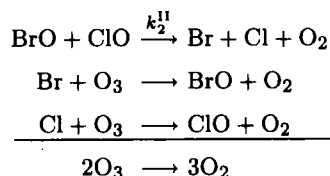
time throughout the mission, using the Hayman *et al.* [1986] rate constant; Figure 16b does the same using the Sander *et al.* [1989] rate constant.

Finally, we can integrate over both space and time to define a single fraction of observed O₃ loss attributed to mechanism I. For the Hayman *et al.* [1986] rate constant, 82% of the observed loss is subsumed by mechanism I; for the Sander *et al.* [1989] rate constant, 38% of the observed loss is subsumed by mechanism I.

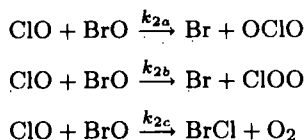
Mechanism II

The second mechanism in this class, proposed by McElroy *et al.* [1986], couples the chlorine and bromine family together:

Mechanism II



While the first reaction is rate limiting, and we will use k_2^{II} for our ozone loss calculation, it is important to note that there are three significant product channels for this reaction [see Sander and Friedl, 1989; Friedl and Sander, 1989; and Toohey and Anderson, 1988]:



for which the kinetics are now well-defined. Given that ClOO thermally dissociates to Cl + O₂ and that BrCl photodissociates on a very short time scale, we will set

$$k_2^{\text{II}} = k_{2b} + k_{2c}$$

with

$$\begin{aligned}
 k_{2b} &= 2.9 \times 10^{-12} \exp(217/T) \text{ cm}^3 \text{ s}^{-1} \\
 k_{2c} &= 5.8 \times 10^{-13} \exp(168/T) \text{ cm}^3 \text{ s}^{-1}
 \end{aligned}$$

based on Sander and Friedl [1989] and Friedl and Sander [1989].

Thus using the same approach taken for mechanism I, we write

$$(-d[\text{O}_3]/dt)_{\text{mech. II}} = 2k_2^{\text{II}}[\text{BrO}][\text{ClO}]$$

The spatial and temporal evolution of [ClO] was defined for mechanism I. We use the same distribution for this calculation. For [BrO]/[M], we will use the altitude-independent distribution of 5 pptv previously discussed.

Given the in situ [ClO] and [BrO] data in combination with the laboratory values for $k_2^{\text{II}} = k_{2b} + k_{2c}$, we can now calculate the amount of ozone destroyed in each diurnal cycle by mechanism II

$$(\Delta\text{O}_3)_{\text{mech. II}} = 2k_2^{\text{II}}[\text{ClO}][\text{BrO}]\Delta t$$

As we did with mechanism I, we can accurately estimate the daily exposure period, Δt , by using a diurnal calculation of ClO and BrO to determine the shape of the diurnally varying product [ClO][BrO], and then normalize the diurnal shape to the observed values of [ClO] and [BrO] at midday. These diurnal waveforms for mechanism II are displayed in Figure 17.

The effective exposure, $Q^{\text{ClO-BrO}}$, analogous to that defined in the previous discussion of mechanism I, is displayed as a function of calendar date throughout the mission in Figure 18. It is interesting to note that $Q^{\text{ClO-BrO}} > Q^{\text{ClO-ClO}}$, because BrO rises significantly faster at sunrise than ClO. For purposes of cross comparison with other approaches, we summarize the results of our ozone loss rate calculation for the potential temperature surfaces 440, 410, 390, and 360 K in Table 2.

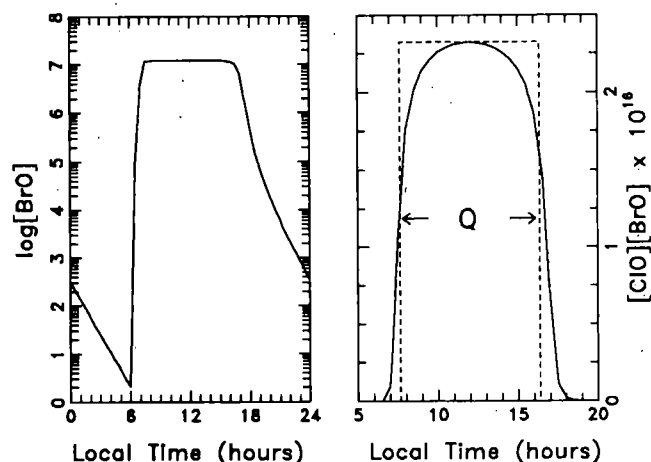
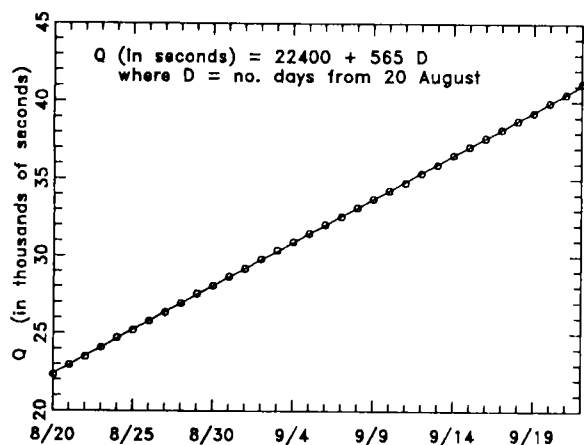


Fig. 17. Diurnal behavior of [ClO][BrO] used in the calculation of $Q^{\text{ClO-BrO}}$.



Q values inside the chemically perturbed region

Fig. 18. Time development of $Q^{\text{ClO-BrO}}$ for mechanism II throughout the course of the ER-2 mission.

TABLE 2. Summary of Ozone Loss on the Potential Temperature Surfaces of 440, 420, 390, and 360 K Resulting From Mechanism II, $\text{ClO} + \text{BrO} \rightarrow \text{Cl} + \text{Br} + \text{O}_2$. Suggested by *McElroy et al.* [1986], Based on ER-2 Observations of ClO and BrO

Day	$[\text{ClO}]$, mol cm^{-3}	$[\text{BrO}]$, mol cm^{-3}	$[M]$, $\times 10^{18} \text{cm}^{-3}$	T , $^{\circ}\text{K}$	k^{II} , $\text{cm}^3 \text{s}^{-1}$	Q , $\times 10^4 \text{s}$	$-\Delta\text{O}_3$, $\text{mol cm}^{-3} \text{d}^{-1}$
440 $\pm$ 5 K Surface							
Aug. 20	1.46×10^9	1.08×10^7	2.16	191.3	1.04×10^{-11}	2.23	7.33×10^9
Aug. 21	1.48×10^9	1.08×10^7	2.16	191.4	1.04×10^{-11}	2.30	7.66×10^9
Aug. 22	1.51×10^9	1.08×10^7	2.16	191.5	1.04×10^{-11}	2.35	7.95×10^9
Aug. 23	1.53×10^9	1.08×10^7	2.15	191.5	1.04×10^{-11}	2.41	8.28×10^9
Aug. 24	1.56×10^9	1.08×10^7	2.15	191.6	1.04×10^{-11}	2.47	8.62×10^9
Aug. 25	1.58×10^9	1.08×10^7	2.15	191.7	1.04×10^{-11}	2.52	8.92×10^9
Aug. 26	1.61×10^9	1.07×10^7	2.15	191.8	1.04×10^{-11}	2.58	9.26×10^9
Aug. 27	1.63×10^9	1.07×10^7	2.15	191.9	1.04×10^{-11}	2.63	9.59×10^9
Aug. 28	1.66×10^9	1.07×10^7	2.15	191.9	1.04×10^{-11}	2.69	9.94×10^9
Aug. 29	1.68×10^9	1.07×10^7	2.15	192.0	1.04×10^{-11}	2.75	1.03×10^{10}
Aug. 30	1.71×10^9	1.07×10^7	2.14	192.1	1.04×10^{-11}	2.81	1.06×10^{10}
Aug. 31	1.73×10^9	1.07×10^7	2.14	192.2	1.04×10^{-11}	2.87	1.10×10^{10}
Sept. 1	1.76×10^9	1.07×10^7	2.14	192.2	1.04×10^{-11}	2.92	1.14×10^{10}
Sept. 2	1.78×10^9	1.07×10^7	2.14	192.3	1.04×10^{-11}	2.98	1.18×10^{10}
Sept. 3	1.81×10^9	1.07×10^7	2.14	192.4	1.03×10^{-11}	3.04	1.21×10^{10}
Sept. 4	1.83×10^9	1.07×10^7	2.14	192.5	1.03×10^{-11}	3.09	1.25×10^{10}
Sept. 5	1.86×10^9	1.07×10^7	2.13	192.5	1.03×10^{-11}	3.15	1.29×10^{10}
Sept. 6	1.88×10^9	1.07×10^7	2.13	192.6	1.03×10^{-11}	3.20	1.33×10^{10}
Sept. 7	1.91×10^9	1.07×10^7	2.13	192.7	1.03×10^{-11}	3.25	1.37×10^{10}
Sept. 8	1.93×10^9	1.06×10^7	2.13	192.8	1.03×10^{-11}	3.32	1.41×10^{10}
Sept. 9	1.95×10^9	1.06×10^7	2.13	192.9	1.03×10^{-11}	3.37	1.45×10^{10}
Sept. 10	1.98×10^9	1.06×10^7	2.13	192.9	1.03×10^{-11}	3.43	1.49×10^{10}
Sept. 11	2.00×10^9	1.06×10^7	2.12	193.0	1.03×10^{-11}	3.48	1.53×10^{10}
Sept. 12	2.03×10^9	1.06×10^7	2.12	193.1	1.03×10^{-11}	3.54	1.57×10^{10}
Sept. 13	2.05×10^9	1.06×10^7	2.12	193.2	1.03×10^{-11}	3.59	1.61×10^{10}
Sept. 14	2.08×10^9	1.06×10^7	2.12	193.2	1.03×10^{-11}	3.65	1.66×10^{10}
Sept. 15	2.10×10^9	1.06×10^7	2.12	193.3	1.03×10^{-11}	3.71	1.70×10^{10}
Sept. 16	2.13×10^9	1.06×10^7	2.12	193.4	1.03×10^{-11}	3.76	1.74×10^{10}
Sept. 17	2.15×10^9	1.06×10^7	2.12	193.5	1.03×10^{-11}	3.82	1.79×10^{10}
Sept. 18	2.18×10^9	1.06×10^7	2.11	193.5	1.03×10^{-11}	3.88	1.83×10^{10}
Sept. 19	2.20×10^9	1.06×10^7	2.11	193.6	1.03×10^{-11}	3.93	1.88×10^{10}
Sept. 20	2.23×10^9	1.06×10^7	2.11	193.7	1.03×10^{-11}	3.99	1.93×10^{10}
Sept. 21	2.25×10^9	1.05×10^7	2.11	193.8	1.03×10^{-11}	4.04	1.97×10^{10}
Sept. 22	2.28×10^9	1.05×10^7	2.11	193.9	1.03×10^{-11}	4.11	2.03×10^{10}

TABLE 2. (continued)

Day	[ClO], mol cm ⁻³	[BrO], mol cm ⁻³	[M], ×10 ¹⁸ cm ⁻³	T, °K	k ^{II} , cm ³ s ⁻¹	Q, ×10 ⁴ s	-ΔO ₃ , mol cm ⁻³ d ⁻¹
<i>420 ± 5 K Surface</i>							
Aug. 20	1.23 × 10 ⁹	1.22 × 10 ⁷	2.45	190.3	1.05 × 10 ⁻¹¹	2.23	7.02 × 10 ⁹
Aug. 21	1.25 × 10 ⁹	1.22 × 10 ⁷	2.45	190.4	1.05 × 10 ⁻¹¹	2.30	7.38 × 10 ⁹
Aug. 22	1.28 × 10 ⁹	1.23 × 10 ⁷	2.45	190.5	1.05 × 10 ⁻¹¹	2.35	7.70 × 10 ⁹
Aug. 23	1.31 × 10 ⁹	1.23 × 10 ⁷	2.45	190.6	1.05 × 10 ⁻¹¹	2.41	8.07 × 10 ⁹
Aug. 24	1.33 × 10 ⁹	1.23 × 10 ⁷	2.45	190.7	1.04 × 10 ⁻¹¹	2.47	8.44 × 10 ⁹
Aug. 25	1.36 × 10 ⁹	1.23 × 10 ⁷	2.46	190.9	1.04 × 10 ⁻¹¹	2.52	8.78 × 10 ⁹
Aug. 26	1.39 × 10 ⁹	1.23 × 10 ⁷	2.46	191.0	1.04 × 10 ⁻¹¹	2.58	9.17 × 10 ⁹
Aug. 27	1.41 × 10 ⁹	1.23 × 10 ⁷	2.46	191.1	1.04 × 10 ⁻¹¹	2.63	9.54 × 10 ⁹
Aug. 28	1.44 × 10 ⁹	1.23 × 10 ⁷	2.46	191.2	1.04 × 10 ⁻¹¹	2.69	9.94 × 10 ⁹
Aug. 29	1.47 × 10 ⁹	1.23 × 10 ⁷	2.46	191.4	1.04 × 10 ⁻¹¹	2.75	1.04 × 10 ¹⁰
Aug. 30	1.49 × 10 ⁹	1.23 × 10 ⁷	2.47	191.5	1.04 × 10 ⁻¹¹	2.81	1.07 × 10 ¹⁰
Aug. 31	1.52 × 10 ⁹	1.23 × 10 ⁷	2.47	191.6	1.04 × 10 ⁻¹¹	2.87	1.12 × 10 ¹⁰
Sept. 1	1.55 × 10 ⁹	1.23 × 10 ⁷	2.47	191.7	1.04 × 10 ⁻¹¹	2.92	1.16 × 10 ¹⁰
Sept. 2	1.57 × 10 ⁹	1.24 × 10 ⁷	2.47	191.9	1.04 × 10 ⁻¹¹	2.98	1.20 × 10 ¹⁰
Sept. 3	1.60 × 10 ⁹	1.24 × 10 ⁷	2.47	192.0	1.04 × 10 ⁻¹¹	3.04	1.25 × 10 ¹⁰
Sept. 4	1.63 × 10 ⁹	1.24 × 10 ⁷	2.47	192.1	1.04 × 10 ⁻¹¹	3.09	1.29 × 10 ¹⁰
Sept. 5	1.65 × 10 ⁹	1.24 × 10 ⁷	2.48	192.2	1.04 × 10 ⁻¹¹	3.15	1.33 × 10 ¹⁰
Sept. 6	1.68 × 10 ⁹	1.24 × 10 ⁷	2.48	192.3	1.04 × 10 ⁻¹¹	3.20	1.38 × 10 ¹⁰
Sept. 7	1.71 × 10 ⁹	1.24 × 10 ⁷	2.48	192.5	1.03 × 10 ⁻¹¹	3.25	1.42 × 10 ¹⁰
Sept. 8	1.73 × 10 ⁹	1.24 × 10 ⁷	2.48	192.6	1.03 × 10 ⁻¹¹	3.32	1.47 × 10 ¹⁰
Sept. 9	1.76 × 10 ⁹	1.24 × 10 ⁷	2.48	192.7	1.03 × 10 ⁻¹¹	3.37	1.52 × 10 ¹⁰
Sept. 10	1.79 × 10 ⁹	1.24 × 10 ⁷	2.49	192.8	1.03 × 10 ⁻¹¹	3.43	1.57 × 10 ¹⁰
Sept. 11	1.81 × 10 ⁹	1.24 × 10 ⁷	2.49	193.0	1.03 × 10 ⁻¹¹	3.48	1.62 × 10 ¹⁰
Sept. 12	1.84 × 10 ⁹	1.24 × 10 ⁷	2.49	193.1	1.03 × 10 ⁻¹¹	3.54	1.67 × 10 ¹⁰
Sept. 13	1.87 × 10 ⁹	1.25 × 10 ⁷	2.49	193.2	1.03 × 10 ⁻¹¹	3.59	1.72 × 10 ¹⁰
Sept. 14	1.89 × 10 ⁹	1.25 × 10 ⁷	2.49	193.3	1.03 × 10 ⁻¹¹	3.65	1.77 × 10 ¹⁰
Sept. 15	1.92 × 10 ⁹	1.25 × 10 ⁷	2.49	193.5	1.03 × 10 ⁻¹¹	3.71	1.83 × 10 ¹⁰
Sept. 16	1.95 × 10 ⁹	1.25 × 10 ⁷	2.50	193.6	1.03 × 10 ⁻¹¹	3.76	1.88 × 10 ¹⁰
Sept. 17	1.97 × 10 ⁹	1.25 × 10 ⁷	2.50	193.7	1.03 × 10 ⁻¹¹	3.82	1.93 × 10 ¹⁰
Sept. 18	2.00 × 10 ⁹	1.25 × 10 ⁷	2.50	193.8	1.03 × 10 ⁻¹¹	3.88	1.99 × 10 ¹⁰
Sept. 19	2.03 × 10 ⁹	1.25 × 10 ⁷	2.50	194.0	1.03 × 10 ⁻¹¹	3.93	2.04 × 10 ¹⁰
Sept. 20	2.05 × 10 ⁹	1.25 × 10 ⁷	2.50	194.1	1.02 × 10 ⁻¹¹	3.99	2.10 × 10 ¹⁰
Sept. 21	2.08 × 10 ⁹	1.25 × 10 ⁷	2.50	194.2	1.02 × 10 ⁻¹¹	4.04	2.16 × 10 ¹⁰
Sept. 22	2.11 × 10 ⁹	1.25 × 10 ⁷	2.51	194.3	1.02 × 10 ⁻¹¹	4.11	2.22 × 10 ¹⁰
<i>390 ± 5 K Surface</i>							
Aug. 20	8.60 × 10 ⁸	1.57 × 10 ⁷	3.13	190.6	1.05 × 10 ⁻¹¹	2.23	6.29 × 10 ⁹
Aug. 21	8.85 × 10 ⁸	1.57 × 10 ⁷	3.14	190.8	1.04 × 10 ⁻¹¹	2.30	6.66 × 10 ⁹
Aug. 22	9.09 × 10 ⁸	1.57 × 10 ⁷	3.15	191.0	1.04 × 10 ⁻¹¹	2.35	7.00 × 10 ⁹
Aug. 23	9.33 × 10 ⁸	1.58 × 10 ⁷	3.15	191.2	1.04 × 10 ⁻¹¹	2.41	7.39 × 10 ⁹
Aug. 24	9.57 × 10 ⁸	1.58 × 10 ⁷	3.16	191.3	1.04 × 10 ⁻¹¹	2.47	7.79 × 10 ⁹
Aug. 25	9.82 × 10 ⁸	1.58 × 10 ⁷	3.17	191.5	1.04 × 10 ⁻¹¹	2.52	8.15 × 10 ⁹
Aug. 26	1.01 × 10 ⁹	1.59 × 10 ⁷	3.18	191.7	1.04 × 10 ⁻¹¹	2.58	8.56 × 10 ⁹
Aug. 27	1.03 × 10 ⁹	1.59 × 10 ⁷	3.18	191.9	1.04 × 10 ⁻¹¹	2.63	8.96 × 10 ⁹
Aug. 28	1.05 × 10 ⁹	1.60 × 10 ⁷	3.19	192.1	1.04 × 10 ⁻¹¹	2.69	9.39 × 10 ⁹
Aug. 29	1.08 × 10 ⁹	1.60 × 10 ⁷	3.20	192.3	1.04 × 10 ⁻¹¹	2.75	9.84 × 10 ⁹
Aug. 30	1.10 × 10 ⁹	1.60 × 10 ⁷	3.21	192.5	1.03 × 10 ⁻¹¹	2.81	1.03 × 10 ¹⁰
Aug. 31	1.13 × 10 ⁹	1.61 × 10 ⁷	3.21	192.6	1.03 × 10 ⁻¹¹	2.87	1.07 × 10 ¹⁰
Sept. 1	1.15 × 10 ⁹	1.61 × 10 ⁷	3.22	192.8	1.03 × 10 ⁻¹¹	2.92	1.12 × 10 ¹⁰
Sept. 2	1.18 × 10 ⁹	1.61 × 10 ⁷	3.23	193.0	1.03 × 10 ⁻¹¹	2.98	1.17 × 10 ¹⁰
Sept. 3	1.20 × 10 ⁹	1.62 × 10 ⁷	3.24	193.2	1.03 × 10 ⁻¹¹	3.04	1.21 × 10 ¹⁰
Sept. 4	1.22 × 10 ⁹	1.62 × 10 ⁷	3.24	193.4	1.03 × 10 ⁻¹¹	3.09	1.26 × 10 ¹⁰
Sept. 5	1.25 × 10 ⁹	1.63 × 10 ⁷	3.25	193.6	1.03 × 10 ⁻¹¹	3.15	1.31 × 10 ¹⁰
Sept. 6	1.27 × 10 ⁹	1.63 × 10 ⁷	3.26	193.8	1.03 × 10 ⁻¹¹	3.20	1.36 × 10 ¹⁰
Sept. 7	1.30 × 10 ⁹	1.63 × 10 ⁷	3.27	194.0	1.03 × 10 ⁻¹¹	3.25	1.41 × 10 ¹⁰
Sept. 8	1.32 × 10 ⁹	1.64 × 10 ⁷	3.27	194.1	1.02 × 10 ⁻¹¹	3.32	1.47 × 10 ¹⁰
Sept. 9	1.35 × 10 ⁹	1.64 × 10 ⁷	3.28	194.3	1.02 × 10 ⁻¹¹	3.37	1.52 × 10 ¹⁰
Sept. 10	1.37 × 10 ⁹	1.64 × 10 ⁷	3.29	194.5	1.02 × 10 ⁻¹¹	3.43	1.58 × 10 ¹⁰
Sept. 11	1.39 × 10 ⁹	1.65 × 10 ⁷	3.30	194.7	1.02 × 10 ⁻¹¹	3.48	1.63 × 10 ¹⁰
Sept. 12	1.42 × 10 ⁹	1.65 × 10 ⁷	3.30	194.9	1.02 × 10 ⁻¹¹	3.54	1.69 × 10 ¹⁰
Sept. 13	1.44 × 10 ⁹	1.66 × 10 ⁷	3.31	195.1	1.02 × 10 ⁻¹¹	3.59	1.75 × 10 ¹⁰
Sept. 14	1.47 × 10 ⁹	1.66 × 10 ⁷	3.32	195.3	1.02 × 10 ⁻¹¹	3.65	1.81 × 10 ¹⁰
Sept. 15	1.49 × 10 ⁹	1.66 × 10 ⁷	3.33	195.5	1.02 × 10 ⁻¹¹	3.71	1.87 × 10 ¹⁰
Sept. 16	1.52 × 10 ⁹	1.67 × 10 ⁷	3.33	195.6	1.02 × 10 ⁻¹¹	3.76	1.93 × 10 ¹⁰
Sept. 17	1.54 × 10 ⁹	1.67 × 10 ⁷	3.34	195.8	1.02 × 10 ⁻¹¹	3.82	2.00 × 10 ¹⁰

TABLE 2. (continued)

