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Recent Research Results

and

Ongoing and Planned Activities Relevant to the World Plan of Action on the Ozone Layer

Contribution

by

The Chemical Manufacturers Association

Chemical Manufacturers Association Fluorocarbon Program: Recent and Ongoing Research Activities

MODELING

In 1980-81 a full chemical scheme was successfully incorporated into the 2-D model funded by CMA FPP. During 1981-82 considerable effort was spent on the further refinement and optimization of several key components of the 2-D code.

Incorporating detailed simulation of diurnal behavior of radical species permits comprehensive comparisons of model calculations with the concentrations of those observed species known to vary significantly during a diurnal cycle. This unique capability is useful and perhaps essential in the interpretation of certain phenomena. For example, some improvement between the calculated and observed column NO_2 can be achieved by use of a fully diurnal, instead of a diurnally averaged, 2-D model. This model, however, still cannot fully account for the observed NO_2 minimum occurring at high latitudes during winter months, leading to the belief that certain conversion processes for NO_2 are not included in the presently accepted chemical scheme.

Much of the major overestimation by models of the HNO_3 concentrations at around 35 km has been removed by incorporating the diurnal variations of OH and NO_2 into the model. Analysis of difficulties in reconciling the NO_2 observations at high latitudes during wintertime suggests that current theory may be missing a stratospheric sink for N_2O_5. N