Day	[ClO], mol cm ⁻³	[BrO], mol cm ⁻³	[M], ×10 ¹⁸ cm ⁻³	T, °K	k ^{II} , cm ³ s ⁻¹	Q, ×10 ⁴ s	-ΔO ₃ , mol cm ⁻³ d ⁻¹
390 ± 5 K Surface (continued)							
Sept. 18	1.56 × 10 ⁹	1.67 × 10 ⁷	3.35	196.0	1.01 × 10 ⁻¹¹	3.88	2.06 × 10 ¹⁰
Sept. 19	1.59 × 10 ⁹	1.68 × 10 ⁷	3.36	196.2	1.01 × 10 ⁻¹¹	3.93	2.12 × 10 ¹⁰
Sept. 20	1.61 × 10 ⁹	1.68 × 10 ⁷	3.36	196.4	1.01 × 10 ⁻¹¹	3.99	2.19 × 10 ¹⁰
Sept. 21	1.64 × 10 ⁹	1.69 × 10 ⁷	3.37	196.6	1.01 × 10 ⁻¹¹	4.04	2.26 × 10 ¹⁰
Sept. 22	1.66 × 10 ⁹	1.69 × 10 ⁷	3.38	196.8	1.01 × 10 ⁻¹¹	4.11	2.33 × 10 ¹⁰
360 ± 5 K Surface							
Aug. 20	5.37 × 10 ⁸	1.95 × 10 ⁷	3.89	190.5	1.05 × 10 ⁻¹¹	2.23	4.88 × 10 ⁹
Aug. 21	5.48 × 10 ⁸	1.96 × 10 ⁷	3.92	190.8	1.04 × 10 ⁻¹¹	2.30	5.15 × 10 ⁹
Aug. 22	5.59 × 10 ⁸	1.97 × 10 ⁷	3.94	191.1	1.04 × 10 ⁻¹¹	2.35	5.39 × 10 ⁹
Aug. 23	5.69 × 10 ⁸	1.98 × 10 ⁷	3.97	191.4	1.04 × 10 ⁻¹¹	2.41	5.66 × 10 ⁹
Aug. 24	5.80 × 10 ⁸	2.00 × 10 ⁷	3.99	191.8	1.04 × 10 ⁻¹¹	2.47	5.94 × 10 ⁹
Aug. 25	5.91 × 10 ⁸	2.01 × 10 ⁷	4.02	192.1	1.04 × 10 ⁻¹¹	2.52	6.20 × 10 ⁹
Aug. 26	6.01 × 10 ⁸	2.02 × 10 ⁷	4.05	192.4	1.03 × 10 ⁻¹¹	2.58	6.49 × 10 ⁹
Aug. 27	6.12 × 10 ⁸	2.04 × 10 ⁷	4.07	192.7	1.03 × 10 ⁻¹¹	2.63	6.78 × 10 ⁹
Aug. 28	6.23 × 10 ⁸	2.05 × 10 ⁷	4.10	193.0	1.03 × 10 ⁻¹¹	2.69	7.08 × 10 ⁹
Aug. 29	6.33 × 10 ⁸	2.06 × 10 ⁷	4.12	193.3	1.03 × 10 ⁻¹¹	2.75	7.40 × 10 ⁹
Aug. 30	6.44 × 10 ⁸	2.07 × 10 ⁷	4.15	193.7	1.03 × 10 ⁻¹¹	2.81	7.70 × 10 ⁹
Aug. 31	6.55 × 10 ⁸	2.09 × 10 ⁷	4.17	194.0	1.03 × 10 ⁻¹¹	2.87	8.03 × 10 ⁹
Sept. 1	6.66 × 10 ⁸	2.10 × 10 ⁷	4.20	194.3	1.02 × 10 ⁻¹¹	2.92	8.35 × 10 ⁹
Sept. 2	6.76 × 10 ⁸	2.11 × 10 ⁷	4.23	194.6	1.02 × 10 ⁻¹¹	2.98	8.70 × 10 ⁹
Sept. 3	6.87 × 10 ⁸	2.13 × 10 ⁷	4.25	194.9	1.02 × 10 ⁻¹¹	3.04	9.04 × 10 ⁹
Sept. 4	6.98 × 10 ⁸	2.14 × 10 ⁷	4.28	195.3	1.02 × 10 ⁻¹¹	3.09	9.40 × 10 ⁹
Sept. 5	7.08 × 10 ⁸	2.15 × 10 ⁷	4.30	195.6	1.02 × 10 ⁻¹¹	3.15	9.75 × 10 ⁹
Sept. 6	7.19 × 10 ⁸	2.16 × 10 ⁷	4.33	195.9	1.01 × 10 ⁻¹¹	3.20	1.01 × 10 ¹⁰
Sept. 7	7.30 × 10 ⁸	2.18 × 10 ⁷	4.35	196.2	1.01 × 10 ⁻¹¹	3.25	1.05 × 10 ¹⁰
Sept. 8	7.40 × 10 ⁸	2.19 × 10 ⁷	4.38	196.5	1.01 × 10 ⁻¹¹	3.32	1.09 × 10 ¹⁰
Sept. 9	7.51 × 10 ⁸	2.20 × 10 ⁷	4.41	196.8	1.01 × 10 ⁻¹¹	3.37	1.13 × 10 ¹⁰
Sept. 10	7.62 × 10 ⁸	2.22 × 10 ⁷	4.43	197.2	1.01 × 10 ⁻¹¹	3.43	1.17 × 10 ¹⁰
Sept. 11	7.73 × 10 ⁸	2.23 × 10 ⁷	4.46	197.5	1.01 × 10 ⁻¹¹	3.48	1.20 × 10 ¹⁰
Sept. 12	7.83 × 10 ⁸	2.24 × 10 ⁷	4.48	197.8	1.00 × 10 ⁻¹¹	3.54	1.25 × 10 ¹⁰
Sept. 13	7.94 × 10 ⁸	2.25 × 10 ⁷	4.51	198.1	1.00 × 10 ⁻¹¹	3.59	1.29 × 10 ¹⁰
Sept. 14	8.05 × 10 ⁸	2.27 × 10 ⁷	4.53	198.4	1.00 × 10 ⁻¹¹	3.65	1.33 × 10 ¹⁰
Sept. 15	8.15 × 10 ⁸	2.28 × 10 ⁷	4.56	198.7	9.99 × 10 ⁻¹²	3.71	1.38 × 10 ¹⁰
Sept. 16	8.26 × 10 ⁸	2.29 × 10 ⁷	4.59	199.1	9.98 × 10 ⁻¹²	3.76	1.42 × 10 ¹⁰
Sept. 17	8.37 × 10 ⁸	2.31 × 10 ⁷	4.61	199.4	9.96 × 10 ⁻¹²	3.82	1.47 × 10 ¹⁰
Sept. 18	8.47 × 10 ⁸	2.32 × 10 ⁷	4.64	199.7	9.94 × 10 ⁻¹²	3.88	1.51 × 10 ¹⁰
Sept. 19	8.58 × 10 ⁸	2.33 × 10 ⁷	4.66	200.0	9.92 × 10 ⁻¹²	3.93	1.56 × 10 ¹⁰
Sept. 20	8.69 × 10 ⁸	2.34 × 10 ⁷	4.69	200.3	9.91 × 10 ⁻¹²	3.99	1.61 × 10 ¹⁰
Sept. 21	8.79 × 10 ⁸	2.36 × 10 ⁷	4.71	200.7	9.89 × 10 ⁻¹²	4.04	1.66 × 10 ¹⁰
Sept. 22	8.90 × 10 ⁸	2.37 × 10 ⁷	4.74	201.0	9.88 × 10 ⁻¹²	4.11	1.71 × 10 ¹⁰

Values of ClO and BrO from ER-2 observations are given in columns two and three. The fourth and fifth columns cite total atmospheric concentration and temperature, also obtained from the ER-2. The sixth column tracks the bimolecular rate for the formation of Cl and Br, reported recently by *Sander and Friedl* [1989] and *Friedl and Sander* [1989]. Effective exposure time in each 24-hour period, *Q*, is given in column seven. The final column represents the amount of ozone removal in each 24-hour period by mechanism II.

Turning to the lower Θ surfaces, Figure 21 demonstrates that the choice of rate constant again critically affects the results. With the *Hayman et al.* [1986] rate constant the sum of mechanisms I and II adequately describes the observed O₃ loss down to $\Theta \sim 370$ K, but with the *Sander et al.* [1989] rate constant mechanisms I and II fail dramatically in describing the observed loss rates.

We can again summarize the results in three ways. Figure 23a compares the observed absolute O₃ loss as a function of potential temperature with the contribution from mechanism I and mechanisms I and II, using the *Hayman et al.* [1986] rate constant; Figure 23b does the same us-

ing the *Sander et al.* [1989] rate constant. The contrast is dramatic. Figure 24 traces the fractional contributions to observed O₃ loss resulting from mechanism II as a function of time throughout the mission. At the beginning of the flight series, mechanism II constitutes 29% of the observed loss; by the end of the mission it constitutes about 17%. We can then integrate over both space and time to determine the percentage contribution of mechanism II to the observed O₃ loss from the beginning of the mission to the end over Θ surfaces from 360 to 450 K. We find a 21% contribution from mechanism II when compared with observed O₃ loss. Experimental uncertainties are discussed in the final section.

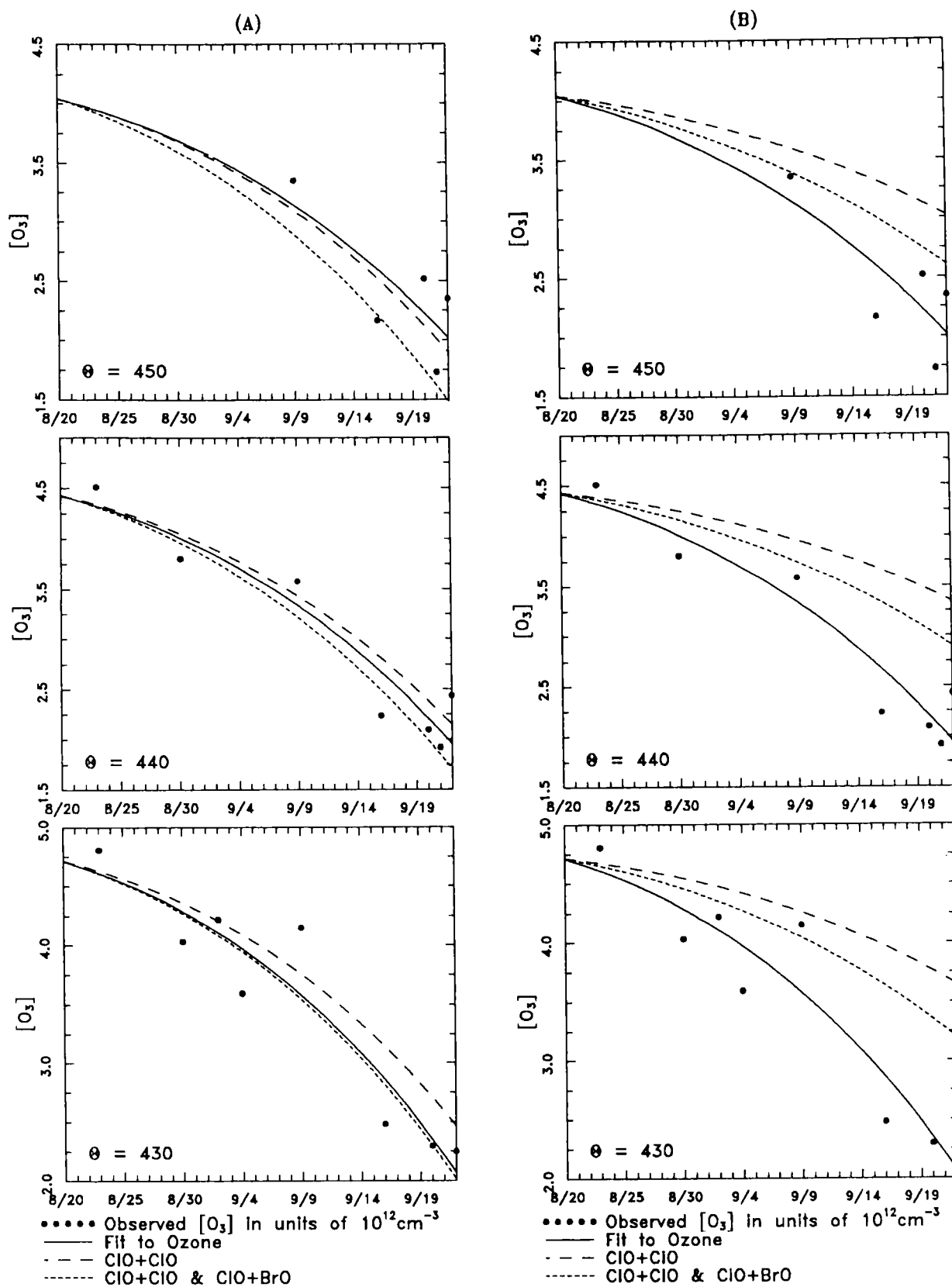


Fig. 19. Comparison between ozone loss rates resulting from mechanism I and the sum of mechanisms I and II using (a) the Hayman et al. [1986] value for k_1^{III} , and (b) the Sander et al. [1989] value for k_1^{III} . Potential temperature surfaces 450, 440, and 430 K are shown.

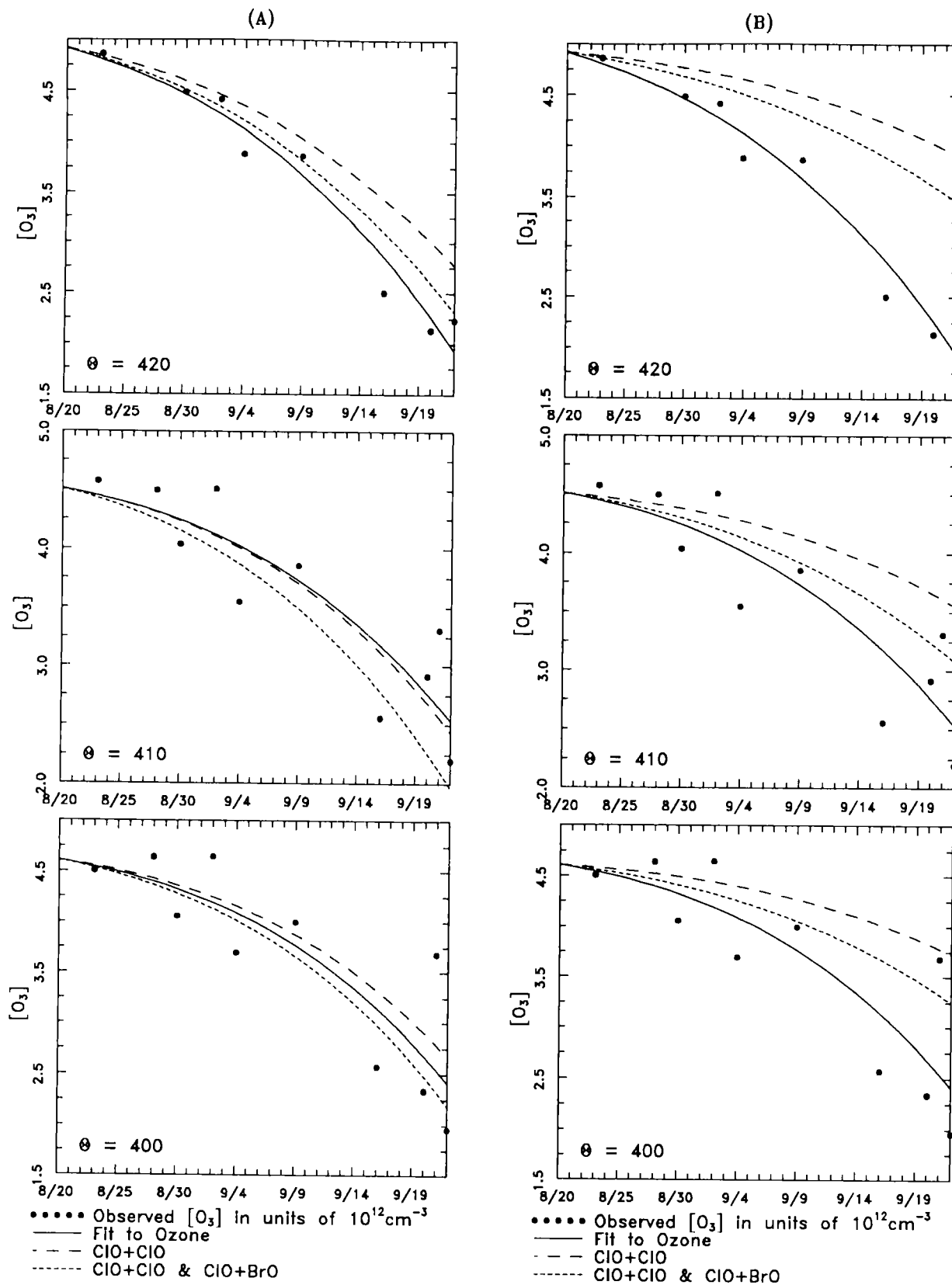


Fig. 20. Comparison between ozone loss rates resulting from mechanism I and the sum of mechanisms I and II using (a) the Hayman *et al.* [1986] value for k_1^{III} , and (b) the Sander *et al.* [1989] value for k_1^{III} . Potential temperature surfaces 420, 410, and 400 K are shown.

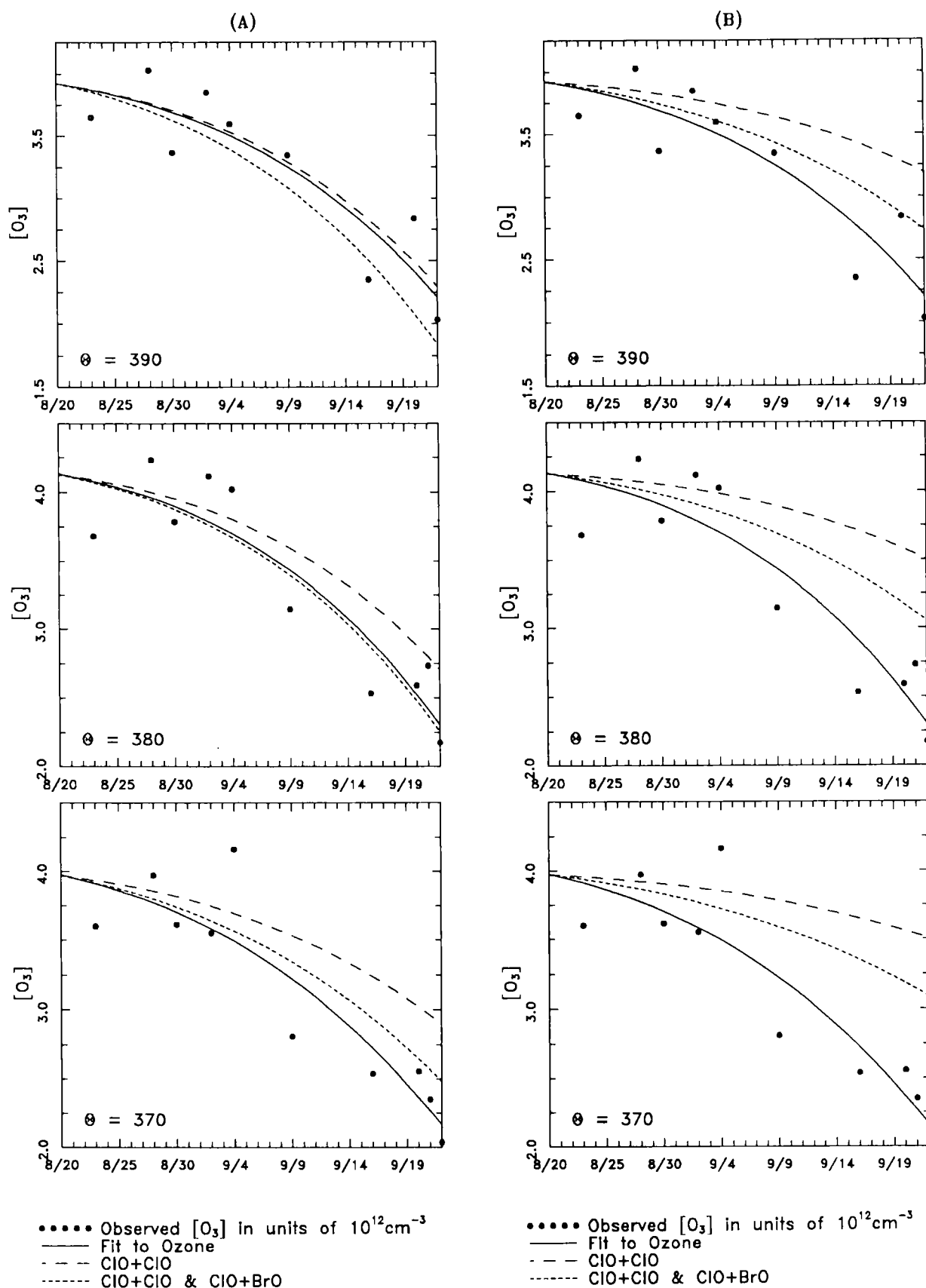


Fig. 21. Comparison between ozone loss rates resulting from mechanism I and the sum of mechanisms I and II using (a) the Hayman *et al.* [1986] value for k_1^{III} , and (b) the Sander *et al.* [1989] value for k_1^{III} . Potential temperature surfaces 390, 380, and 370 K are shown.

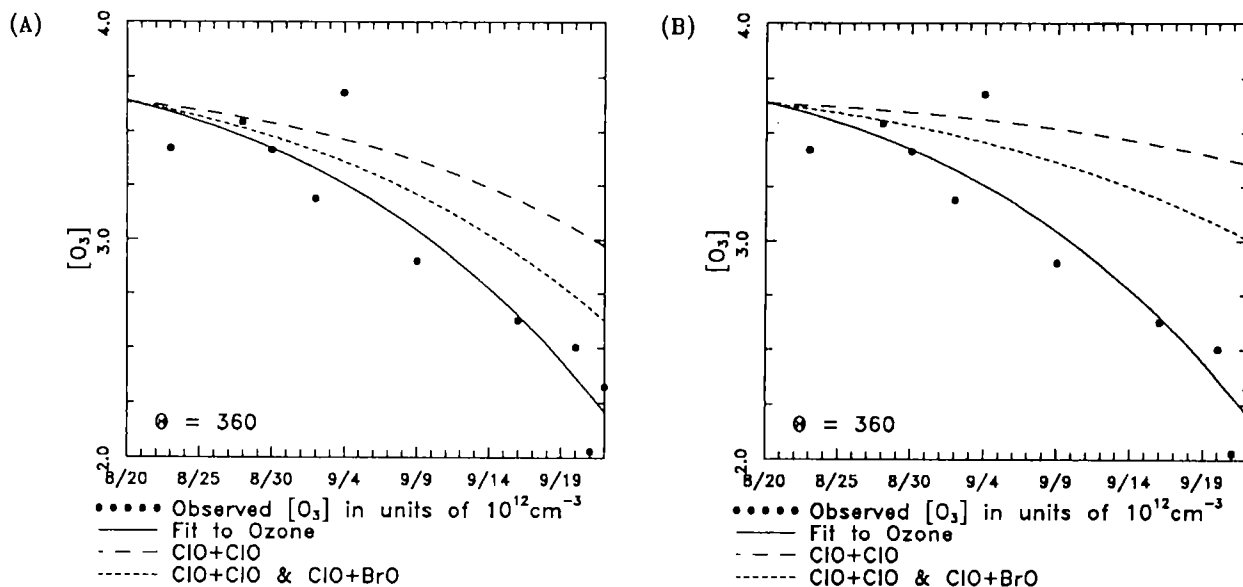
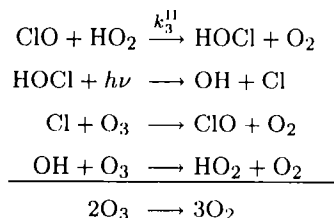


Fig. 22. Comparison between ozone loss rates resulting from mechanism I and the sum of mechanisms I and II using (a) the Hayman et al. [1986] value for k_1^{III} , and (b) the Sander et al. [1989] value for k_1^{III} . Potential temperature surface 360 is shown.

Mechanism III

We consider next the $\text{ClO}_x\text{-HO}_x$ catalytic cycle proposed by Solomon et al. [1986]:

Mechanism III



For this reaction sequence, the first reaction is rate limiting (although $\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$ can compete at certain times):

$$\Delta\text{O}_3 = 2k_3^{II}[\text{ClO}][\text{HO}_2]\Delta t$$

The kinetics of this step are well understood. We adopt a bimolecular rate

$$k_3^{II} = 4.8 \times 10^{-13} \exp(700/T) \text{ cm}^3 \text{ s}^{-1}$$

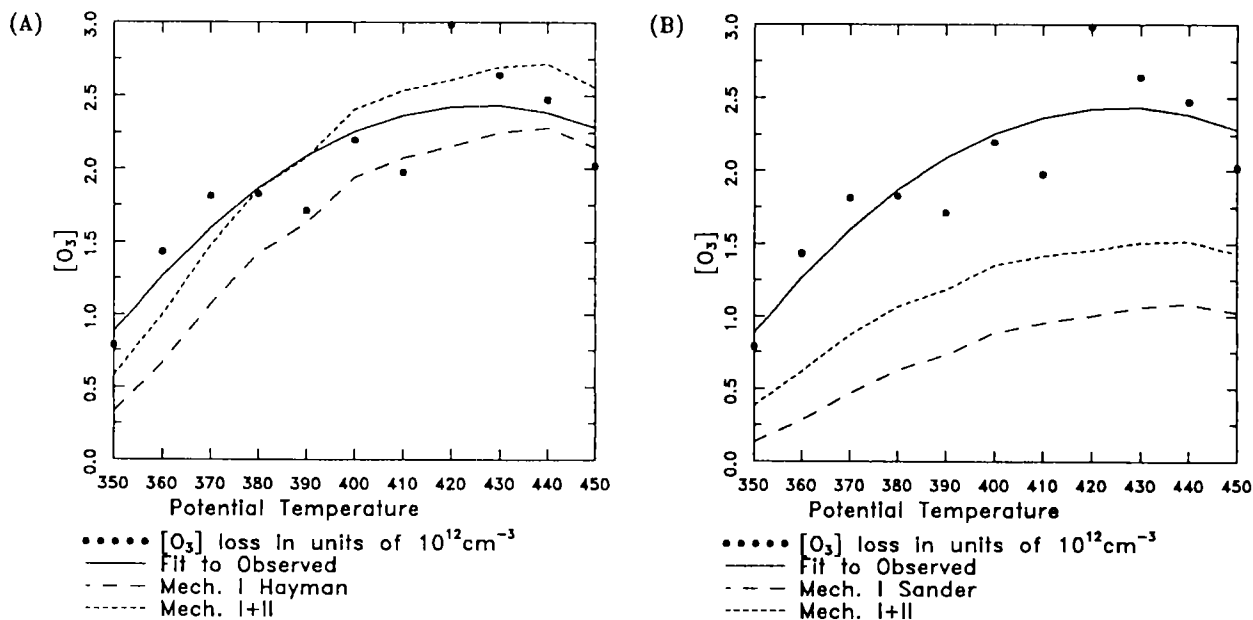


Fig. 23. Comparison between observed and calculated O_3 loss rates as a function of potential temperature surface. (a) Loss rates for mechanism I and mechanisms I plus II, using the Hayman et al. [1986] rate for k_1^{III} . (b) Loss rates for the same quantities, using the Sander et al. [1989] rate for k_1^{III} .

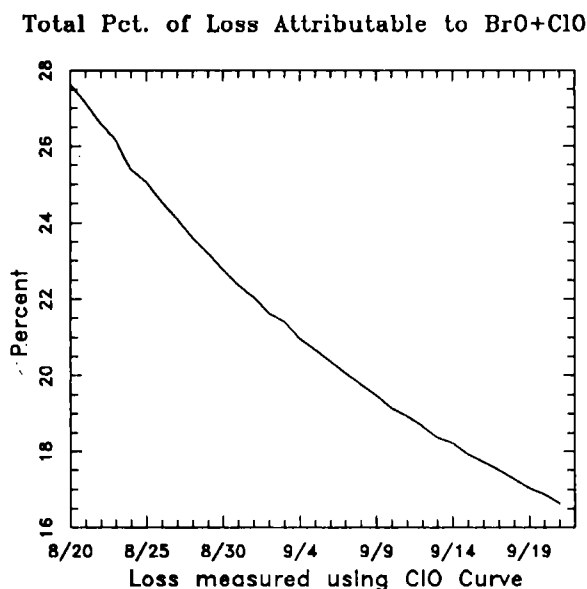


Fig. 24. Fractional contribution to total observed ozone loss as a function of time throughout the mission resulting from mechanism II.

based on the analysis by *DeMore et al.* [1987], drawn primarily from the temperature dependent work of *Stimpfle et al.* [1979] and the room temperature work of *Reimann and Kaufman* [1978] and *Leck et al.* [1980].

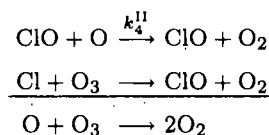
The major uncertainty in this calculation is the appropriate value for HO_2 , a radical for which no observations exist within the Antarctic vortex. The absence of HO_2 or OH data represents a significant compromise in this analysis, particularly because the class of heterogeneous reactions

which liberate ClO could also augment the HO_x budget within the vortex. We will use $[\text{HO}_2]$ values consistent with those of *Jones et al.* [this issue] and *Rodriguez et al.* [1989] to estimate the contribution from mechanism III. Effective exposure times, $Q^{\text{ClO}-\text{HO}_2}$, for mechanism III are calculated using the same diurnal analysis referred to for mechanisms I and II. We will assume an HO_2 mixing ratio of 1 pptv over the altitude range encompassed by the 360–450 K surfaces. This is an upper limit, based on conventional wisdom extracted from current models. However, it represents a simple benchmark, convenient for scaling our results to any choice for the HO_2 distribution. Table 3 summarizes the results on the 440, 420, 390, and 360 K surfaces. We conclude that a contribution of $\sim 4\%$ can be accounted for by mechanism III if the mixing ratio for HO_2 is 1 pptv.

Mechanism IV

For completeness we include the time-honored catalytic couplet

Mechanism IV



Given that (1) we have ClO and O_3 observations, (2) the kinetics of the reaction are precisely defined, and (3) we can calculate the $\text{O}(^3\text{P})$ concentration by the simple steady-state relationship between ozone and atomic oxygen, we can establish the rate of O_3 destruction resulting from mechanism IV.

TABLE 3. Summary of Ozone Loss on Potential Temperature Surfaces 440, 420, 390, and 360 K Resulting From Mechanism III, $\text{ClO} + \text{HO}_2 \rightarrow \text{HOCl} + \text{O}_2$, Suggested by *Solomon et al.* [1986]

Day	$[\text{ClO}]$, mol cm^{-3}	$[\text{HO}_2]$, mol cm^{-3}	$[M]$, $\times 10^{18} \text{cm}^{-3}$	T , $^\circ\text{K}$	k_4^{II} , $\text{cm}^3 \text{s}^{-1}$	Q , $\times 10^4 \text{s}$	$-\Delta\text{O}_3$, $\text{mol cm}^{-3} \text{d}^{-1}$
440 $\pm$ 5 K Surface							
Aug. 20	1.46×10^9	2.16×10^6	2.16	191.3	1.86×10^{-11}	1.26	1.48×10^9
Aug. 21	1.48×10^9	2.16×10^6	2.16	191.4	1.86×10^{-11}	1.28	1.53×10^9
Aug. 22	1.51×10^9	2.16×10^6	2.16	191.5	1.86×10^{-11}	1.29	1.56×10^9
Aug. 23	1.53×10^9	2.15×10^6	2.15	191.5	1.86×10^{-11}	1.32	1.62×10^9
Aug. 24	1.56×10^9	2.15×10^6	2.15	191.6	1.85×10^{-11}	1.35	1.68×10^9
Aug. 25	1.58×10^9	2.15×10^6	2.15	191.7	1.85×10^{-11}	1.36	1.71×10^9
Aug. 26	1.61×10^9	2.15×10^6	2.15	191.8	1.85×10^{-11}	1.38	1.76×10^9
Aug. 27	1.63×10^9	2.15×10^6	2.15	191.9	1.84×10^{-11}	1.40	1.81×10^9
Aug. 28	1.66×10^9	2.15×10^6	2.15	191.9	1.84×10^{-11}	1.42	1.86×10^9
Aug. 29	1.68×10^9	2.15×10^6	2.15	192.0	1.84×10^{-11}	1.45	1.92×10^9
Aug. 30	1.71×10^9	2.14×10^6	2.14	192.1	1.84×10^{-11}	1.46	1.96×10^9
Aug. 31	1.73×10^9	2.14×10^6	2.14	192.2	1.83×10^{-11}	1.49	2.02×10^9
Sept. 1	1.76×10^9	2.14×10^6	2.14	192.2	1.83×10^{-11}	1.49	2.05×10^9
Sept. 2	1.78×10^9	2.14×10^6	2.14	192.3	1.83×10^{-11}	1.52	2.12×10^9
Sept. 3	1.81×10^9	2.14×10^6	2.14	192.4	1.83×10^{-11}	1.53	2.16×10^9
Sept. 4	1.83×10^9	2.14×10^6	2.14	192.5	1.82×10^{-11}	1.56	2.23×10^9
Sept. 5	1.86×10^9	2.13×10^6	2.13	192.5	1.82×10^{-11}	1.57	2.26×10^9
Sept. 6	1.88×10^9	2.13×10^6	2.13	192.6	1.82×10^{-11}	1.60	2.34×10^9

TABLE 3. (continued)

Day	[ClO], mol cm ⁻³	[HO ₂], mol cm ⁻³	[M], × 10 ¹⁸ cm ⁻³	T, °K	k ^{II} , cm ³ s ⁻¹	Q, × 10 ⁴ s	-ΔO ₃ , mol cm ⁻³ d ⁻¹
<i>440 ± 5 K Surface (continued)</i>							
Sept. 7	1.91 × 10 ⁹	2.13 × 10 ⁶	2.13	192.7	1.81 × 10 ⁻¹¹	1.62	2.39 × 10 ⁹
Sept. 8	1.93 × 10 ⁹	2.13 × 10 ⁶	2.13	192.8	1.81 × 10 ⁻¹¹	1.64	2.44 × 10 ⁹
Sept. 9	1.95 × 10 ⁹	2.13 × 10 ⁶	2.13	192.9	1.81 × 10 ⁻¹¹	1.66	2.49 × 10 ⁹
Sept. 10	1.98 × 10 ⁹	2.13 × 10 ⁶	2.13	192.9	1.81 × 10 ⁻¹¹	1.69	2.57 × 10 ⁹
Sept. 11	2.00 × 10 ⁹	2.12 × 10 ⁶	2.12	193.0	1.80 × 10 ⁻¹¹	1.69	2.60 × 10 ⁹
Sept. 12	2.03 × 10 ⁹	2.12 × 10 ⁶	2.12	193.1	1.80 × 10 ⁻¹¹	1.72	2.67 × 10 ⁹
Sept. 13	2.05 × 10 ⁹	2.12 × 10 ⁶	2.12	193.2	1.80 × 10 ⁻¹¹	1.74	2.72 × 10 ⁹
Sept. 14	2.08 × 10 ⁹	2.12 × 10 ⁶	2.12	193.2	1.80 × 10 ⁻¹¹	1.75	2.77 × 10 ⁹
Sept. 15	2.10 × 10 ⁹	2.12 × 10 ⁶	2.12	193.3	1.79 × 10 ⁻¹¹	1.78	2.84 × 10 ⁹
Sept. 16	2.13 × 10 ⁹	2.12 × 10 ⁶	2.12	193.4	1.79 × 10 ⁻¹¹	1.79	2.88 × 10 ⁹
Sept. 17	2.15 × 10 ⁹	2.12 × 10 ⁶	2.12	193.5	1.79 × 10 ⁻¹¹	1.81	2.96 × 10 ⁹
Sept. 18	2.18 × 10 ⁹	2.11 × 10 ⁶	2.11	193.5	1.79 × 10 ⁻¹¹	1.82	2.99 × 10 ⁹
Sept. 19	2.20 × 10 ⁹	2.11 × 10 ⁶	2.11	193.6	1.78 × 10 ⁻¹¹	1.85	3.06 × 10 ⁹
Sept. 20	2.23 × 10 ⁹	2.11 × 10 ⁶	2.11	193.7	1.78 × 10 ⁻¹¹	1.86	3.11 × 10 ⁹
Sept. 21	2.25 × 10 ⁹	2.11 × 10 ⁶	2.11	193.8	1.78 × 10 ⁻¹¹	1.88	3.18 × 10 ⁹
Sept. 22	2.28 × 10 ⁹	2.11 × 10 ⁶	2.11	193.9	1.78 × 10 ⁻¹¹	1.89	3.22 × 10 ⁹
<i>420 ± 5 K Surface</i>							
Aug. 20	1.23 × 10 ⁹	2.45 × 10 ⁶	2.45	190.3	1.90 × 10 ⁻¹¹	1.26	1.44 × 10 ⁹
Aug. 21	1.25 × 10 ⁹	2.45 × 10 ⁶	2.45	190.4	1.90 × 10 ⁻¹¹	1.28	1.50 × 10 ⁹
Aug. 22	1.28 × 10 ⁹	2.45 × 10 ⁶	2.45	190.5	1.89 × 10 ⁻¹¹	1.29	1.54 × 10 ⁹
Aug. 23	1.31 × 10 ⁹	2.45 × 10 ⁶	2.45	190.6	1.89 × 10 ⁻¹¹	1.32	1.60 × 10 ⁹
Aug. 24	1.33 × 10 ⁹	2.45 × 10 ⁶	2.45	190.7	1.88 × 10 ⁻¹¹	1.35	1.66 × 10 ⁹
Aug. 25	1.36 × 10 ⁹	2.46 × 10 ⁶	2.46	190.9	1.88 × 10 ⁻¹¹	1.36	1.70 × 10 ⁹
Aug. 26	1.39 × 10 ⁹	2.46 × 10 ⁶	2.46	191.0	1.87 × 10 ⁻¹¹	1.38	1.76 × 10 ⁹
Aug. 27	1.41 × 10 ⁹	2.46 × 10 ⁶	2.46	191.1	1.87 × 10 ⁻¹¹	1.40	1.82 × 10 ⁹
Aug. 28	1.44 × 10 ⁹	2.46 × 10 ⁶	2.46	191.2	1.87 × 10 ⁻¹¹	1.42	1.88 × 10 ⁹
Aug. 29	1.47 × 10 ⁹	2.46 × 10 ⁶	2.46	191.4	1.86 × 10 ⁻¹¹	1.45	1.95 × 10 ⁹
Aug. 30	1.49 × 10 ⁹	2.47 × 10 ⁶	2.47	191.5	1.86 × 10 ⁻¹¹	1.46	1.99 × 10 ⁹
Aug. 31	1.52 × 10 ⁹	2.47 × 10 ⁶	2.47	191.6	1.85 × 10 ⁻¹¹	1.49	2.07 × 10 ⁹
Sept. 1	1.55 × 10 ⁹	2.47 × 10 ⁶	2.47	191.7	1.85 × 10 ⁻¹¹	1.49	2.11 × 10 ⁹
Sept. 2	1.57 × 10 ⁹	2.47 × 10 ⁶	2.47	191.9	1.84 × 10 ⁻¹¹	1.52	2.19 × 10 ⁹
Sept. 3	1.60 × 10 ⁹	2.47 × 10 ⁶	2.47	192.0	1.84 × 10 ⁻¹¹	1.53	2.23 × 10 ⁹
Sept. 4	1.63 × 10 ⁹	2.47 × 10 ⁶	2.47	192.1	1.84 × 10 ⁻¹¹	1.56	2.31 × 10 ⁹
Sept. 5	1.65 × 10 ⁹	2.48 × 10 ⁶	2.48	192.2	1.83 × 10 ⁻¹¹	1.57	2.35 × 10 ⁹
Sept. 6	1.68 × 10 ⁹	2.48 × 10 ⁶	2.48	192.3	1.83 × 10 ⁻¹¹	1.60	2.44 × 10 ⁹
Sept. 7	1.71 × 10 ⁹	2.48 × 10 ⁶	2.48	192.5	1.82 × 10 ⁻¹¹	1.62	2.50 × 10 ⁹
Sept. 8	1.73 × 10 ⁹	2.48 × 10 ⁶	2.48	192.6	1.82 × 10 ⁻¹¹	1.64	2.56 × 10 ⁹
Sept. 9	1.76 × 10 ⁹	2.48 × 10 ⁶	2.48	192.7	1.81 × 10 ⁻¹¹	1.66	2.63 × 10 ⁹
Sept. 10	1.79 × 10 ⁹	2.49 × 10 ⁶	2.49	192.8	1.81 × 10 ⁻¹¹	1.69	2.71 × 10 ⁹
Sept. 11	1.81 × 10 ⁹	2.49 × 10 ⁶	2.49	193.0	1.81 × 10 ⁻¹¹	1.69	2.75 × 10 ⁹
Sept. 12	1.84 × 10 ⁹	2.49 × 10 ⁶	2.49	193.1	1.80 × 10 ⁻¹¹	1.72	2.84 × 10 ⁹
Sept. 13	1.87 × 10 ⁹	2.49 × 10 ⁶	2.49	193.2	1.80 × 10 ⁻¹¹	1.74	2.90 × 10 ⁹
Sept. 14	1.89 × 10 ⁹	2.49 × 10 ⁶	2.49	193.3	1.79 × 10 ⁻¹¹	1.75	2.96 × 10 ⁹
Sept. 15	1.92 × 10 ⁹	2.49 × 10 ⁶	2.49	193.5	1.79 × 10 ⁻¹¹	1.78	3.05 × 10 ⁹
Sept. 16	1.95 × 10 ⁹	2.50 × 10 ⁶	2.50	193.6	1.79 × 10 ⁻¹¹	1.79	3.10 × 10 ⁹
Sept. 17	1.97 × 10 ⁹	2.50 × 10 ⁶	2.50	193.7	1.78 × 10 ⁻¹¹	1.81	3.19 × 10 ⁹
Sept. 18	2.00 × 10 ⁹	2.50 × 10 ⁶	2.50	193.8	1.78 × 10 ⁻¹¹	1.82	3.24 × 10 ⁹
Sept. 19	2.03 × 10 ⁹	2.50 × 10 ⁶	2.50	194.0	1.77 × 10 ⁻¹¹	1.85	3.32 × 10 ⁹
Sept. 20	2.05 × 10 ⁹	2.50 × 10 ⁶	2.50	194.1	1.77 × 10 ⁻¹¹	1.86	3.38 × 10 ⁹
Sept. 21	2.08 × 10 ⁹	2.50 × 10 ⁶	2.50	194.2	1.76 × 10 ⁻¹¹	1.88	3.46 × 10 ⁹
Sept. 22	2.11 × 10 ⁹	2.51 × 10 ⁶	2.51	194.3	1.76 × 10 ⁻¹¹	1.89	3.52 × 10 ⁹
<i>390 ± 5 K Surface</i>							
Aug. 20	8.60 × 10 ⁸	3.13 × 10 ⁶	3.13	190.6	1.89 × 10 ⁻¹¹	1.26	1.28 × 10 ⁹
Aug. 21	8.85 × 10 ⁸	3.14 × 10 ⁶	3.14	190.8	1.88 × 10 ⁻¹¹	1.28	1.34 × 10 ⁹
Aug. 22	9.09 × 10 ⁸	3.15 × 10 ⁶	3.15	191.0	1.88 × 10 ⁻¹¹	1.29	1.39 × 10 ⁹
Aug. 23	9.33 × 10 ⁸	3.15 × 10 ⁶	3.15	191.2	1.87 × 10 ⁻¹¹	1.32	1.45 × 10 ⁹
Aug. 24	9.57 × 10 ⁸	3.16 × 10 ⁶	3.16	191.3	1.86 × 10 ⁻¹¹	1.35	1.52 × 10 ⁹
Aug. 25	9.82 × 10 ⁸	3.17 × 10 ⁶	3.17	191.5	1.86 × 10 ⁻¹¹	1.36	1.57 × 10 ⁹
Aug. 26	1.01 × 10 ⁹	3.18 × 10 ⁶	3.18	191.7	1.85 × 10 ⁻¹¹	1.38	1.63 × 10 ⁹
Aug. 27	1.03 × 10 ⁹	3.18 × 10 ⁶	3.18	191.9	1.84 × 10 ⁻¹¹	1.40	1.69 × 10 ⁹
Aug. 28	1.05 × 10 ⁹	3.19 × 10 ⁶	3.19	192.1	1.84 × 10 ⁻¹¹	1.42	1.76 × 10 ⁹
Aug. 29	1.08 × 10 ⁹	3.20 × 10 ⁶	3.20	192.3	1.83 × 10 ⁻¹¹	1.45	1.83 × 10 ⁹
Aug. 30	1.10 × 10 ⁹	3.21 × 10 ⁶	3.21	192.5	1.82 × 10 ⁻¹¹	1.46	1.88 × 10 ⁹

TABLE 3. (continued)

Day	[ClO], mol cm ⁻³	[HO ₂], mol cm ⁻³	[M], ×10 ¹⁸ cm ⁻³	T, °K	k ^{II} , cm ³ s ⁻¹	Q, ×10 ⁴ s	-ΔO ₃ , mol cm ⁻³ d ⁻¹
<i>390 ± 5 K Surface (continued)</i>							
Aug. 31	1.13 × 10 ⁹	3.21 × 10 ⁶	3.21	192.6	1.82 × 10 ⁻¹¹	1.49	1.96 × 10 ⁹
Sept. 1	1.15 × 10 ⁹	3.22 × 10 ⁶	3.22	192.8	1.81 × 10 ⁻¹¹	1.49	2.00 × 10 ⁹
Sept. 2	1.18 × 10 ⁹	3.23 × 10 ⁶	3.23	193.0	1.80 × 10 ⁻¹¹	1.52	2.09 × 10 ⁹
Sept. 3	1.20 × 10 ⁹	3.24 × 10 ⁶	3.24	193.2	1.80 × 10 ⁻¹¹	1.53	2.14 × 10 ⁹
Sept. 4	1.22 × 10 ⁹	3.24 × 10 ⁶	3.24	193.4	1.79 × 10 ⁻¹¹	1.56	2.22 × 10 ⁹
Sept. 5	1.25 × 10 ⁹	3.25 × 10 ⁶	3.25	193.6	1.79 × 10 ⁻¹¹	1.57	2.27 × 10 ⁹
Sept. 6	1.27 × 10 ⁹	3.26 × 10 ⁶	3.26	193.8	1.78 × 10 ⁻¹¹	1.60	2.37 × 10 ⁹
Sept. 7	1.30 × 10 ⁹	3.27 × 10 ⁶	3.27	194.0	1.77 × 10 ⁻¹¹	1.62	2.43 × 10 ⁹
Sept. 8	1.32 × 10 ⁹	3.27 × 10 ⁶	3.27	194.1	1.77 × 10 ⁻¹¹	1.64	2.51 × 10 ⁹
Sept. 9	1.35 × 10 ⁹	3.28 × 10 ⁶	3.28	194.3	1.76 × 10 ⁻¹¹	1.66	2.58 × 10 ⁹
Sept. 10	1.37 × 10 ⁹	3.29 × 10 ⁶	3.29	194.5	1.75 × 10 ⁻¹¹	1.69	2.67 × 10 ⁹
Sept. 11	1.39 × 10 ⁹	3.30 × 10 ⁶	3.30	194.7	1.75 × 10 ⁻¹¹	1.69	2.72 × 10 ⁹
Sept. 12	1.42 × 10 ⁹	3.30 × 10 ⁶	3.30	194.9	1.74 × 10 ⁻¹¹	1.72	2.81 × 10 ⁹
Sept. 13	1.44 × 10 ⁹	3.31 × 10 ⁶	3.31	195.1	1.74 × 10 ⁻¹¹	1.74	2.88 × 10 ⁹
Sept. 14	1.47 × 10 ⁹	3.32 × 10 ⁶	3.32	195.3	1.73 × 10 ⁻¹¹	1.75	2.95 × 10 ⁹
Sept. 15	1.49 × 10 ⁹	3.33 × 10 ⁶	3.33	195.5	1.72 × 10 ⁻¹¹	1.78	3.04 × 10 ⁹
Sept. 16	1.52 × 10 ⁹	3.33 × 10 ⁶	3.33	195.6	1.72 × 10 ⁻¹¹	1.79	3.10 × 10 ⁹
Sept. 17	1.54 × 10 ⁹	3.34 × 10 ⁶	3.34	195.8	1.71 × 10 ⁻¹¹	1.81	3.20 × 10 ⁹
Sept. 18	1.56 × 10 ⁹	3.35 × 10 ⁶	3.35	196.0	1.71 × 10 ⁻¹¹	1.82	3.26 × 10 ⁹
Sept. 19	1.59 × 10 ⁹	3.36 × 10 ⁶	3.36	196.2	1.70 × 10 ⁻¹¹	1.85	3.35 × 10 ⁹
Sept. 20	1.61 × 10 ⁹	3.36 × 10 ⁶	3.36	196.4	1.70 × 10 ⁻¹¹	1.86	3.41 × 10 ⁹
Sept. 21	1.64 × 10 ⁹	3.37 × 10 ⁶	3.37	196.6	1.69 × 10 ⁻¹¹	1.88	3.51 × 10 ⁹
Sept. 22	1.66 × 10 ⁹	3.38 × 10 ⁶	3.38	196.8	1.68 × 10 ⁻¹¹	1.89	3.57 × 10 ⁹
<i>360 ± 5 K Surface</i>							
Aug. 20	5.37 × 10 ⁸	3.89 × 10 ⁶	3.89	190.5	1.89 × 10 ⁻¹¹	1.26	9.98 × 10 ⁸
Aug. 21	5.48 × 10 ⁸	3.92 × 10 ⁶	3.92	190.8	1.88 × 10 ⁻¹¹	1.28	1.04 × 10 ⁹
Aug. 22	5.59 × 10 ⁸	3.94 × 10 ⁶	3.94	191.1	1.87 × 10 ⁻¹¹	1.29	1.07 × 10 ⁹
Aug. 23	5.69 × 10 ⁸	3.97 × 10 ⁶	3.97	191.4	1.86 × 10 ⁻¹¹	1.32	1.11 × 10 ⁹
Aug. 24	5.80 × 10 ⁸	3.99 × 10 ⁶	3.99	191.8	1.85 × 10 ⁻¹¹	1.35	1.16 × 10 ⁹
Aug. 25	5.91 × 10 ⁸	4.02 × 10 ⁶	4.02	192.1	1.84 × 10 ⁻¹¹	1.36	1.18 × 10 ⁹
Aug. 26	6.01 × 10 ⁸	4.05 × 10 ⁶	4.05	192.4	1.83 × 10 ⁻¹¹	1.38	1.23 × 10 ⁹
Aug. 27	6.12 × 10 ⁸	4.07 × 10 ⁶	4.07	192.7	1.81 × 10 ⁻¹¹	1.40	1.26 × 10 ⁹
Aug. 28	6.23 × 10 ⁸	4.10 × 10 ⁶	4.10	193.0	1.80 × 10 ⁻¹¹	1.42	1.31 × 10 ⁹
Aug. 29	6.33 × 10 ⁸	4.12 × 10 ⁶	4.12	193.3	1.79 × 10 ⁻¹¹	1.45	1.36 × 10 ⁹
Aug. 30	6.44 × 10 ⁸	4.15 × 10 ⁶	4.15	193.7	1.78 × 10 ⁻¹¹	1.46	1.39 × 10 ⁹
Aug. 31	6.55 × 10 ⁸	4.17 × 10 ⁶	4.17	194.0	1.77 × 10 ⁻¹¹	1.49	1.44 × 10 ⁹
Sept. 1	6.66 × 10 ⁸	4.20 × 10 ⁶	4.20	194.3	1.76 × 10 ⁻¹¹	1.49	1.47 × 10 ⁹
Sept. 2	6.76 × 10 ⁸	4.23 × 10 ⁶	4.23	194.6	1.75 × 10 ⁻¹¹	1.52	1.53 × 10 ⁹
Sept. 3	6.87 × 10 ⁸	4.25 × 10 ⁶	4.25	194.9	1.74 × 10 ⁻¹¹	1.53	1.56 × 10 ⁹
Sept. 4	6.98 × 10 ⁸	4.28 × 10 ⁶	4.28	195.3	1.73 × 10 ⁻¹¹	1.56	1.61 × 10 ⁹
Sept. 5	7.08 × 10 ⁸	4.30 × 10 ⁶	4.30	195.6	1.72 × 10 ⁻¹¹	1.57	1.64 × 10 ⁹
Sept. 6	7.19 × 10 ⁸	4.33 × 10 ⁶	4.33	195.9	1.71 × 10 ⁻¹¹	1.60	1.71 × 10 ⁹
Sept. 7	7.30 × 10 ⁸	4.35 × 10 ⁶	4.35	196.2	1.70 × 10 ⁻¹¹	1.62	1.75 × 10 ⁹
Sept. 8	7.40 × 10 ⁸	4.38 × 10 ⁶	4.38	196.5	1.69 × 10 ⁻¹¹	1.64	1.80 × 10 ⁹
Sept. 9	7.51 × 10 ⁸	4.41 × 10 ⁶	4.41	196.8	1.68 × 10 ⁻¹¹	1.66	1.84 × 10 ⁹
Sept. 10	7.62 × 10 ⁸	4.43 × 10 ⁶	4.43	197.2	1.67 × 10 ⁻¹¹	1.69	1.90 × 10 ⁹
Sept. 11	7.73 × 10 ⁸	4.46 × 10 ⁶	4.46	197.5	1.66 × 10 ⁻¹¹	1.69	1.94 × 10 ⁹
Sept. 12	7.83 × 10 ⁸	4.48 × 10 ⁶	4.48	197.8	1.65 × 10 ⁻¹¹	1.72	1.99 × 10 ⁹
Sept. 13	7.94 × 10 ⁸	4.51 × 10 ⁶	4.51	198.1	1.64 × 10 ⁻¹¹	1.74	2.04 × 10 ⁹
Sept. 14	8.05 × 10 ⁸	4.53 × 10 ⁶	4.53	198.4	1.63 × 10 ⁻¹¹	1.75	2.09 × 10 ⁹
Sept. 15	8.15 × 10 ⁸	4.56 × 10 ⁶	4.56	198.7	1.63 × 10 ⁻¹¹	1.78	2.15 × 10 ⁹
Sept. 16	8.26 × 10 ⁸	4.59 × 10 ⁶	4.59	199.1	1.62 × 10 ⁻¹¹	1.79	2.19 × 10 ⁹
Sept. 17	8.37 × 10 ⁸	4.61 × 10 ⁶	4.61	199.4	1.61 × 10 ⁻¹¹	1.81	2.25 × 10 ⁹
Sept. 18	8.47 × 10 ⁸	4.64 × 10 ⁶	4.64	199.7	1.60 × 10 ⁻¹¹	1.82	2.29 × 10 ⁹
Sept. 19	8.58 × 10 ⁸	4.66 × 10 ⁶	4.66	200.0	1.59 × 10 ⁻¹¹	1.85	2.35 × 10 ⁹
Sept. 20	8.69 × 10 ⁸	4.69 × 10 ⁶	4.69	200.3	1.58 × 10 ⁻¹¹	1.86	2.39 × 10 ⁹
Sept. 21	8.79 × 10 ⁸	4.71 × 10 ⁶	4.71	200.7	1.57 × 10 ⁻¹¹	1.88	2.45 × 10 ⁹
Sept. 22	8.90 × 10 ⁸	4.74 × 10 ⁶	4.74	201.0	1.56 × 10 ⁻¹¹	1.89	2.49 × 10 ⁹

ClO observed from the ER-2 appears in column two. HO₂ concentration based on an altitude-dependent 1-pptv distribution is given in column three. Columns four and five report [M] and T observations from the ER-2, and the bimolecular reaction rate constant for the rate-limiting reaction is given in column six. Effective exposure time, Q, and ozone loss rate, ΔO₃, for each 24-hour period are given in the last two columns. A distribution of 1 pptv for HO₂ represents an upper bound from photochemical models of the Antarctic vortex region.

We use the NASA Evaluation Panel recommendation for the bimolecular rate

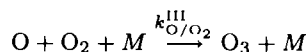
$$k_4^{\text{II}} = 3.0 \times 10^{-11} \exp(70 \pm 70/T) \text{ cm}^3 \text{ s}^{-1}$$

from *DeMore et al.* [1987].

Atomic oxygen densities are determined from the measured $[\text{O}_3]$ densities, using the expression

$$[\text{O}(^3\text{P})] = \frac{J_{\text{O}_3}[\text{O}_3]}{k_{\text{O}/\text{O}_2}^{\text{III}}[\text{M}][\text{O}_2]}$$

where J_{O_3} is the relevant photolysis rate for $[\text{O}_3]$, and $k_{\text{O}/\text{O}_2}^{\text{III}}$ is the termolecular rate for



The effective exposure time per diurnal cycle, $Q^{\text{ClO-O}}$, is calculated as before. Table 4 summarizes the results of this analysis on the 440, 420, 390, and 360 K surfaces. Again, the contribution is not large enough to warrant graphical representation. We find that approximately 3% of the observed O_3 loss is attributable to this mechanism.

This leaves us with a situation best summarized by revisiting Figure 23. We have concluded, as noted before, that the laboratory results reported by *Hayman et al.* [1986], defining the kinetics of Cl_2O_2 formation from ClO, are in error and that the *Sander et al.* [1989] determination of k_1^{II} is correct within experimental error. Thus we conclude that Figure 23b, with an additional increment of $\sim 7\%$ from the sum of mechanisms III and IV, best summarizes the quantitative relationship between observed O_3 loss and that which results from the sum of mechanisms I–IV, given our in situ measurements of ClO and BrO.

The implication is that, while 60–70% of the observed O_3 loss can be accounted for quantitatively, there remains a deficit of 30–40% (or larger if consideration is taken of dynamically imported O_3 ; see *Hartmann et al.* [1989]) between observed and calculated decay rates. Thus either our reported ClO observations are low by $\sim 25\%$, or the complement of catalytic mechanisms is incomplete. A detailed analysis of experimental uncertainty is offered in the concluding section of this paper. Therefore we consider briefly other catalytic processes involving ClO and BrO radicals, which could quantitatively affect the rate of ozone removal.

TABLE 4. Summary of Ozone Loss on Potential Temperature Surfaces 440, 420, 390, and 360 K Resulting From Mechanism IV, $\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2$, Suggested by *Molina and Rowland* [1974]

Day	$[\text{ClO}]$, mol cm^{-3}	$[\text{O}(^3\text{P})]$, mol cm^{-3}	$[\text{M}]$, $\times 10^{18} \text{ cm}^{-3}$	T , $^{\circ}\text{K}$	k_4^{II} , $\text{cm}^3 \text{ s}^{-1}$	Q , $\times 10^4 \text{ s}$	$-\Delta\text{O}_3$, $\text{mol cm}^{-3} \text{ d}^{-1}$
<i>440 $\pm$ 5 K Surface</i>							
Aug. 20	1.46×10^9	7.02×10^5	2.16	191.3	4.33×10^{-11}	1.96	1.74×10^9
Aug. 21	1.48×10^9	7.06×10^5	2.16	191.4	4.32×10^{-11}	2.02	1.83×10^9
Aug. 22	1.51×10^9	7.13×10^5	2.16	191.5	4.32×10^{-11}	2.06	1.92×10^9
Aug. 23	1.53×10^9	7.15×10^5	2.15	191.5	4.32×10^{-11}	2.12	2.01×10^9
Aug. 24	1.56×10^9	7.15×10^5	2.15	191.6	4.32×10^{-11}	2.18	2.10×10^9
Aug. 25	1.58×10^9	7.20×10^5	2.15	191.7	4.32×10^{-11}	2.22	2.19×10^9
Aug. 26	1.61×10^9	7.19×10^5	2.15	191.8	4.32×10^{-11}	2.28	2.27×10^9
Aug. 27	1.63×10^9	7.22×10^5	2.15	191.9	4.32×10^{-11}	2.32	2.36×10^9
Aug. 28	1.66×10^9	7.19×10^5	2.15	191.9	4.32×10^{-11}	2.37	2.44×10^9
Aug. 29	1.68×10^9	7.15×10^5	2.15	192.0	4.32×10^{-11}	2.44	2.53×10^9
Aug. 30	1.71×10^9	7.14×10^5	2.14	192.1	4.32×10^{-11}	2.47	2.60×10^9
Aug. 31	1.73×10^9	7.10×10^5	2.14	192.2	4.32×10^{-11}	2.54	2.69×10^9
Sept. 1	1.76×10^9	7.07×10^5	2.14	192.2	4.32×10^{-11}	2.57	2.76×10^9
Sept. 2	1.78×10^9	7.01×10^5	2.14	192.3	4.32×10^{-11}	2.63	2.84×10^9
Sept. 3	1.81×10^9	6.97×10^5	2.14	192.4	4.32×10^{-11}	2.67	2.90×10^9
Sept. 4	1.83×10^9	6.89×10^5	2.14	192.5	4.32×10^{-11}	2.73	2.98×10^9
Sept. 5	1.86×10^9	6.81×10^5	2.13	192.5	4.32×10^{-11}	2.77	3.02×10^9
Sept. 6	1.88×10^9	6.71×10^5	2.13	192.6	4.31×10^{-11}	2.83	3.08×10^9
Sept. 7	1.91×10^9	6.63×10^5	2.13	192.7	4.31×10^{-11}	2.87	3.13×10^9
Sept. 8	1.93×10^9	6.52×10^5	2.13	192.8	4.31×10^{-11}	2.93	3.18×10^9
Sept. 9	1.95×10^9	6.41×10^5	2.13	192.9	4.31×10^{-11}	2.97	3.21×10^9
Sept. 10	1.98×10^9	6.29×10^5	2.13	192.9	4.31×10^{-11}	3.03	3.25×10^9
Sept. 11	2.00×10^9	6.16×10^5	2.12	193.0	4.31×10^{-11}	3.06	3.26×10^9
Sept. 12	2.03×10^9	6.01×10^5	2.12	193.1	4.31×10^{-11}	3.12	3.28×10^9
Sept. 13	2.05×10^9	5.86×10^5	2.12	193.2	4.31×10^{-11}	3.17	3.28×10^9
Sept. 14	2.08×10^9	5.69×10^5	2.12	193.2	4.31×10^{-11}	3.21	3.27×10^9
Sept. 15	2.10×10^9	5.52×10^5	2.12	193.3	4.31×10^{-11}	3.26	3.27×10^9
Sept. 16	2.13×10^9	5.34×10^5	2.12	193.4	4.31×10^{-11}	3.31	3.25×10^9
Sept. 17	2.15×10^9	5.15×10^5	2.12	193.5	4.31×10^{-11}	3.36	3.21×10^9
Sept. 18	2.18×10^9	4.94×10^5	2.11	193.5	4.31×10^{-11}	3.41	3.16×10^9
Sept. 19	2.20×10^9	4.73×10^5	2.11	193.6	4.31×10^{-11}	3.45	3.10×10^9
Sept. 20	2.23×10^9	4.50×10^5	2.11	193.7	4.31×10^{-11}	3.51	3.03×10^9
Sept. 21	2.25×10^9	4.26×10^5	2.11	193.8	4.31×10^{-11}	3.55	2.93×10^9
Sept. 22	2.28×10^9	4.01×10^5	2.11	193.9	4.30×10^{-11}	3.60	2.83×10^9

TABLE 4. (continued)

Day	$[ClO]$, mol cm^{-3}	$[O(^3P)]$, mol cm^{-3}	$[M]$, $\times 10^{18} \text{cm}^{-3}$	T , $^{\circ}\text{K}$	k^{II} , $\text{cm}^3 \text{s}^{-1}$	Q , $\times 10^4 \text{s}$	$-\Delta O_3$, $\text{mol cm}^{-3} \text{d}^{-1}$
<i>420 ± 5 K Surface</i>							
Aug. 20	1.23×10^9	7.80×10^5	2.45	190.3	4.33×10^{-11}	1.96	1.63×10^9
Aug. 21	1.25×10^9	7.84×10^5	2.45	190.4	4.33×10^{-11}	2.02	1.72×10^9
Aug. 22	1.28×10^9	7.93×10^5	2.45	190.5	4.33×10^{-11}	2.06	1.81×10^9
Aug. 23	1.31×10^9	7.95×10^5	2.45	190.6	4.33×10^{-11}	2.12	1.90×10^9
Aug. 24	1.33×10^9	7.96×10^5	2.45	190.7	4.33×10^{-11}	2.18	2.00×10^9
Aug. 25	1.36×10^9	8.02×10^5	2.46	190.9	4.33×10^{-11}	2.22	2.09×10^9
Aug. 26	1.39×10^9	8.00×10^5	2.46	191.0	4.33×10^{-11}	2.28	2.19×10^9
Aug. 27	1.41×10^9	8.04×10^5	2.46	191.1	4.33×10^{-11}	2.32	2.28×10^9
Aug. 28	1.44×10^9	8.00×10^5	2.46	191.2	4.33×10^{-11}	2.37	2.37×10^9
Aug. 29	1.47×10^9	7.96×10^5	2.46	191.4	4.32×10^{-11}	2.44	2.46×10^9
Aug. 30	1.49×10^9	7.94×10^5	2.47	191.5	4.32×10^{-11}	2.47	2.54×10^9
Aug. 31	1.52×10^9	7.90×10^5	2.47	191.6	4.32×10^{-11}	2.54	2.63×10^9
Sept. 1	1.55×10^9	7.86×10^5	2.47	191.7	4.32×10^{-11}	2.57	2.71×10^9
Sept. 2	1.57×10^9	7.79×10^5	2.47	191.9	4.32×10^{-11}	2.63	2.79×10^9
Sept. 3	1.60×10^9	7.73×10^5	2.47	192.0	4.32×10^{-11}	2.67	2.86×10^9
Sept. 4	1.63×10^9	7.64×10^5	2.47	192.1	4.32×10^{-11}	2.73	2.94×10^9
Sept. 5	1.65×10^9	7.55×10^5	2.48	192.2	4.32×10^{-11}	2.77	2.98×10^9
Sept. 6	1.68×10^9	7.43×10^5	2.48	192.3	4.32×10^{-11}	2.83	3.05×10^9
Sept. 7	1.71×10^9	7.32×10^5	2.48	192.5	4.32×10^{-11}	2.87	3.10×10^9
Sept. 8	1.73×10^9	7.19×10^5	2.48	192.6	4.31×10^{-11}	2.93	3.15×10^9
Sept. 9	1.76×10^9	7.05×10^5	2.48	192.7	4.31×10^{-11}	2.97	3.18×10^9
Sept. 10	1.79×10^9	6.90×10^5	2.49	192.8	4.31×10^{-11}	3.03	3.22×10^9
Sept. 11	1.81×10^9	6.74×10^5	2.49	193.0	4.31×10^{-11}	3.06	3.22×10^9
Sept. 12	1.84×10^9	6.55×10^5	2.49	193.1	4.31×10^{-11}	3.12	3.25×10^9
Sept. 13	1.87×10^9	6.36×10^5	2.49	193.2	4.31×10^{-11}	3.17	3.24×10^9
Sept. 14	1.89×10^9	6.14×10^5	2.49	193.3	4.31×10^{-11}	3.21	3.22×10^9
Sept. 15	1.92×10^9	5.93×10^5	2.49	193.5	4.31×10^{-11}	3.26	3.20×10^9
Sept. 16	1.95×10^9	5.70×10^5	2.50	193.6	4.31×10^{-11}	3.31	3.17×10^9
Sept. 17	1.97×10^9	5.45×10^5	2.50	193.7	4.31×10^{-11}	3.36	3.11×10^9
Sept. 18	2.00×10^9	5.18×10^5	2.50	193.8	4.30×10^{-11}	3.41	3.04×10^9
Sept. 19	2.03×10^9	4.91×10^5	2.50	194.0	4.30×10^{-11}	3.45	2.96×10^9
Sept. 20	2.05×10^9	4.61×10^5	2.50	194.1	4.30×10^{-11}	3.51	2.86×10^9
Sept. 21	2.08×10^9	4.30×10^5	2.50	194.2	4.30×10^{-11}	3.55	2.73×10^9
Sept. 22	2.11×10^9	3.97×10^5	2.51	194.3	4.30×10^{-11}	3.60	2.59×10^9
<i>390 ± 5 K Surface</i>							
Aug. 20	8.60×10^8	6.23×10^5	3.13	190.6	4.33×10^{-11}	1.96	9.11×10^8
Aug. 21	8.85×10^8	6.28×10^5	3.14	190.8	4.33×10^{-11}	2.02	9.73×10^8
Aug. 22	9.09×10^8	6.36×10^5	3.15	191.0	4.33×10^{-11}	2.06	1.03×10^9
Aug. 23	9.33×10^8	6.40×10^5	3.15	191.2	4.33×10^{-11}	2.12	1.09×10^9
Aug. 24	9.57×10^8	6.43×10^5	3.16	191.3	4.33×10^{-11}	2.18	1.16×10^9
Aug. 25	9.82×10^8	6.50×10^5	3.17	191.5	4.32×10^{-11}	2.22	1.22×10^9
Aug. 26	1.01×10^9	6.51×10^5	3.18	191.7	4.32×10^{-11}	2.28	1.29×10^9
Aug. 27	1.03×10^9	6.57×10^5	3.18	191.9	4.32×10^{-11}	2.32	1.36×10^9
Aug. 28	1.05×10^9	6.56×10^5	3.19	192.1	4.32×10^{-11}	2.37	1.42×10^9
Aug. 29	1.08×10^9	6.55×10^5	3.20	192.3	4.32×10^{-11}	2.44	1.49×10^9
Aug. 30	1.10×10^9	6.57×10^5	3.21	192.5	4.32×10^{-11}	2.47	1.55×10^9
Aug. 31	1.13×10^9	6.57×10^5	3.21	192.6	4.31×10^{-11}	2.54	1.62×10^9
Sept. 1	1.15×10^9	6.57×10^5	3.22	192.8	4.31×10^{-11}	2.57	1.68×10^9
Sept. 2	1.18×10^9	6.55×10^5	3.23	193.0	4.31×10^{-11}	2.63	1.75×10^9
Sept. 3	1.20×10^9	6.54×10^5	3.24	193.2	4.31×10^{-11}	2.67	1.81×10^9
Sept. 4	1.22×10^9	6.50×10^5	3.24	193.4	4.31×10^{-11}	2.73	1.88×10^9
Sept. 5	1.25×10^9	6.47×10^5	3.25	193.6	4.31×10^{-11}	2.77	1.93×10^9
Sept. 6	1.27×10^9	6.41×10^5	3.26	193.8	4.31×10^{-11}	2.83	1.99×10^9
Sept. 7	1.30×10^9	6.37×10^5	3.27	194.0	4.30×10^{-11}	2.87	2.04×10^9
Sept. 8	1.32×10^9	6.31×10^5	3.27	194.1	4.30×10^{-11}	2.93	2.10×10^9
Sept. 9	1.35×10^9	6.24×10^5	3.28	194.3	4.30×10^{-11}	2.97	2.14×10^9
Sept. 10	1.37×10^9	6.17×10^5	3.29	194.5	4.30×10^{-11}	3.03	2.20×10^9
Sept. 11	1.39×10^9	6.09×10^5	3.30	194.7	4.30×10^{-11}	3.06	2.23×10^9
Sept. 12	1.42×10^9	5.99×10^5	3.30	194.9	4.30×10^{-11}	3.12	2.28×10^9
Sept. 13	1.44×10^9	5.89×10^5	3.31	195.1	4.29×10^{-11}	3.17	2.31×10^9
Sept. 14	1.47×10^9	5.77×10^5	3.32	195.3	4.29×10^{-11}	3.21	2.34×10^9
Sept. 15	1.49×10^9	5.66×10^5	3.33	195.5	4.29×10^{-11}	3.26	2.37×10^9
Sept. 16	1.52×10^9	5.53×10^5	3.33	195.6	4.29×10^{-11}	3.31	2.39×10^9

TABLE 4. (continued)

Day	[ClO], mol cm ⁻³	[O(³ P)], mol cm ⁻³	[M], × 10 ¹⁸ cm ⁻³	T, °K	k ^{II} , cm ³ s ⁻¹	Q, × 10 ⁴ s	-ΔO ₃ , mol cm ⁻³ d ⁻¹
390 ± 5 K Surface (continued)							
Sept. 17	1.54 × 10 ⁹	5.40 × 10 ⁵	3.34	195.8	4.29 × 10 ⁻¹¹	3.36	2.40 × 10 ⁹
Sept. 18	1.56 × 10 ⁹	5.24 × 10 ⁵	3.35	196.0	4.29 × 10 ⁻¹¹	3.41	2.40 × 10 ⁹
Sept. 19	1.59 × 10 ⁹	5.10 × 10 ⁵	3.36	196.2	4.29 × 10 ⁻¹¹	3.45	2.39 × 10 ⁹
Sept. 20	1.61 × 10 ⁹	4.92 × 10 ⁵	3.36	196.4	4.28 × 10 ⁻¹¹	3.51	2.39 × 10 ⁹
Sept. 21	1.64 × 10 ⁹	4.74 × 10 ⁵	3.37	196.6	4.28 × 10 ⁻¹¹	3.55	2.36 × 10 ⁹
Sept. 22	1.66 × 10 ⁹	4.55 × 10 ⁵	3.38	196.8	4.28 × 10 ⁻¹¹	3.60	2.33 × 10 ⁹
360 ± 5 K Surface							
Aug. 20	5.37 × 10 ⁸	5.78 × 10 ⁵	3.89	190.5	4.33 × 10 ⁻¹¹	1.96	5.28 × 10 ⁸
Aug. 21	5.48 × 10 ⁸	5.83 × 10 ⁵	3.92	190.8	4.33 × 10 ⁻¹¹	2.02	5.59 × 10 ⁸
Aug. 22	5.59 × 10 ⁸	5.90 × 10 ⁵	3.94	191.1	4.33 × 10 ⁻¹¹	2.06	5.88 × 10 ⁸
Aug. 23	5.69 × 10 ⁸	5.94 × 10 ⁵	3.97	191.4	4.32 × 10 ⁻¹¹	2.12	6.19 × 10 ⁸
Aug. 24	5.80 × 10 ⁸	5.96 × 10 ⁵	3.99	191.8	4.32 × 10 ⁻¹¹	2.18	6.51 × 10 ⁸
Aug. 25	5.91 × 10 ⁸	6.02 × 10 ⁵	4.02	192.1	4.32 × 10 ⁻¹¹	2.22	6.81 × 10 ⁸
Aug. 26	6.01 × 10 ⁸	6.04 × 10 ⁵	4.05	192.4	4.32 × 10 ⁻¹¹	2.28	7.13 × 10 ⁸
Aug. 27	6.12 × 10 ⁸	6.09 × 10 ⁵	4.07	192.7	4.31 × 10 ⁻¹¹	2.32	7.45 × 10 ⁸
Aug. 28	6.23 × 10 ⁸	6.08 × 10 ⁵	4.10	193.0	4.31 × 10 ⁻¹¹	2.37	7.75 × 10 ⁸
Aug. 29	6.33 × 10 ⁸	6.07 × 10 ⁵	4.12	193.3	4.31 × 10 ⁻¹¹	2.44	8.08 × 10 ⁸
Aug. 30	6.44 × 10 ⁸	6.09 × 10 ⁵	4.15	193.7	4.31 × 10 ⁻¹¹	2.47	8.36 × 10 ⁸
Aug. 31	6.55 × 10 ⁸	6.09 × 10 ⁵	4.17	194.0	4.30 × 10 ⁻¹¹	2.54	8.70 × 10 ⁸
Sept. 1	6.66 × 10 ⁸	6.10 × 10 ⁵	4.20	194.3	4.30 × 10 ⁻¹¹	2.57	8.98 × 10 ⁸
Sept. 2	6.76 × 10 ⁸	6.08 × 10 ⁵	4.23	194.6	4.30 × 10 ⁻¹¹	2.63	9.30 × 10 ⁸
Sept. 3	6.87 × 10 ⁸	6.07 × 10 ⁵	4.25	194.9	4.30 × 10 ⁻¹¹	2.67	9.59 × 10 ⁸
Sept. 4	6.98 × 10 ⁸	6.05 × 10 ⁵	4.28	195.3	4.29 × 10 ⁻¹¹	2.73	9.90 × 10 ⁸
Sept. 5	7.08 × 10 ⁸	6.02 × 10 ⁵	4.30	195.6	4.29 × 10 ⁻¹¹	2.77	1.01 × 10 ⁹
Sept. 6	7.19 × 10 ⁸	5.97 × 10 ⁵	4.33	195.9	4.29 × 10 ⁻¹¹	2.83	1.04 × 10 ⁹
Sept. 7	7.30 × 10 ⁸	5.94 × 10 ⁵	4.35	196.2	4.29 × 10 ⁻¹¹	2.87	1.07 × 10 ⁹
Sept. 8	7.40 × 10 ⁸	5.89 × 10 ⁵	4.38	196.5	4.28 × 10 ⁻¹¹	2.93	1.09 × 10 ⁹
Sept. 9	7.51 × 10 ⁸	5.84 × 10 ⁵	4.41	196.8	4.28 × 10 ⁻¹¹	2.97	1.11 × 10 ⁹
Sept. 10	7.62 × 10 ⁸	5.78 × 10 ⁵	4.43	197.2	4.28 × 10 ⁻¹¹	3.03	1.14 × 10 ⁹
Sept. 11	7.73 × 10 ⁸	5.72 × 10 ⁵	4.46	197.5	4.28 × 10 ⁻¹¹	3.06	1.16 × 10 ⁹
Sept. 12	7.83 × 10 ⁸	5.65 × 10 ⁵	4.48	197.8	4.27 × 10 ⁻¹¹	3.12	1.18 × 10 ⁹
Sept. 13	7.94 × 10 ⁸	5.57 × 10 ⁵	4.51	198.1	4.27 × 10 ⁻¹¹	3.17	1.20 × 10 ⁹
Sept. 14	8.05 × 10 ⁸	5.47 × 10 ⁵	4.53	198.4	4.27 × 10 ⁻¹¹	3.21	1.21 × 10 ⁹
Sept. 15	8.15 × 10 ⁸	5.39 × 10 ⁵	4.56	198.7	4.27 × 10 ⁻¹¹	3.26	1.22 × 10 ⁹
Sept. 16	8.26 × 10 ⁸	5.29 × 10 ⁵	4.59	199.1	4.26 × 10 ⁻¹¹	3.31	1.24 × 10 ⁹
Sept. 17	8.37 × 10 ⁸	5.19 × 10 ⁵	4.61	199.4	4.26 × 10 ⁻¹¹	3.36	1.24 × 10 ⁹
Sept. 18	8.47 × 10 ⁸	5.07 × 10 ⁵	4.64	199.7	4.26 × 10 ⁻¹¹	3.41	1.25 × 10 ⁹
Sept. 19	8.58 × 10 ⁸	4.96 × 10 ⁵	4.66	200.0	4.26 × 10 ⁻¹¹	3.45	1.25 × 10 ⁹
Sept. 20	8.69 × 10 ⁸	4.83 × 10 ⁵	4.69	200.3	4.25 × 10 ⁻¹¹	3.51	1.25 × 10 ⁹
Sept. 21	8.79 × 10 ⁸	4.69 × 10 ⁵	4.71	200.7	4.25 × 10 ⁻¹¹	3.55	1.24 × 10 ⁹
Sept. 22	8.90 × 10 ⁸	4.55 × 10 ⁵	4.74	201.0	4.25 × 10 ⁻¹¹	3.60	1.24 × 10 ⁹

Values in the second, fourth, and fifth columns were obtained in situ from the ER-2. The atomic oxygen concentrations were obtained from in situ observations of ozone, using a steady-state relationship between O(³P) and O₃, given in text. The bimolecular rate for ClO + O → Cl + O₂, which is well-defined from laboratory studies, is given in column six. Exposure times per 24 hours and ozone removal per 24 hours appear in the last two columns.

POTENTIALLY IMPORTANT CATALYTIC PROCESSES

The intention of this discussion is twofold. First, we wish to underline the fact that there are a great many possibilities for catalyzed ozone destruction by halogen/oxygen cycles that have not been previously noted in the literature. Second, a great deal of detailed laboratory work remains in order to quantify the effect of these cycles under the conditions encountered in the Antarctic.

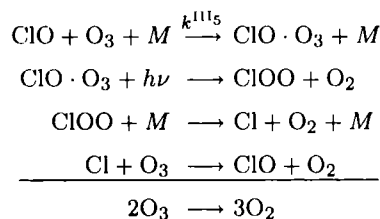
While there are many ways in which to organize this discussion, we will adopt a pragmatic tack: we will investigate

the catalytic cycles in order of their reactant concentrations in the rate limiting step of the proposed cycle. This will identify their potential importance apart from the reaction rate constant for the selected step; we will then discuss what is known about the kinetics to estimate the possible contribution. Alternatively, since we know how much ClO and BrO exists in the vortex and we know the rate of O₃ disappearance, we can calculate how fast the rate-limiting step of a given cycle must be to explain any difference between the sum of mechanisms I-IV and the observed O₃ loss.

Mechanism V

The first catalytic cycle we consider in this class is a mechanism rate limited by the termolecular reaction between ClO and O₃, forming the complex ClO · O₃:

Mechanism V



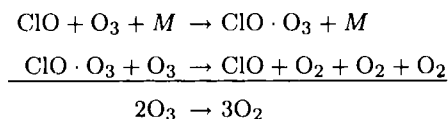
Typical intravortex concentrations of ClO and O₃ are $2 \times 10^9 \text{ cm}^{-3}$ and $5 \times 10^{12} \text{ cm}^{-3}$, respectively, which yields a concentration product of $\sim 10^{22} \text{ cm}^{-6}$.

This cycle is speculative at this point, because no laboratory data exist that could define k_5^{III} . However, we can specify the magnitude of k_5^{III} required to account for the deficit between the sum of mechanisms I–IV and the observed rate of O₃ loss by setting the contribution of mechanism V equal to that deficit at the upper potential temperature surface and then solving for the required k_5^{III} . This yields a value of k_5^{III} equal to $2 \times 10^{-35} \text{ cm}^6 \text{ s}^{-1}$ at 200 K, corresponding to a reaction probability per collision of 10^{-6} .

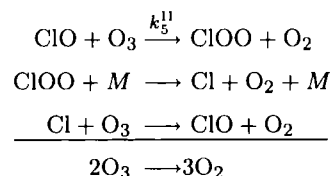
We indulge in another assumption: that the product of ClO · O₃ photolysis is either ClOO + O₂ or Cl + O₂ + O₂. This is obviously an issue to be settled in laboratory studies.

Table 5 summarizes the speculative rate of ozone destruction by mechanism V on potential temperature surfaces 440, 420, 390, and 360 K. Figure 25 graphically characterizes the relationship between calculated and observed O₃ loss. We show the impact of mechanism V by plotting the time rate of change of O₃ resulting from the sum of mechanisms I–IV and that resulting from the sum of mechanisms I–V on Θ

surfaces of 440, 400, and 360 K. Several points require comment. First, for a very slow third-order rate, this termolecular mechanism makes a significant contribution to the loss rate of ozone throughout the entire altitude interval. Second, the altitude distribution of O₃ destruction by mechanism V rectifies the deficit apparent at lower potential temperatures for the sum of mechanisms I–IV, no matter which rate constant is used for k_1^{III} . Third, there are a number of potentially interesting companion processes which merit laboratory investigation. If ClO reacts with O₃, then we must also consider the catalytic couplet:



which could be important at night. In addition, the bimolecular process:



has been reported to be extremely slow. An upper limit of $10^{-18} \text{ cm}^3 \text{ s}^{-1}$ at 300 K is recommended by the NASA Evaluation Panel [DeMore *et al.*, 1987]. The direct determination of k_5^{II} presents formidable difficulties in most laboratory studies because the channel of interest produces Cl atoms that immediately react with O₃ to reform ClO. Nevertheless, it is extremely important to obtain direct rate data on k_5^{II} because it only need be $1 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$ to be of major significance to ozone destruction in the Antarctic polar vortex.

TABLE 5. Analysis of Ozone Loss Based on the Speculation That ClO Radicals Combine with O₃ to Form ClO · O₃ in a Termolecular Process Described by a Third-Order Rate Constant $k_5^{\text{III}} = 3 \times 10^{-35} \text{ cm}^6 \text{ s}^{-1}$ at 200 K

Day	[ClO], mol cm ⁻³	[O ₃], mol cm ⁻³	[M], × 10 ¹⁸ cm ⁻³	T, °K	k_5^{III} , cm ⁶ s ⁻¹	Q, × 10 ⁴ s	−ΔO ₃ , mol cm ⁻³ d ⁻¹
440 ± 5 K Surface							
Aug. 20	1.46 × 10 ⁹	4.42 × 10 ¹²	2.16	191.3	4.32 × 10 ⁻¹⁷	3.05	1.70 × 10 ¹⁰
Aug. 21	1.48 × 10 ⁹	4.39 × 10 ¹²	2.16	191.4	4.32 × 10 ⁻¹⁷	3.10	1.75 × 10 ¹⁰
Aug. 22	1.51 × 10 ⁹	4.36 × 10 ¹²	2.16	191.5	4.31 × 10 ⁻¹⁷	3.14	1.78 × 10 ¹⁰
Aug. 23	1.53 × 10 ⁹	4.32 × 10 ¹²	2.15	191.5	4.31 × 10 ⁻¹⁷	3.19	1.83 × 10 ¹⁰
Aug. 24	1.56 × 10 ⁹	4.29 × 10 ¹²	2.15	191.6	4.31 × 10 ⁻¹⁷	3.25	1.87 × 10 ¹⁰
Aug. 25	1.58 × 10 ⁹	4.25 × 10 ¹²	2.15	191.7	4.30 × 10 ⁻¹⁷	3.29	1.90 × 10 ¹⁰
Aug. 26	1.61 × 10 ⁹	4.20 × 10 ¹²	2.15	191.8	4.30 × 10 ⁻¹⁷	3.34	1.94 × 10 ¹⁰
Aug. 27	1.63 × 10 ⁹	4.16 × 10 ¹²	2.15	191.9	4.30 × 10 ⁻¹⁷	3.39	1.98 × 10 ¹⁰
Aug. 28	1.66 × 10 ⁹	4.11 × 10 ¹²	2.15	191.9	4.29 × 10 ⁻¹⁷	3.44	2.01 × 10 ¹⁰
Aug. 29	1.68 × 10 ⁹	4.06 × 10 ¹²	2.15	192.0	4.29 × 10 ⁻¹⁷	3.49	2.05 × 10 ¹⁰
Aug. 30	1.71 × 10 ⁹	4.01 × 10 ¹²	2.14	192.1	4.29 × 10 ⁻¹⁷	3.54	2.08 × 10 ¹⁰
Aug. 31	1.73 × 10 ⁹	3.96 × 10 ¹²	2.14	192.2	4.28 × 10 ⁻¹⁷	3.59	2.11 × 10 ¹⁰
Sept. 1	1.76 × 10 ⁹	3.90 × 10 ¹²	2.14	192.2	4.28 × 10 ⁻¹⁷	3.64	2.14 × 10 ¹⁰
Sept. 2	1.78 × 10 ⁹	3.84 × 10 ¹²	2.14	192.3	4.28 × 10 ⁻¹⁷	3.69	2.16 × 10 ¹⁰
Sept. 3	1.81 × 10 ⁹	3.78 × 10 ¹²	2.14	192.4	4.27 × 10 ⁻¹⁷	3.74	2.18 × 10 ¹⁰
Sept. 4	1.83 × 10 ⁹	3.71 × 10 ¹²	2.14	192.5	4.27 × 10 ⁻¹⁷	3.80	2.20 × 10 ¹⁰
Sept. 5	1.86 × 10 ⁹	3.64 × 10 ¹²	2.13	192.5	4.27 × 10 ⁻¹⁷	3.84	2.22 × 10 ¹⁰
Sept. 6	1.88 × 10 ⁹	3.57 × 10 ¹²	2.13	192.6	4.27 × 10 ⁻¹⁷	3.89	2.23 × 10 ¹⁰

TABLE 5. (continued)

Day	[ClO], mol cm ⁻³	[O ₃], mol cm ⁻³	[M], × 10 ¹⁸ cm ⁻³	T, °K	k ^{II} , cm ³ s ⁻¹	Q, × 10 ⁴ s	-ΔO ₃ , mol cm ⁻³ d ⁻¹
<i>440 ± 5 K Surface (continued)</i>							
Sept. 7	1.91 × 10 ⁹	3.50 × 10 ¹²	2.13	192.7	4.26 × 10 ⁻¹⁷	3.94	2.24 × 10 ¹⁰
Sept. 8	1.93 × 10 ⁹	3.42 × 10 ¹²	2.13	192.8	4.26 × 10 ⁻¹⁷	3.99	2.25 × 10 ¹⁰
Sept. 9	1.95 × 10 ⁹	3.34 × 10 ¹²	2.13	192.9	4.26 × 10 ⁻¹⁷	4.04	2.25 × 10 ¹⁰
Sept. 10	1.98 × 10 ⁹	3.26 × 10 ¹²	2.13	192.9	4.25 × 10 ⁻¹⁷	4.09	2.24 × 10 ¹⁰
Sept. 11	2.00 × 10 ⁹	3.17 × 10 ¹²	2.12	193.0	4.25 × 10 ⁻¹⁷	4.15	2.24 × 10 ¹⁰
Sept. 12	2.03 × 10 ⁹	3.08 × 10 ¹²	2.12	193.1	4.25 × 10 ⁻¹⁷	4.20	2.23 × 10 ¹⁰
Sept. 13	2.05 × 10 ⁹	2.98 × 10 ¹²	2.12	193.2	4.24 × 10 ⁻¹⁷	4.25	2.21 × 10 ¹⁰
Sept. 14	2.08 × 10 ⁹	2.88 × 10 ¹²	2.12	193.2	4.24 × 10 ⁻¹⁷	4.30	2.19 × 10 ¹⁰
Sept. 15	2.10 × 10 ⁹	2.78 × 10 ¹²	2.12	193.3	4.24 × 10 ⁻¹⁷	4.36	2.16 × 10 ¹⁰
Sept. 16	2.13 × 10 ⁹	2.67 × 10 ¹²	2.12	193.4	4.23 × 10 ⁻¹⁷	4.41	2.12 × 10 ¹⁰
Sept. 17	2.15 × 10 ⁹	2.56 × 10 ¹²	2.12	193.5	4.23 × 10 ⁻¹⁷	4.46	2.08 × 10 ¹⁰
Sept. 18	2.18 × 10 ⁹	2.45 × 10 ¹²	2.11	193.5	4.23 × 10 ⁻¹⁷	4.51	2.04 × 10 ¹⁰
Sept. 19	2.20 × 10 ⁹	2.33 × 10 ¹²	2.11	193.6	4.22 × 10 ⁻¹⁷	4.57	1.98 × 10 ¹⁰
Sept. 20	2.23 × 10 ⁹	2.21 × 10 ¹²	2.11	193.7	4.22 × 10 ⁻¹⁷	4.62	1.92 × 10 ¹⁰
Sept. 21	2.25 × 10 ⁹	2.08 × 10 ¹²	2.11	193.8	4.22 × 10 ⁻¹⁷	4.67	1.85 × 10 ¹⁰
Sept. 22	2.28 × 10 ⁹	1.95 × 10 ¹²	2.11	193.9	4.21 × 10 ⁻¹⁷	4.73	1.77 × 10 ¹⁰
<i>420 ± 5 K Surface</i>							
Aug. 20	1.23 × 10 ⁹	4.91 × 10 ¹²	2.45	190.3	4.90 × 10 ⁻¹⁷	3.05	1.80 × 10 ¹⁰
Aug. 21	1.25 × 10 ⁹	4.88 × 10 ¹²	2.45	190.4	4.90 × 10 ⁻¹⁷	3.10	1.86 × 10 ¹⁰
Aug. 22	1.28 × 10 ⁹	4.85 × 10 ¹²	2.45	190.5	4.90 × 10 ⁻¹⁷	3.14	1.91 × 10 ¹⁰
Aug. 23	1.31 × 10 ⁹	4.81 × 10 ¹²	2.45	190.6	4.91 × 10 ⁻¹⁷	3.19	1.97 × 10 ¹⁰
Aug. 24	1.33 × 10 ⁹	4.77 × 10 ¹²	2.45	190.7	4.91 × 10 ⁻¹⁷	3.25	2.03 × 10 ¹⁰
Aug. 25	1.36 × 10 ⁹	4.72 × 10 ¹²	2.46	190.9	4.91 × 10 ⁻¹⁷	3.29	2.08 × 10 ¹⁰
Aug. 26	1.39 × 10 ⁹	4.68 × 10 ¹²	2.46	191.0	4.92 × 10 ⁻¹⁷	3.34	2.13 × 10 ¹⁰
Aug. 27	1.41 × 10 ⁹	4.63 × 10 ¹²	2.46	191.1	4.92 × 10 ⁻¹⁷	3.39	2.18 × 10 ¹⁰
Aug. 28	1.44 × 10 ⁹	4.58 × 10 ¹²	2.46	191.2	4.92 × 10 ⁻¹⁷	3.44	2.23 × 10 ¹⁰
Aug. 29	1.47 × 10 ⁹	4.52 × 10 ¹²	2.46	191.4	4.93 × 10 ⁻¹⁷	3.49	2.28 × 10 ¹⁰
Aug. 30	1.49 × 10 ⁹	4.46 × 10 ¹²	2.47	191.5	4.93 × 10 ⁻¹⁷	3.54	2.33 × 10 ¹⁰
Aug. 31	1.52 × 10 ⁹	4.40 × 10 ¹²	2.47	191.6	4.93 × 10 ⁻¹⁷	3.59	2.37 × 10 ¹⁰
Sept. 1	1.55 × 10 ⁹	4.34 × 10 ¹²	2.47	191.7	4.94 × 10 ⁻¹⁷	3.64	2.41 × 10 ¹⁰
Sept. 2	1.57 × 10 ⁹	4.27 × 10 ¹²	2.47	191.9	4.94 × 10 ⁻¹⁷	3.69	2.45 × 10 ¹⁰
Sept. 3	1.60 × 10 ⁹	4.19 × 10 ¹²	2.47	192.0	4.95 × 10 ⁻¹⁷	3.74	2.48 × 10 ¹⁰
Sept. 4	1.63 × 10 ⁹	4.12 × 10 ¹²	2.47	192.1	4.95 × 10 ⁻¹⁷	3.80	2.52 × 10 ¹⁰
Sept. 5	1.65 × 10 ⁹	4.04 × 10 ¹²	2.48	192.2	4.95 × 10 ⁻¹⁷	3.84	2.54 × 10 ¹⁰
Sept. 6	1.68 × 10 ⁹	3.95 × 10 ¹²	2.48	192.3	4.96 × 10 ⁻¹⁷	3.89	2.56 × 10 ¹⁰
Sept. 7	1.71 × 10 ⁹	3.86 × 10 ¹²	2.48	192.5	4.96 × 10 ⁻¹⁷	3.94	2.58 × 10 ¹⁰
Sept. 8	1.73 × 10 ⁹	3.77 × 10 ¹²	2.48	192.6	4.96 × 10 ⁻¹⁷	3.99	2.59 × 10 ¹⁰
Sept. 9	1.76 × 10 ⁹	3.67 × 10 ¹²	2.48	192.7	4.97 × 10 ⁻¹⁷	4.04	2.60 × 10 ¹⁰
Sept. 10	1.79 × 10 ⁹	3.57 × 10 ¹²	2.49	192.8	4.97 × 10 ⁻¹⁷	4.09	2.60 × 10 ¹⁰
Sept. 11	1.81 × 10 ⁹	3.46 × 10 ¹²	2.49	193.0	4.97 × 10 ⁻¹⁷	4.15	2.59 × 10 ¹⁰
Sept. 12	1.84 × 10 ⁹	3.35 × 10 ¹²	2.49	193.1	4.98 × 10 ⁻¹⁷	4.20	2.58 × 10 ¹⁰
Sept. 13	1.87 × 10 ⁹	3.24 × 10 ¹²	2.49	193.2	4.98 × 10 ⁻¹⁷	4.25	2.56 × 10 ¹⁰
Sept. 14	1.89 × 10 ⁹	3.11 × 10 ¹²	2.49	193.3	4.98 × 10 ⁻¹⁷	4.30	2.53 × 10 ¹⁰
Sept. 15	1.92 × 10 ⁹	2.99 × 10 ¹²	2.49	193.5	4.99 × 10 ⁻¹⁷	4.36	2.49 × 10 ¹⁰
Sept. 16	1.95 × 10 ⁹	2.85 × 10 ¹²	2.50	193.6	4.99 × 10 ⁻¹⁷	4.41	2.44 × 10 ¹⁰
Sept. 17	1.97 × 10 ⁹	2.71 × 10 ¹²	2.50	193.7	5.00 × 10 ⁻¹⁷	4.46	2.39 × 10 ¹⁰
Sept. 18	2.00 × 10 ⁹	2.57 × 10 ¹²	2.50	193.8	5.00 × 10 ⁻¹⁷	4.51	2.32 × 10 ¹⁰
Sept. 19	2.03 × 10 ⁹	2.42 × 10 ¹²	2.50	194.0	5.00 × 10 ⁻¹⁷	4.57	2.24 × 10 ¹⁰
Sept. 20	2.05 × 10 ⁹	2.26 × 10 ¹²	2.50	194.1	5.01 × 10 ⁻¹⁷	4.62	2.15 × 10 ¹⁰
Sept. 21	2.08 × 10 ⁹	2.10 × 10 ¹²	2.50	194.2	5.01 × 10 ⁻¹⁷	4.67	2.04 × 10 ¹⁰
Sept. 22	2.11 × 10 ⁹	1.93 × 10 ¹²	2.51	194.3	5.01 × 10 ⁻¹⁷	4.73	1.93 × 10 ¹⁰
<i>390 ± 5 K Surface</i>							
Aug. 20	8.60 × 10 ⁸	3.92 × 10 ¹²	3.13	190.6	6.26 × 10 ⁻¹⁷	3.05	1.29 × 10 ¹⁰
Aug. 21	8.85 × 10 ⁸	3.91 × 10 ¹²	3.14	190.8	6.28 × 10 ⁻¹⁷	3.10	1.35 × 10 ¹⁰
Aug. 22	9.09 × 10 ⁸	3.89 × 10 ¹²	3.15	191.0	6.29 × 10 ⁻¹⁷	3.14	1.40 × 10 ¹⁰
Aug. 23	9.33 × 10 ⁸	3.87 × 10 ¹²	3.15	191.2	6.31 × 10 ⁻¹⁷	3.19	1.46 × 10 ¹⁰
Aug. 24	9.57 × 10 ⁸	3.85 × 10 ¹²	3.16	191.3	6.32 × 10 ⁻¹⁷	3.25	1.51 × 10 ¹⁰
Aug. 25	9.82 × 10 ⁸	3.83 × 10 ¹²	3.17	191.5	6.34 × 10 ⁻¹⁷	3.29	1.57 × 10 ¹⁰
Aug. 26	1.01 × 10 ⁹	3.81 × 10 ¹²	3.18	191.7	6.35 × 10 ⁻¹⁷	3.34	1.63 × 10 ¹⁰
Aug. 27	1.03 × 10 ⁹	3.78 × 10 ¹²	3.18	191.9	6.37 × 10 ⁻¹⁷	3.39	1.68 × 10 ¹⁰
Aug. 28	1.05 × 10 ⁹	3.75 × 10 ¹²	3.19	192.1	6.38 × 10 ⁻¹⁷	3.44	1.74 × 10 ¹⁰
Aug. 29	1.08 × 10 ⁹	3.72 × 10 ¹²	3.20	192.3	6.40 × 10 ⁻¹⁷	3.49	1.80 × 10 ¹⁰

TABLE 5. (continued)

Day	[ClO], mol cm ⁻³	[O ₃], mol cm ⁻³	[M], ×10 ¹⁸ cm ⁻³	T, °K	k ^{II} , cm ³ s ⁻¹	Q, ×10 ⁴ s	-ΔO ₃ , mol cm ⁻³ d ⁻¹
390 ± 5 K Surface (continued)							
Aug. 30	1.10 × 10 ⁹	3.69 × 10 ¹²	3.21	192.5	6.41 × 10 ⁻¹⁷	3.54	1.85 × 10 ¹⁰
Aug. 31	1.13 × 10 ⁹	3.66 × 10 ¹²	3.21	192.6	6.43 × 10 ⁻¹⁷	3.59	1.91 × 10 ¹⁰
Sept. 1	1.15 × 10 ⁹	3.62 × 10 ¹²	3.22	192.8	6.44 × 10 ⁻¹⁷	3.64	1.96 × 10 ¹⁰
Sept. 2	1.18 × 10 ⁹	3.59 × 10 ¹²	3.23	193.0	6.46 × 10 ⁻¹⁷	3.69	2.01 × 10 ¹⁰
Sept. 3	1.20 × 10 ⁹	3.55 × 10 ¹²	3.24	193.2	6.47 × 10 ⁻¹⁷	3.74	2.06 × 10 ¹⁰
Sept. 4	1.22 × 10 ⁹	3.50 × 10 ¹²	3.24	193.4	6.49 × 10 ⁻¹⁷	3.80	2.11 × 10 ¹⁰
Sept. 5	1.25 × 10 ⁹	3.46 × 10 ¹²	3.25	193.6	6.50 × 10 ⁻¹⁷	3.84	2.16 × 10 ¹⁰
Sept. 6	1.27 × 10 ⁹	3.41 × 10 ¹²	3.26	193.8	6.52 × 10 ⁻¹⁷	3.89	2.20 × 10 ¹⁰
Sept. 7	1.30 × 10 ⁹	3.36 × 10 ¹²	3.27	194.0	6.53 × 10 ⁻¹⁷	3.94	2.24 × 10 ¹⁰
Sept. 8	1.32 × 10 ⁹	3.31 × 10 ¹²	3.27	194.1	6.55 × 10 ⁻¹⁷	3.99	2.29 × 10 ¹⁰
Sept. 9	1.35 × 10 ⁹	3.25 × 10 ¹²	3.28	194.3	6.56 × 10 ⁻¹⁷	4.04	2.32 × 10 ¹⁰
Sept. 10	1.37 × 10 ⁹	3.19 × 10 ¹²	3.29	194.5	6.58 × 10 ⁻¹⁷	4.09	2.36 × 10 ¹⁰
Sept. 11	1.39 × 10 ⁹	3.13 × 10 ¹²	3.30	194.7	6.59 × 10 ⁻¹⁷	4.15	2.39 × 10 ¹⁰
Sept. 12	1.42 × 10 ⁹	3.07 × 10 ¹²	3.30	194.9	6.61 × 10 ⁻¹⁷	4.20	2.41 × 10 ¹⁰
Sept. 13	1.44 × 10 ⁹	3.00 × 10 ¹²	3.31	195.1	6.62 × 10 ⁻¹⁷	4.25	2.44 × 10 ¹⁰
Sept. 14	1.47 × 10 ⁹	2.93 × 10 ¹²	3.32	195.3	6.64 × 10 ⁻¹⁷	4.30	2.45 × 10 ¹⁰
Sept. 15	1.49 × 10 ⁹	2.85 × 10 ¹²	3.33	195.5	6.65 × 10 ⁻¹⁷	4.36	2.47 × 10 ¹⁰
Sept. 16	1.52 × 10 ⁹	2.77 × 10 ¹²	3.33	195.6	6.67 × 10 ⁻¹⁷	4.41	2.47 × 10 ¹⁰
Sept. 17	1.54 × 10 ⁹	2.69 × 10 ¹²	3.34	195.8	6.68 × 10 ⁻¹⁷	4.46	2.47 × 10 ¹⁰
Sept. 18	1.56 × 10 ⁹	2.60 × 10 ¹²	3.35	196.0	6.70 × 10 ⁻¹⁷	4.51	2.46 × 10 ¹⁰
Sept. 19	1.59 × 10 ⁹	2.51 × 10 ¹²	3.36	196.2	6.71 × 10 ⁻¹⁷	4.57	2.45 × 10 ¹⁰
Sept. 20	1.61 × 10 ⁹	2.42 × 10 ¹²	3.36	196.4	6.73 × 10 ⁻¹⁷	4.62	2.42 × 10 ¹⁰
Sept. 21	1.64 × 10 ⁹	2.32 × 10 ¹²	3.37	196.6	6.74 × 10 ⁻¹⁷	4.67	2.39 × 10 ¹⁰
Sept. 22	1.66 × 10 ⁹	2.21 × 10 ¹²	3.38	196.8	6.76 × 10 ⁻¹⁷	4.73	2.35 × 10 ¹⁰
360 ± 5 K Surface							
Aug. 20	5.37 × 10 ⁸	3.64 × 10 ¹²	3.89	190.5	7.78 × 10 ⁻¹⁷	3.05	9.30 × 10 ⁹
Aug. 21	5.48 × 10 ⁸	3.63 × 10 ¹²	3.92	190.8	7.83 × 10 ⁻¹⁷	3.10	9.66 × 10 ⁹
Aug. 22	5.59 × 10 ⁸	3.61 × 10 ¹²	3.94	191.1	7.89 × 10 ⁻¹⁷	3.14	9.99 × 10 ⁹
Aug. 23	5.69 × 10 ⁸	3.59 × 10 ¹²	3.97	191.4	7.94 × 10 ⁻¹⁷	3.19	1.04 × 10 ¹⁰
Aug. 24	5.80 × 10 ⁸	3.57 × 10 ¹²	3.99	191.8	7.99 × 10 ⁻¹⁷	3.25	1.07 × 10 ¹⁰
Aug. 25	5.91 × 10 ⁸	3.55 × 10 ¹²	4.02	192.1	8.04 × 10 ⁻¹⁷	3.29	1.11 × 10 ¹⁰
Aug. 26	6.01 × 10 ⁸	3.53 × 10 ¹²	4.05	192.4	8.09 × 10 ⁻¹⁷	3.34	1.15 × 10 ¹⁰
Aug. 27	6.12 × 10 ⁸	3.50 × 10 ¹²	4.07	192.7	8.14 × 10 ⁻¹⁷	3.39	1.18 × 10 ¹⁰
Aug. 28	6.23 × 10 ⁸	3.48 × 10 ¹²	4.10	193.0	8.19 × 10 ⁻¹⁷	3.44	1.22 × 10 ¹⁰
Aug. 29	6.33 × 10 ⁸	3.45 × 10 ¹²	4.12	193.3	8.25 × 10 ⁻¹⁷	3.49	1.26 × 10 ¹⁰
Aug. 30	6.44 × 10 ⁸	3.42 × 10 ¹²	4.15	193.7	8.30 × 10 ⁻¹⁷	3.54	1.29 × 10 ¹⁰
Aug. 31	6.55 × 10 ⁸	3.39 × 10 ¹²	4.17	194.0	8.35 × 10 ⁻¹⁷	3.59	1.33 × 10 ¹⁰
Sept. 1	6.66 × 10 ⁸	3.36 × 10 ¹²	4.20	194.3	8.40 × 10 ⁻¹⁷	3.64	1.37 × 10 ¹⁰
Sept. 2	6.76 × 10 ⁸	3.33 × 10 ¹²	4.23	194.6	8.45 × 10 ⁻¹⁷	3.69	1.41 × 10 ¹⁰
Sept. 3	6.87 × 10 ⁸	3.29 × 10 ¹²	4.25	194.9	8.50 × 10 ⁻¹⁷	3.74	1.44 × 10 ¹⁰
Sept. 4	6.98 × 10 ⁸	3.26 × 10 ¹²	4.28	195.3	8.55 × 10 ⁻¹⁷	3.80	1.48 × 10 ¹⁰
Sept. 5	7.08 × 10 ⁸	3.22 × 10 ¹²	4.30	195.6	8.61 × 10 ⁻¹⁷	3.84	1.51 × 10 ¹⁰
Sept. 6	7.19 × 10 ⁸	3.18 × 10 ¹²	4.33	195.9	8.66 × 10 ⁻¹⁷	3.89	1.54 × 10 ¹⁰
Sept. 7	7.30 × 10 ⁸	3.14 × 10 ¹²	4.35	196.2	8.71 × 10 ⁻¹⁷	3.94	1.57 × 10 ¹⁰
Sept. 8	7.40 × 10 ⁸	3.09 × 10 ¹²	4.38	196.5	8.76 × 10 ⁻¹⁷	3.99	1.60 × 10 ¹⁰
Sept. 9	7.51 × 10 ⁸	3.04 × 10 ¹²	4.41	196.8	8.81 × 10 ⁻¹⁷	4.04	1.63 × 10 ¹⁰
Sept. 10	7.62 × 10 ⁸	2.99 × 10 ¹²	4.43	197.2	8.86 × 10 ⁻¹⁷	4.09	1.66 × 10 ¹⁰
Sept. 11	7.73 × 10 ⁸	2.94 × 10 ¹²	4.46	197.5	8.91 × 10 ⁻¹⁷	4.15	1.68 × 10 ¹⁰
Sept. 12	7.83 × 10 ⁸	2.89 × 10 ¹²	4.48	197.8	8.97 × 10 ⁻¹⁷	4.20	1.70 × 10 ¹⁰
Sept. 13	7.94 × 10 ⁸	2.83 × 10 ¹²	4.51	198.1	9.02 × 10 ⁻¹⁷	4.25	1.72 × 10 ¹⁰
Sept. 14	8.05 × 10 ⁸	2.77 × 10 ¹²	4.53	198.4	9.07 × 10 ⁻¹⁷	4.30	1.74 × 10 ¹⁰
Sept. 15	8.15 × 10 ⁸	2.71 × 10 ¹²	4.56	198.7	9.12 × 10 ⁻¹⁷	4.36	1.76 × 10 ¹⁰
Sept. 16	8.26 × 10 ⁸	2.65 × 10 ¹²	4.59	199.1	9.17 × 10 ⁻¹⁷	4.41	1.77 × 10 ¹⁰
Sept. 17	8.37 × 10 ⁸	2.58 × 10 ¹²	4.61	199.4	9.22 × 10 ⁻¹⁷	4.46	1.78 × 10 ¹⁰
Sept. 18	8.47 × 10 ⁸	2.51 × 10 ¹²	4.64	199.7	9.27 × 10 ⁻¹⁷	4.51	1.78 × 10 ¹⁰
Sept. 19	8.58 × 10 ⁸	2.44 × 10 ¹²	4.66	200.0	9.32 × 10 ⁻¹⁷	4.57	1.79 × 10 ¹⁰
Sept. 20	8.69 × 10 ⁸	2.37 × 10 ¹²	4.69	200.3	9.38 × 10 ⁻¹⁷	4.62	1.78 × 10 ¹⁰
Sept. 21	8.79 × 10 ⁸	2.29 × 10 ¹²	4.71	200.7	9.43 × 10 ⁻¹⁷	4.67	1.77 × 10 ¹⁰
Sept. 22	8.90 × 10 ⁸	2.21 × 10 ¹²	4.74	201.0	9.48 × 10 ⁻¹⁷	4.73	1.76 × 10 ¹⁰

Values in columns two through five are taken from the in situ ER-2 data. The sixth column tracks the effective second-order reaction rate constant, assuming $k_5^{\text{II}} = 3 \times 10^{-35} \text{ cm}^6 \text{ s}^{-1}$ at 200 K. This third-order rate is selected such that the loss rate of ozone resulting from mechanism V equals that resulting from mechanism I at the 440 K surface. Columns seven and eight track the effective exposure time, Q , and the ozone removal in each 24-hour period.

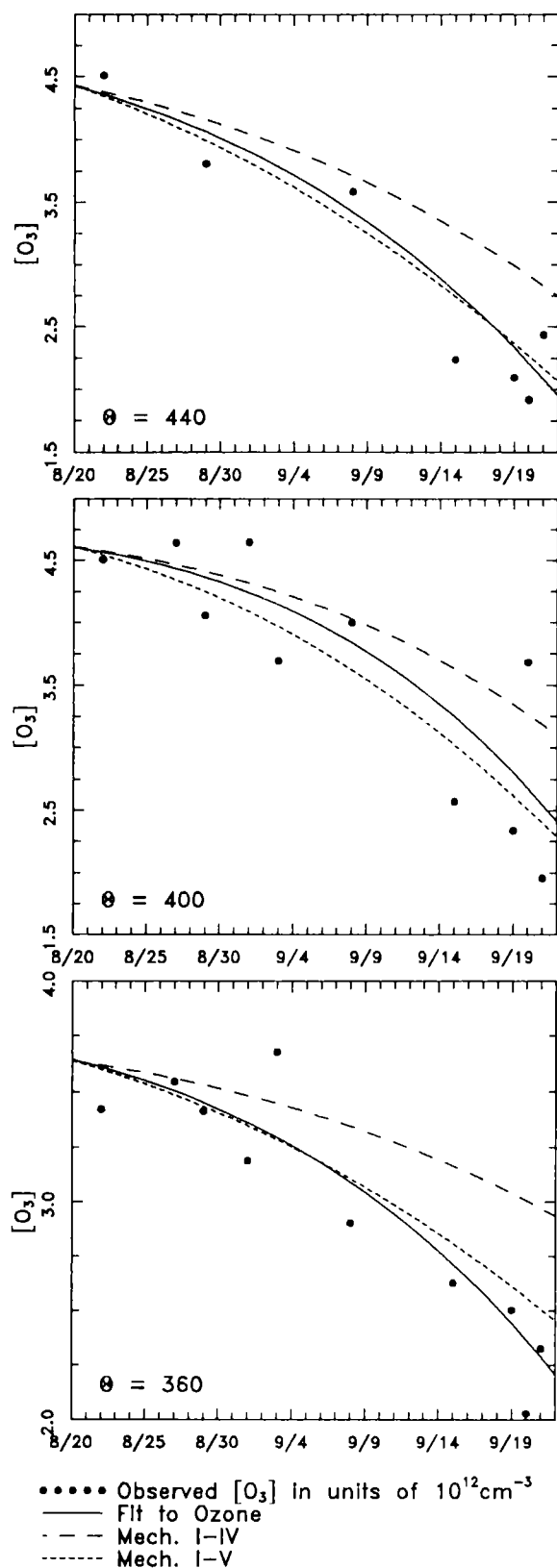
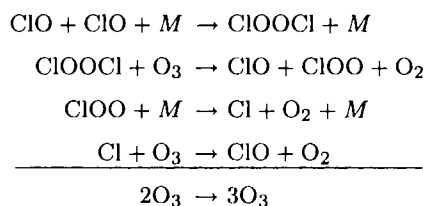


Fig. 25. Summary of the impact of mechanism V, rate limited by $\text{ClO} + \text{O}_3 + M \rightarrow \text{ClO} \cdot \text{O}_3 + M$, on the time rate of change of O_3 on the 440, 400, and 360 K surfaces, assuming a $\text{ClO} \cdot \text{O}_3$ termolecular formation rate of $k_5^{\text{III}} = 2 \times 10^{-35} \text{ cm}^6 \text{ s}^{-1}$. The solid curve is the best fit to observed O_3 , the dotted curve is the sum of mechanisms I-IV, and the dashed curve is the sum of mechanisms I-V.

Mechanism VI

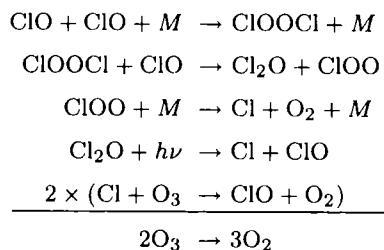
A kindred cycle to that of mechanism V is the reaction sequence rate limited by the reaction of the ClO dimer with ozone:

Mechanism VI



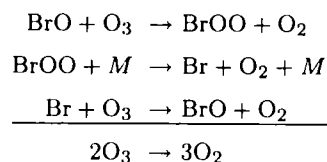
While this sequence may be important at night, note that we have already accounted for any cycle in which ClO dimer formation is rate limiting, no matter what subsequent elementary reactions are invoked. We have used the forward rate of the first step to calculate the ozone destruction rate in mechanism I assuming every dimer formed is photolyzed to yield two Cl atoms. Any deviation from this assumption can only slow the net effect of mechanism I.

This reaction is not without consequence at night, however, since it could serve as an important source of ClO recycling. A similar circumstance surrounds a catalytic cycle of the form:



Again, since we have used the full dimer formation rate in our calculations associated with mechanism I, such a cycle cannot enhance the rate of O_3 destruction.

The product of the ClO (or ClO dimer) and O_3 concentration is $\sim 10^{22} \text{ cm}^{-6}$. Stepping to the next tier is the BrO- O_3 concentration product, which is of the order of 10^{20} cm^{-6} within the vortex. In order for the direct reaction between BrO and O_3 to initiate a cycle which catalytically destroys O_3

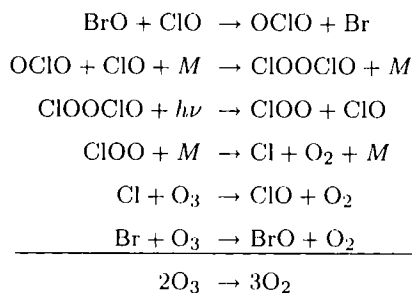


at a rate comparable with that of mechanism I, a bimolecular rate of $10^{-14} \text{ cm}^3 \text{ s}^{-1}$ or greater at 200 K is required. This exceeds the room temperature upper limit to the rate constant reported by Sander and Watson [1981], an experiment that provided a direct measurement of the rate constant. While it would be of great interest to study this reaction at low temperature and at elevated pressure, the bimolecular reaction of BrO and O_3 does not appear to be important.

Mechanism VII

The next halogen-oxygen reactant-product concentration tier is occupied by mechanisms I and II, which we have already treated. The $[\text{ClO}]^2$ regime is approximately $5 \times 10^{18} \text{ cm}^{-6}$, the $[\text{BrO}][\text{ClO}]$ regime is $\sim 5 \times 10^{16} \text{ cm}^{-6}$.

A broad class of catalytic cycles rate limited by OCIO occupy the next regime. For example, the $\text{BrO} + \text{ClO}$ product channel, which is not used in mechanism II, produces OCIO, which can then react with ClO to yield the following cycle:



We can place an upper limit on the rate-limiting step, $\text{OCIO} + \text{ClO} \rightarrow \text{ClOOCIO}$, using the column density measurements of OCIO by Solomon *et al.* [1987]. Those experiments indicate a daytime column concentration of $3 \times 10^{13} \text{ cm}^{-2}$, which corresponds to an $[\text{OCIO}]$ upper limit of $\sim 3 \times 10^7 \text{ cm}^{-3}$. This in turn implies a $[\text{ClO}][\text{OCIO}]$ product of $\sim 5 \times 10^{16} \text{ cm}^{-6}$, so the bimolecular rate constant for this step must be of the order of $5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ in order to contribute significantly. A rate constant this large at 200 K is highly unlikely. Nevertheless, this step is receiving careful attention in laboratory experiments.

There are a manifold of other possibilities, but they are rate limited by reaction steps that we have already "used." We are thus left with a situation that requires strong input from laboratory studies to define critical rates in an extensive subset of catalytic processes.

ANALYSIS OF EXPERIMENTAL UNCERTAINTY

Table 6 defines the mechanism, experimental uncertainty, percentage contribution by each cycle, and finally, key observational or laboratory data, which are both critical to the quantitative analysis and incomplete.

A significant issue, which is highlighted in Table 6, is the relationship between (1) the rate of ozone loss observed by the ER-2 and (2) the magnitude of the photochemical sink required to explain that loss of ozone. A very important companion analysis to ours by Hartmann *et al.* [1989] concludes that transport of ozone into the CPR contributes an additional 20% to the photochemical sink required for quantitative agreement between calculated and observed O_3 loss rates. The implication is that the time rate of change of ozone resulting from the sum of all photochemical cycles must be 1.2 ± 0.1 times the observed decay rate of O_3 . We emphasize this point by appropriate renormalization of the fractional loss represented by each mechanism.

SUMMARY AND COMPARISON

In this paper we seek to define the fraction of observed ozone loss within the chemically perturbed region of the Antarctic polar vortex that can be accounted for by halogen

radical catalysis. We present an analysis of ozone destruction rates at 72°S latitude, based on simultaneous, in situ observations of ClO, BrO, and O_3 obtained from the ER-2 aircraft. The analysis examines a manifold of possible catalytic cycles, some with incomplete specification of kinetic parameters. The rate of ozone destruction for each mechanism is analyzed for a period corresponding to a set of 10 ER-2 missions, extending from August 23 to September 22, 1987, which left Punta Arenas, Chile (54°S latitude), crossed the Drake Passage, followed the western extremity of the Palmer Peninsula to 72°S latitude, turned north, and rapidly descended from 18.2 to 13.7 km, then returned to 18.2 km for the homebound leg. Our analysis isolates the dive region of the flight trajectory at 72°S latitude, which covers the isentropic surfaces from 360 to 450 K (13.5–18.3 km).

Figure 26 summarizes our results in graphical form, displaying the absolute amount of ozone destroyed by the sum of mechanisms I–IV within the vortex as a function of potential temperature (altitude). Experimental uncertainties, reviewed in Table 6, are superposed in Figure 26 to emphasize the importance of this issue, particularly given the quadratic dependence of ozone loss rates on experimentally determined concentrations in this analysis.

We can summarize our results from another point of view. In Figure 27 we present the time evolution of the percentage contribution from each mechanism integrated over all potential temperatures (360–450 K) and thus over the entire altitude interval covered by the ER-2 in the dive segment of the flight trajectory (13.5–18.3 km).

While obviously a major fraction of the observed ozone loss is accounted for by the sum of mechanisms I–IV, we can speculate on what the explanation might be for the discrepancy implied in Figure 26 between the calculated and observed O_3 loss. Of the potentially important catalytic cycles reviewed in Table 6, perhaps the most promising is mechanism V, which is rate limited by the termolecular reaction of ClO with O_3 . Using a third-order rate constant for k_5^{III} of $2 \times 10^{-35} \text{ cm}^6 \text{ s}^{-1}$ and the observed concentration of ClO and O_3 (see Table 5) we can sum mechanism V with the results displayed in Figure 26 for mechanisms I–IV to compare the altitude distribution of O_3 loss. This comparison is shown in Figure 28, the absolute ozone loss as a function of potential temperature (altitude). It is clear that for an exceedingly small reaction rate constant for $\text{ClO} + \text{O}_3 + M \rightarrow \text{ClO} \cdot \text{O}_3 + M$, both the shape of the altitude dependent O_3 loss and the absolute magnitude of the O_3 loss are quantitatively matched. We do not offer this as a method for rate constant determination. Rather, we present this analysis to demonstrate how an exceedingly slow kinetic process between ClO and O_3 can significantly impact the rate of catalytic destruction. To complete this speculative component of the analysis, we trace, in Figure 29, the temporal development of the percentage contribution of mechanism V with that of the catalytic cycles already discussed. In comparison, we note that Barrett *et al.* [1988] published an analysis of ozone loss rates within the Antarctic vortex based on ClO concentrations obtained from ground-based millimeter wave emission experiments observed on September 20–24, 1987 from McMurdo Station (77°S) and the Hayman *et al.* [1986] value for k_1^{III} . They concluded that "both the rate and altitude range of ozone depletion can be accounted for by the dimer mechanism," that is, by mechanism I alone.

TABLE 6. Error Analysis of Catalytic Cycles That Contribute to Ozone Destruction Within the Antarctic Vortex

Mechanism	Experimental Uncertainty	Fraction of Observed Ozone Loss	Comments
$\begin{array}{l} \text{ClO} + \text{ClO} + M \xrightarrow{k_1^{\text{III}}} \text{ClOOC}l + M \\ \text{ClOOC}l + h\nu \longrightarrow \text{Cl} + \text{ClOO} \\ \text{ClOO} + M \longrightarrow \text{Cl} + \text{O}_2 + M \\ 2 \times (\text{Cl} + \text{O}_3 \longrightarrow \text{ClO} + \text{O}_2) \\ \hline 2\text{O}_3 \longrightarrow 3\text{O}_2 \end{array}$ Rate-limiting step is taken to be the rate of dimer formation. However, if the product of that reaction does not photolyze to form ClOO + Cl, then reaction 2 will be rate limiting.	ClO concentration $\pm 25\%$ k_1^{III} $\pm 20\%$ Q, equivalent exposure time $\pm 10\%$ pressure, temperature $\pm 5\%$ rms uncertainty: $\pm 42\%$	Taken directly from observed O₃ decay over course of mission (August 23–September 25, 1987): $38 \pm 15\%$. Adjusted for amount of O₃ transported into vortex (estimated to be $\sim 20\%$ by Hartmann <i>et al.</i> [1989]): $32 \pm 13\%$.	We adopt the recent determination of k_1^{III} by Sander <i>et al.</i> [1989] which is more than a factor of 2 lower than the previous work by Hayman <i>et al.</i> [1986]. This drops the fractional contribution of mechanism I proportionally. Two critical issues remain: (1) What is the structure of the dimer formed by ClO self reaction? (2) What are the products of ClO dimer photolysis?
$\begin{array}{l} \text{ClO} + \text{BrO} \xrightarrow{k_2^{\text{II}}} \text{Cl} + \text{Br} + \text{O}_2 \\ \text{Cl} + \text{O}_3 \longrightarrow \text{ClO} + \text{O}_2 \\ \text{Br} + \text{O}_3 \longrightarrow \text{BrO} + \text{O}_2 \\ \hline 2\text{O}_3 \longrightarrow 3\text{O}_2 \end{array}$ Rate-limiting step is the bimolecular reaction of ClO and BrO to yield Cl and Br.	ClO concentration $\pm 25\%$ BrO concentration $\pm 31\%$ k_2^{II} $\pm 15\%$ Q, equivalent exposure time $\pm 10\%$ pressure, temperature $\pm 5\%$ rms uncertainty: $\pm 44\%$	Taken directly from observed O₃ decay over course of mission (August 23–September 25, 1987): $21 \pm 8\%$. Adjusted for amount of O₃ transported into vortex (estimated to be $\sim 20\%$ by Hartmann <i>et al.</i> [1989]): $15 \pm 6\%$.	Kinetics well-defined by recent work of Friedl and Sander [1989]; Sander and Friedl [1989]; Toohey and Anderson [1988]: $\begin{array}{l} \text{ClO} + \text{BrO} \xrightarrow{k_{2a}} \text{Br} + \text{OC}l\text{O} \\ \xrightarrow{k_{2b}} \text{Br} + \text{ClOO} \\ \xrightarrow{k_{2c}} \text{BrCl} + \text{O}_2 \end{array}$ $\begin{array}{l} k_{2a} = 1.6 \times 10^{-12} \exp(426/T) \\ k_{2b} = 2.9 \times 10^{-12} \exp(217/T) \\ k_{2c} = 5.8 \times 10^{-13} \exp(168/T) \end{array}$ For the rate limiting step we take $k_2^{\text{II}} = k_{2b} + k_{2c}$
$\begin{array}{l} \text{ClO} + \text{HO}_2 \xrightarrow{k_3^{\text{II}}} \text{HOCl} + \text{O}_2 \\ \text{HOCl} + h\nu \longrightarrow \text{OH} + \text{Cl} \\ \text{OH} + \text{O}_3 \longrightarrow \text{HO}_2 + \text{O}_2 \\ \text{Cl} + \text{O}_3 \longrightarrow \text{ClO} + \text{O}_2 \\ \hline 2\text{O}_3 \longrightarrow 3\text{O}_2 \end{array}$ Rate-limiting step is the bimolecular reaction of ClO and HO₂ to form HOCl.	ClO concentration $\pm 25\%$ HO₂ concentration unknown k_3^{II} $\pm 15\%$ Q, equivalent exposure time $\pm 10\%$ pressure, temperature $\pm 5\%$ rms uncertainty: unknown	Taken directly from observed O₃ decay over course of mission (August 23–September 25, 1987): 4%. Adjusted for amount of O₃ transported into vortex (estimated to be $\sim 20\%$ by Hartmann <i>et al.</i> [1989]): 3%.	Analysis crippled by absence of HO₂ measurements. Kinetics well-defined in literature. See DeMore <i>et al.</i> [1987].
$\begin{array}{l} \text{ClO} + \text{O} \xrightarrow{k_4^{\text{II}}} \text{Cl} + \text{O}_2 \\ \text{Cl} + \text{O}_3 \longrightarrow \text{ClO} + \text{O}_2 \\ \hline \text{O} + \text{O}_3 \longrightarrow 2\text{O}_2 \end{array}$ Rate limited by bimolecular reaction of ClO with O.	ClO concentration $\pm 25\%$ O(³P) concentration based on observed O₃ $\pm 15\%$ k_4^{II} $\pm 10\%$ Q, equivalent exposure time $\pm 10\%$ pressure, temperature $\pm 5\%$ rms uncertainty: $\pm 33\%$	Taken directly from observed O₃ decay over course of mission (August 23–September 25, 1987): $38 \pm 15\%$. Adjusted for amount of O₃ transported into vortex (estimated to be $\sim 20\%$ by Hartmann <i>et al.</i> [1989]): $32 \pm 13\%$.	Kinetics very well-defined. Analysis based on photochemical steady-state relationship between O(³P) and O₃: $\text{O}(\text{}^3\text{P}) = \frac{J_{\text{O}_3}[\text{O}_3]}{k^{\text{III}}[\text{O}_2][M]}$ using observed O₃.

TABLE 6. (continued)

Mechanism	Experimental Uncertainty	Fraction of Observed Ozone Loss	Comments
$\begin{array}{l} \text{ClO} + \text{O}_3 + M \xrightarrow{k_{5a}^{III}} \text{ClO} \cdot \text{O}_3 + M \\ \text{ClO} \cdot \text{O}_3 + h\nu \longrightarrow \text{Cl} + \text{O}_2 + \text{O}_2 \\ + M \longrightarrow \text{Cl} + \text{O}_2 + \text{O}_2 \\ \text{Cl} + \text{O}_3 \longrightarrow \text{ClO} + \text{O}_2 \\ \hline 2\text{O}_3 \longrightarrow 3\text{O}_2 \\ \text{and} \\ \text{ClO} + \text{O}_3 + M \longrightarrow \text{ClO} \cdot \text{O}_3 + M \\ \text{ClO} \cdot \text{O}_3 + \text{O}_3 \longrightarrow \text{ClO} + \text{O}_2 + \text{O}_2 + \text{O}_2 \\ \hline 2\text{O}_3 \longrightarrow 3\text{O}_2 \end{array}$	ClO concentration $\pm 25\%$ O ₃ concentration $\pm 5\%$ k_{5a}^{III} unknown Q , equivalent exposure time $\pm 10\%$ pressure, temperature $\pm 5\%$ rms uncertainty: unknown	This cycle can compare quantitatively with mechanism I if k_{5a}^{III} is 1×10^{-35} cm ⁶ s ⁻¹ or larger; see analysis in text. The reaction between ClO · O ₃ and O ₃ could be important at night as a source for ClO.	No laboratory data exist which could define the rate of ClO-O ₃ association to form ClO · O ₃ , the required termolecular rate corresponds to a reaction probability per collision of 10 ⁻⁶ . Data are also required to establish the photolysis products of step 2.
$\begin{array}{l} \text{ClO} + \text{O}_3 \xrightarrow{k_{5b}^{II}} \text{ClOO} + \text{O}_2 \\ \text{ClOO} + M \longrightarrow \text{Cl} + \text{O}_2 + M \\ \text{Cl} + \text{O}_3 \longrightarrow \text{ClO} + \text{O}_2 \\ \hline 2\text{O}_3 \longrightarrow 3\text{O}_2 \end{array}$	ClO concentration $\pm 25\%$ O ₃ concentration $\pm 5\%$ k_{5b}^{II} unknown Q , equivalent exposure time $\pm 10\%$ pressure, temperature $\pm 5\%$ rms uncertainty: unknown	Taken directly from observed O ₃ decay over course of mission (August 23–September 25, 1987): $21 \pm 8\%$. Adjusted for amount of O ₃ transported into vortex (estimated to be ~20% by Hartmann <i>et al.</i> [1989]): $15 \pm 6\%$.	Kinetics poorly defined, only available data indicates $k_5^{II} < 10^{-18}$ cm ³ s ⁻¹ at 298 K, this upper limit is very small for a radical-molecule reaction.
$\begin{array}{l} \text{ClO} + \text{ClO} + M \longrightarrow \text{ClOOC} + M \\ \text{ClOOC} + \text{O}_3 \xrightarrow{k_6^{II}} \text{ClO} + \text{ClOO} + \text{O}_2 \\ \text{ClOO} + M \longrightarrow \text{Cl} + \text{O}_2 + M \\ \text{Cl} + \text{O}_3 \longrightarrow \text{ClO} + \text{O}_2 \\ \hline 2\text{O}_3 \longrightarrow 3\text{O}_2 \end{array}$	ClO concentration $\pm 25\%$ O ₃ concentration $\pm 5\%$ k_6^{II} unknown Q , equivalent exposure time $\pm 10\%$ pressure, temperature $\pm 5\%$ rms uncertainty: unknown	Less than 1%. May be important at night, but cannot enhance rate of O ₃ destruction by ClO because mechanism I above has already assumed that every ClOOC formed leads to loss of 2 O ₃ molecules. Same conclusion if ClOOC + O ₃ → ClOO + O ₂ is replaced by ClOOC + ClO → ClOO + Cl ₂ O.	No laboratory data exist for the O ₃ reaction with the ClO dimer. The product channel for this reaction is also of critical importance.
$\begin{array}{l} \text{BrO} + \text{O}_3 \xrightarrow{k_7^{II}} \text{BrOO} + \text{O}_2 \\ \text{BrOO} + M \longrightarrow \text{Br} + \text{O}_2 + M \\ \text{Br} + \text{O}_3 \longrightarrow \text{BrO} + \text{O}_2 \\ \hline 2\text{O}_3 \longrightarrow 3\text{O}_2 \end{array}$	BrO concentration $\pm 31\%$ O ₃ concentration $\pm 5\%$ k_7^{II} upper limit Q , equivalent exposure time $\pm 10\%$ pressure, temperature $\pm 5\%$ rms uncertainty: unknown	Upper limit on bimolecular rate constant reported by Sander and Watson [1981] at 200 K $k_7^{II} \leq 3 \times 10^{-16}$, thus contribution < 1%.	Work of Sander and Watson [1981] confirmed earlier work of Clyne and Cruse [1970]. No evidence for reaction has been observed in laboratory experiments.
$\begin{array}{l} \text{BrO} + \text{ClO} \xrightarrow{k_8^{II}} \text{OC} + \text{Br} \\ \text{OC} + \text{ClO} + M \longrightarrow \text{ClOOC} + M \\ \text{ClOOC} + h\nu \longrightarrow \text{ClOO} + \text{ClO} \\ \text{ClOO} + M \longrightarrow \text{Cl} + \text{O}_2 + M \\ \text{Br} + \text{O}_3 \longrightarrow \text{BrO} + \text{O}_2 \\ \hline 2\text{O}_3 \longrightarrow 3\text{O}_2 \end{array}$	ClO concentration $\pm 25\%$ OC concentration upper limit k_8^{II} unknown Q , equivalent exposure time $\pm 10\%$ pressure, temperature $\pm 5\%$ rms uncertainty: unknown	In situ ClO observations combined with an upper limit on OC obtained by Solomon <i>et al.</i> [1987] requires a rate constant for k_8^{II} , which is $\sim 10^{11}$ cm ⁻³ s ⁻¹ . This is at least 2 orders of magnitude faster than predicted.	This mechanism is a very interesting example of a number of catalytic cycles which are rate limited by ClO + OC →. While they are potentially important, they place extreme demands on the rate of that reaction.

Rate limited by reaction 2.

The catalytic cycle, rate-limiting step, uncertainties associated with quantities involved in the rate-limiting step, the fraction of observed O₃ loss attributed to the particular mechanism, and comments on the current state of mechanism definition are shown.

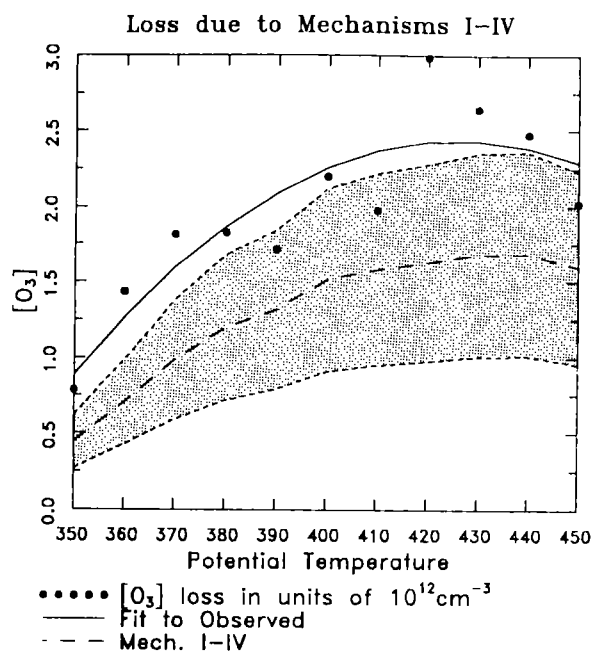


Fig. 26. Summary of the potential temperature (altitude) dependence of absolute ozone loss resulting from the sum of mechanism I ($\text{ClO} + \text{ClO} + M \rightarrow \text{ClOOC}l + M$), mechanism II ($\text{ClO} + \text{BrO} \rightarrow \text{Cl} + \text{Br} + \text{O}_2$), mechanism III ($\text{ClO} + \text{HO}_2 \rightarrow \text{HOCl} + \text{O}_2$), and mechanism IV ($\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2$) compared with observed loss rates of ozone. Experimental uncertainties are indicated by the shaded region.

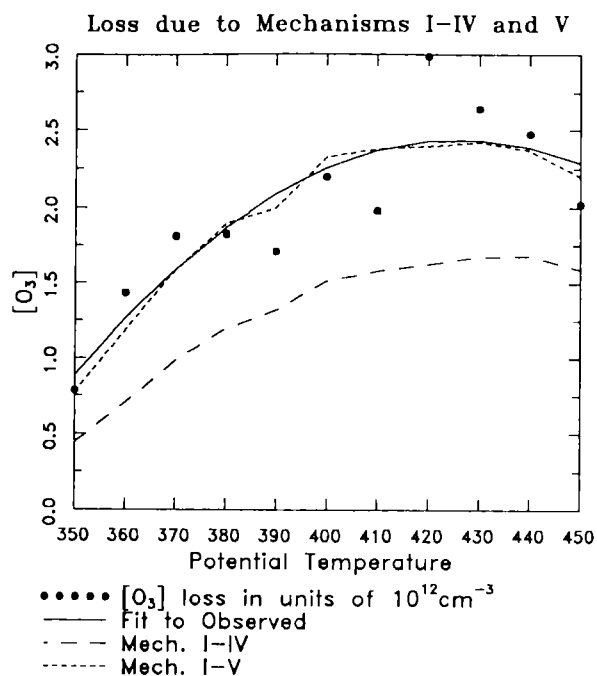


Fig. 28. Summary of absolute ozone destruction rates by the sum of mechanisms I-IV, and the sum of mechanisms I-V, that is, with the addition of $\text{ClO} + \text{O}_3 + M \rightarrow \text{ClO} \cdot \text{O}_3 + M$, assuming a third-order reaction rate constant of $k_{55}^{\text{III}} = 2 \times 10^{-35} \text{ cm}^6 \text{ s}^{-1}$.

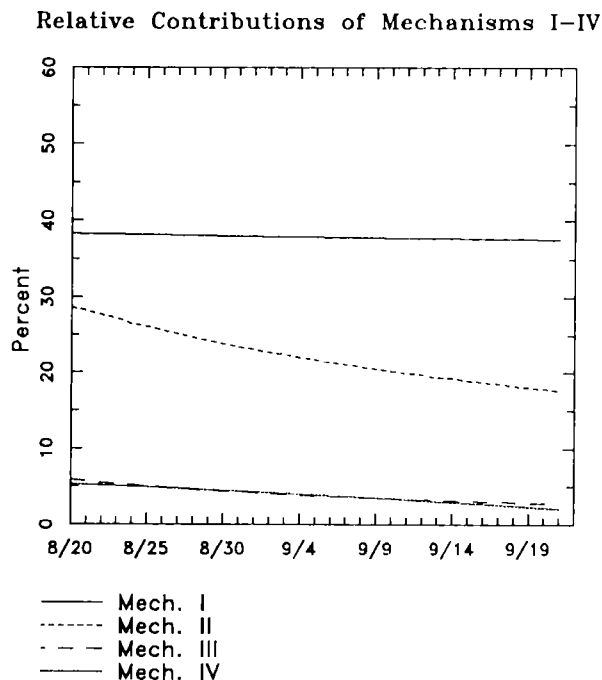


Fig. 27. Temporal evolution of the percentage of observed O_3 destruction accounted for by mechanism I ($\text{ClO} + \text{ClO} + M \rightarrow \text{ClOOC}l + M$), mechanism II ($\text{ClO} + \text{BrO} \rightarrow \text{Cl} + \text{Br} + \text{O}_2$), mechanism III ($\text{ClO} + \text{HO}_2 \rightarrow \text{HOCl} + \text{O}_2$), and mechanism IV ($\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2$) integrated over the full altitude interval covered by the ER-2 within the polar vortex.

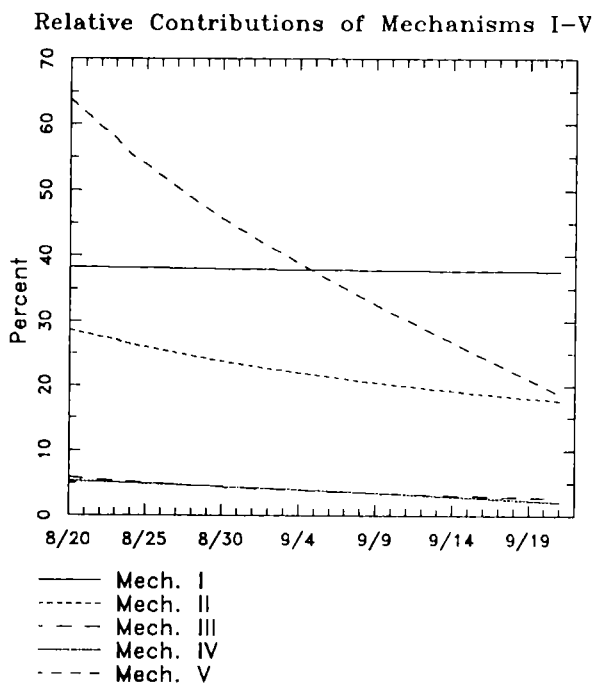


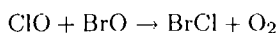
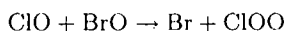
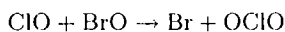
Fig. 29. Temporal development of each mechanism integrated over all altitudes accessible to the ER-2 within the vortex. Mechanism I refers to $\text{ClO} + \text{ClO} + M \rightarrow \text{ClOOC}l + M$, mechanism II refers to $\text{ClO} + \text{BrO} \rightarrow \text{Cl} + \text{Br} + \text{O}_2$, mechanism III refers to $\text{ClO} + \text{HO}_2 \rightarrow \text{HOCl} + \text{O}_2$, mechanism IV refers to $\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2$, and mechanism V refers to $\text{ClO} + \text{O}_3 + M \rightarrow \text{ClO} \cdot \text{O}_3 + M$.

CONCLUSIONS

We conclude the following:

1. Of the catalytic cycles currently offered in the literature, the ClO dimer mechanism suggested by *Molina and Molina* [1987], referred to herein as mechanism I, contributes the greatest fraction of observed O₃ destruction within the chemically perturbed region of the Antarctic polar vortex. In fact, using the only published value for k_1^{III} , the termolecular rate constant for ClO dimer formation reported by *Hayman et al.* [1986], mechanism I constitutes the entire observed loss rate of ozone between Θ surfaces of 370 and 450 K (14.3–18.2 km). However, recent, more direct laboratory measurements of k_1^{III} by *Sander et al.* [1989] in the appropriate temperature (195–250 K) and pressure regime (100–500 torr) reveal that the dimer formation rate is more than a factor of 2 slower than the *Hayman et al.* [1986] rate. We therefore conclude that approximately 40% of the observed ozone loss rate in the period from August 23 to September 22 from 13.5 to 18.3 km results from mechanism I. There still remains the need for critical laboratory studies associated with this mechanism, most notably a direct determination of the structure of ClOOCl and a measurement of the quantum yield of ClOO resulting from dimer photolysis.

2. The contribution to ozone destruction by the coupled ClO–BrO catalytic cycle proposed by *McElroy et al.* [1986], herein referred to as mechanism II, is more accurately defined given recent laboratory results regarding the forward rates of



by *Sander and Friedl* [1989]; *Friedl and Sander* [1989]; and *Toohey and Anderson* [1988]. Over the same time and spatial regime noted in mechanism I, we find that the contributions to ozone loss by mechanism II constitute 21% of the observed O₃ loss.

3. Contributions to O₃ destruction from the catalytic cycle rate limited by $\text{ClO} + \text{HO}_2 \rightarrow \text{HOCl} + \text{O}_2$ suggested by *Solomon et al.* [1986] constitutes 4% of the observed ozone loss assuming an HO₂ mixing ratio of 1 pptv. This HO₂ mixing ratio is perhaps a factor of 2 larger than most photochemical models now predict. It is essential that both the HO₂ and OH concentrations within the vortex be defined experimentally as soon as possible. We find that the classical *Molina and Rowland* [1974] catalytic cycle, $\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2$ (referred to herein as mechanism IV), which is the dominant mechanism in the middle and low latitude stratosphere, constitutes about 3% of the observed ozone loss within the CPR. There are other potentially important catalytic cycles involving halogen radicals which may well be important. As an example, we apply our analysis to a catalytic cycle rate limited by the termolecular process $\text{ClO} + \text{O}_3 + M \rightarrow \text{ClO} \cdot \text{O}_3 + M$. In the analysis we assume a third-order reaction rate constant of $2 \times 10^{-35} \text{ cm}^6 \text{ s}^{-1}$, demonstrating the profound effect such a slow reaction can have on the rate of ozone loss.

4. Analysis by *Hartmann* [1989] of tracer data obtained from the ER-2 simultaneously with the ClO, BrO, and O₃ results cited here indicates that ozone transport into the

vortex “increases the requirement for a photochemical sink by about $20 \pm 10\%$.” Thus our estimate is that the sum of mechanisms I–IV accounts for somewhat more than half of the required ozone destruction rate. Note that *Tuck* [1989] suggests a shorter residence time for air within the vortex region, describing the vortex region as an ozone processor.

Finally, a critical issue which must await further experiments within the chemically perturbed region of the Antarctic polar vortex is the question of how the limited penetration distance of the ER-2 into the vortex distorts our view of the vortex as a whole. It is clear from the ClO data used in the analyses presented here and displayed in detail by *Brune et al.* [1989a] that ClO increases both with altitude and with penetration distance (latitude) into the vortex. While compelling arguments can be given that the ClO and BrO concentrations observed in the flight series define accurately the halogen radical concentrations encountered by ozone during the course of its disappearance, it would nevertheless be of profound value to have a similar observational sequence at 80°S over the altitude region from 12 to 30 km extending through the end of October.

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were from perturbed air at the edge of the vortex during a major warming [Newman et al., 1989]. Thus, vortex air does remain modestly perturbed as it is transported to lower latitudes. Whether or not subsequent mixing of perturbed air to environs outside of the vortex can explain the enhancements of midlatitude ClO throughout the winter remains to be determined. However, it is interesting to note that temperatures were probably not adequate for formation of PSCs within the vortex until sometime in November [P. Newman, personal communication], and that the measurements in late December and thereafter show ClO mixing ratios greater than those observed on 881015. In addition, the horizontal variability of ClO is greatest on 890220 at the vortex edge, less pronounced further from the vortex on 890221, and minimal well outside the vortex on 881205 and 881229. This might be the signature of the mixing of highly perturbed air with midlatitude air. However, enhancements of ClO outside the vortex due to reactions on background aerosols might look similar [J. Rodriguez, personal communication]. An extensive analysis of data from other instruments onboard the ER-2 [A. Tuck, personal communication] should shed some light on this discussion.

Summary

Measurements obtained with the ER-2 aircraft at mid-latitudes in 1988 and 1989 demonstrate that ClO mixing ratios were enhanced in the lower stratosphere throughout the winter. At mixing ratios near 100 pptv, known catalytic cycles, rate limited by the reactions of ClO with BrO and oxygen atoms, can destroy ozone as rapidly as 0.5% per week in a region of the atmosphere where ozone is not replenished rapidly. This rate is about a factor of ten slower than the deduced loss rates within the vortex [Brune et al., 1990a] but greater than loss rates inferred from models which do not account for heterogeneous chemistry [Brune et al., 1988]. Persisting for three months over a geographic area extending from 40°N to 65°N, these underestimated loss processes could represent a significant decrease in global ozone, and may be responsible in part for the ozone losses reported by the Ozone Trends Panel [Watson et al., 1988].

It is tempting to associate the observed enhancements of ClO at midlatitudes with processes occurring within the polar vortex, however, here we have only a few pieces of the puzzle. Our understanding of the seasonality of "normal" midlatitude chlorine chemistry is severely restricted by the lack of continuous, simultaneous observations of ClO, ClONO₂, HCl, NO₂, HNO₃, and dynamical tracers. Thus, we cannot rule out the possibility that unidentified processes occurring outside the vortex, either rare or recurring events, could be responsible for the ClO enhancements. Therefore, until the future (and more frequent) deployment of new instruments, we are unable to resolve this critical issue.

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IN SITU MEASUREMENTS OF MIDLATITUDE ClO IN WINTER

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Abstract. In situ measurements of ClO in the winter lower stratosphere are presented for six flights of the NASA ER-2 aircraft from 38°N to 61°N. Enhanced abundances, increasing in severity with date, were observed below 20 km, where HCl and ClONO₂ dominate the inorganic chlorine budget. The greatest mixing ratios, over 150 pptv, were encountered on February 20 and 21, 1989, as the vortex experienced a major warming. Although the timing of these ClO enhancements and the evidence that vortex air can reach midlatitudes suggest that heterogeneous conversion of chlorine compounds within the vortex influences chemistry at midlatitudes, the enhancements observed early in the winter could have been caused by unknown chemistry occurring outside the vortex. In either case, photochemical loss of ozone due to catalytic reactions involving ClO at these mixing ratios may be responsible in part for the ozone decreases observed at high latitudes in the northern hemisphere.

Introduction

Measurements obtained during the Airborne Antarctic Ozone Experiment (AAOE) demonstrated that halogen-catalyzed reactions destroyed a significant fraction of ozone within the antarctic polar vortex during August and September of 1987 [Anderson et al., 1991]. Within experimental uncertainties, known photochemical reactions of ClO and BrO account for the observed 50% decrease in ozone over the altitude range 12 to 18 km, a region in the polar stratosphere where ozone concentrations are normally greatest. Measurements carried out during the Airborne Arctic Stratospheric Expedition (AASE) in 1989 indicated that a similar perturbation existed over the Arctic throughout the boreal winter. The air there was considered "primed" for the same photochemical ozone destruction as seen over Antarctica [Turco et al., 1990]. Only slight thermal and meteorological differences are thought to be responsible for the different ozone losses observed in the two regions; chemically, they are remarkably similar.

Although the AAOE and AASE missions have identified the mechanisms for ozone loss within the vortex, a number of questions about ozone loss outside the polar regions remain unanswered. The Ozone Trends Panel (OTP) has reported decreases in wintertime ozone between 1965 and 1986 in the northern hemisphere, most pronounced at high latitudes [Watson et al., 1988]. While

it is tempting to associate these losses with changes occurring inside the vortex, the mechanism remains unclear. Does air processed by polar stratospheric clouds (PSCs) within the vortex mix outward to midlatitudes where the sunlight necessary to destroy ozone is more abundant? Or does ozone-poor air from the vortex simply mix outward? Perhaps of more concern is the possibility that unknown chemistry outside the vortex is responsible for midlatitude ozone decreases. To examine the possible role of photochemistry we present measurements of ClO obtained on flights of the NASA ER-2 at midlatitudes in wintertime.

Experiment

The flights reported here were carried out in support of the more extensive AASE mission which is described elsewhere [Turco et al., 1990]. The flights of October 15 and December 5, 1988 (881015 and 881205 in yymmdd notation, respectively) were test flights with the full complement of instruments assembled for that mission, and 881229, 881231, 890220, and 890221 were transit flights, following great circle routes between Moffett Field, Wallops Island, VA, and Stavanger, Norway. For operating ease, the transit flights were flown at fairly constant altitude without vertical profiles at their midpoints.

ClO data were obtained with the Harvard instrument mounted under the left wing of the aircraft. Chlorine atoms, produced by the reaction of NO with ClO, were detected by resonance fluorescence at 118.9 nm with a 32-second response time. A detection limit of 4 pptv (degrading somewhat at lower altitudes) for a S/N≈1 is typically achieved. An offset of 0.7 pptv has been added to account for absorption of 118.9 nm radiation by NO, an effect that has been reproduced in the laboratory and validated on previous flights over Moffett Field at sunrise and sunset in February, 1988 [Brune et al., 1990b]. Potential temperature along the flight was determined from the free-stream pressure and temperature measured with the MMS instrument, as described by Chan et al. [1989].

Since the report of ClO data from the AASE mission [Brune et al., 1990a], extensive tests of the instrument over a wide range of temperatures and pressures have clarified factors which significantly alter previously published data. A comprehensive discussion of these changes is beyond the scope of this letter. Briefly, the pressure dependence of the chlorine atom fluorescence efficiency has now been fully characterized from 5 to 200 torr. The quenching of resonant emission (and hence a decrease in instrumental response) is more strongly pressure dependent than previously assumed. In addition, detailed laboratory tests of the conversion efficiency of ClO to chlorine atoms with pressure, temperature, and ozone mixing ratios that mimic the lower stratosphere provide an empirical correction for incomplete mixing of NO upstream of the detection region. Corroboration is provided by in-flight diagnostics executed during the AAOE and AASE

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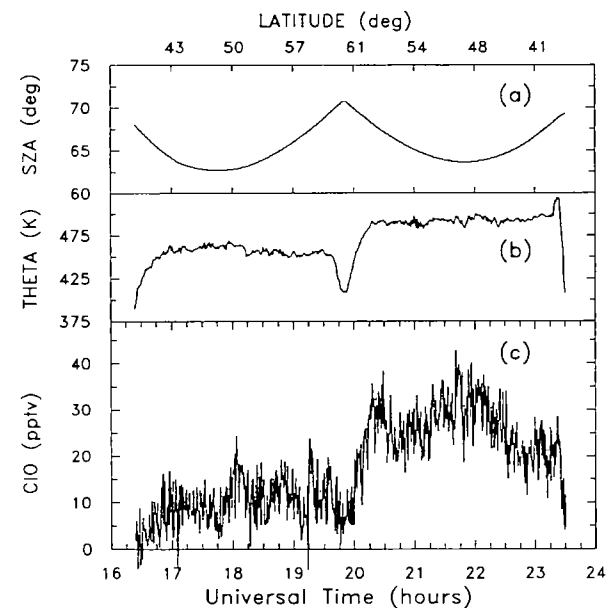


Fig. 1. ClO, potential temperature, and solar zenith angle for 881015, a flight track north from Moffett Field. Latitude is indicated hourly at top of figure.

missions. Combined changes increase the data from earlier reports by 10 to 20% at highest altitudes, and nearly double the values at low altitudes. These changes are incorporated into the data presented here, the AASE CD-ROM disk, a recent summary of the AAOE results [Anderson et al., 1991], and a paper by Douglass et al. [this issue]. A complete update of the remaining ClO data is in preparation.

Results and Discussion

The ClO mixing ratios, potential temperatures, solar zenith angles, and latitudes for five flights are summarized in Figures 1 through 5. Data from 881231 are summarized in Table 1, where ClO mixing ratios were averaged for one hour to reduce statistical errors. This flight occurred almost entirely in darkness, except for several minutes at sunrise as the airplane descended into Stavanger. From these figures it is important to note that the flights of 881015 and 881205 were provided vertical profiles at high latitudes, whereas for the remaining flights, profiles can only be obtained from limited data at the beginning or end of each flight. Thus, meaningful com-

TABLE 1: Results from 881231

Latitude (deg)	Theta (K)	SZA (deg)	ClO (pptv $\pm 1\sigma$)
40 – 45	451	155 – 159	0.8 ± 0.6
45 – 50	470	159 – 148	1.1 ± 0.6
50 – 54	473	148 – 133	1.2 ± 0.6
54 – 57	474	133 – 118	0.7 ± 0.6
57 – 59	468	117 – 103	1.1 ± 0.6
59 – 60	462	103 – 91	0.9 ± 0.6
60 – 59	464	91 – 85	5.2 ± 0.6

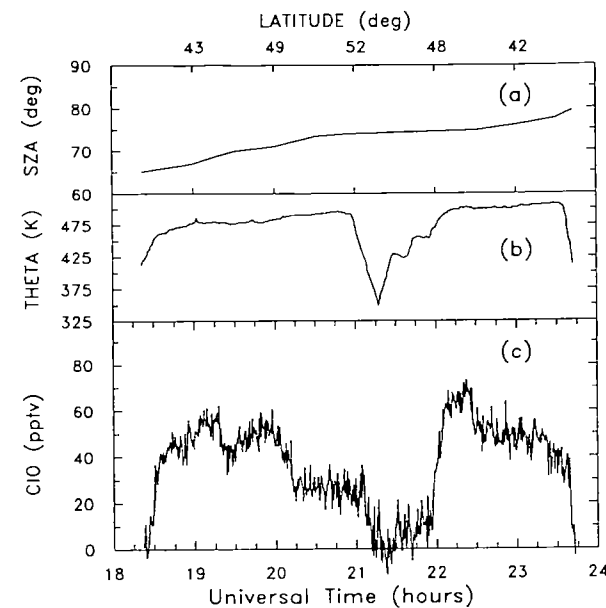


Fig. 2. As Figure 1 for 881205; north from Moffett Field.

parison of data below 450 K is difficult and this paper will focus on the results obtained at cruise altitudes.

We plot ClO mixing ratios versus potential temperature for the five daytime flights in Figure 6. Data from 881015 and 881205 were obtained during the vertical profiles, while data from 881229 and 890221 were binned with respect to potential temperature at 5 K intervals and averaged over the entire flight. For 890220, the range of individual measurements at 32-s intervals is represented by the shaded region. For comparison, we have included updated data from three other flights plotted as solid lines. 880219 shows representative midlatitude ClO measured during a descent over Moffett Field, 880213 shows enhanced ClO from a profile within the edge of the polar

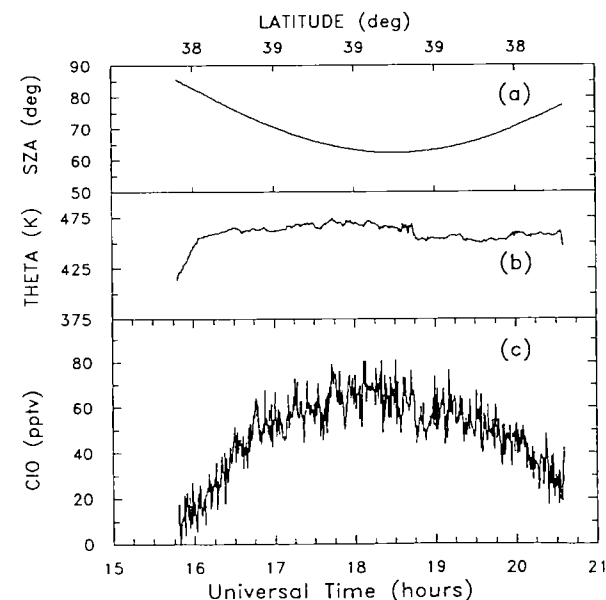


Fig. 3. As Figure 1 for 881229; from Moffett Field to Wallops Island, VA.

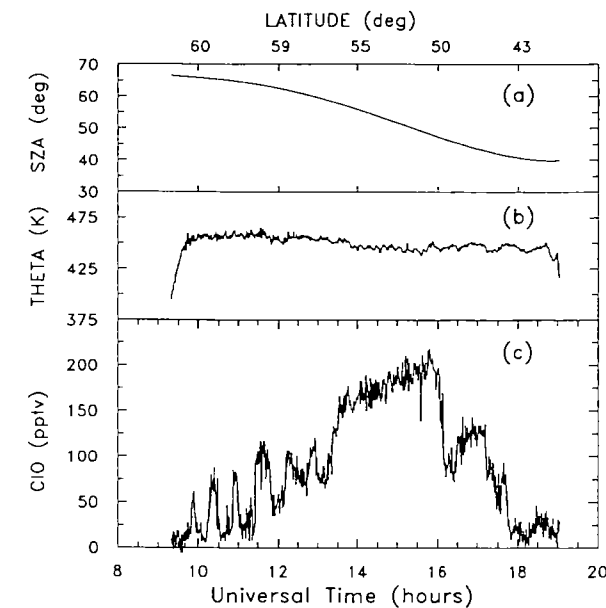


Fig. 4. As Figure 1 for 890220; from Stavanger, Norway, to Wallops Island.

jet at 61°N latitude, and 890210 was a profile obtained in the highly perturbed arctic polar vortex.

The steady increase over time of ClO mixing ratios at fixed potential temperatures is a striking feature of these data. The profile from 881015 is remarkably similar to the “normal” profile obtained on 880219. In contrast, mixing ratios measured on 881205, 881229, and 890221 increase sequentially, ultimately matching enhanced ClO mixing ratios measured on 880213. Higher-than-normal concentrations of ClO can result from several factors, most importantly higher concentrations of available chlorine (and, subsequently, chlorine nitrate), and lower concentrations of reactive odd nitrogen (particularly NO₂).

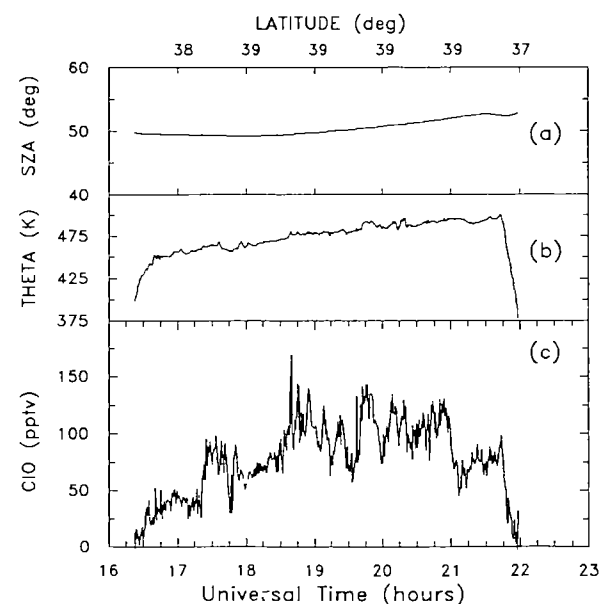


Fig. 5. As Figure 1 for 890221; from Wallops Island to Moffett Field.

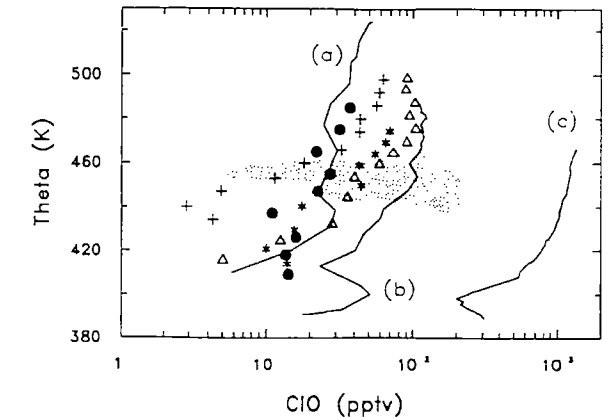


Fig. 6. Summary of ClO mixing ratios versus potential temperature for 881015 (•), 881205 (+), 881229 (*), 890220 (shaded region), 890221 (Δ). Solid lines represent profiles obtained (a) 880219, (b) 880213, and (c) 890210. See text for discussion.

Brune et al. [1988] concluded that the observations from 880213 were best explained by repartitioning within the NO_x family to reduce the available NO₂. A similar explanation could apply for the data obtained after October.

Without a detailed analysis of nitrogen oxides (not available during these flights) and tracers such as N₂O (not measured on every flight reported here), it is difficult to determine if the changes in ClO are due to events occurring outside the vortex or to mixing out of highly perturbed vortex air; it is also difficult to assess the contribution from diabatic descent of air. However, weather maps indicate that the flight tracks for 881205, 881229, and 881231 were not near the polar jet as was the case for 880213. Thus, whatever factors were responsible for the enhancements of ClO, the effects were observed well away from the vortex.

The remaining flights may provide some clues about the nature of the enhancements. Mixing ratios of ClO near 1 pptv measured on 881231 in airmasses that have not been exposed to sunlight in over twelve hours suggests that concentrations of NO₂ were considerably lower than normal. Otherwise, at these altitudes ClO should have dropped to below 0.1 pptv by termolecular formation of chlorine nitrate within several hours of sunset [Brune et al., 1990b]. That enhancements could result from events occurring in the vortex is evident in the flight of 890220, where horizontal variability of ClO from 10 pptv to more than 200 pptv occurs over the mostly level flight. Similar horizontal variability, although less pronounced and occurring further outside the vortex than on the previous day [Newman et al., 1989], is seen on 890221 over the continental United States. These transients of ClO, one in excess of 150 pptv, do not appear in the potential-temperature averaging of Figure 6. They do represent the largest concentrations of midlatitude ClO ever measured at these altitudes. Interestingly, the averaged ClO data over the entire flight look remarkably similar to the profile from 880213.

Comparison of the data from 890220 and 890221 to results from a three-dimensional model lead Douglass et al. [this issue] to conclude that these ClO enhancements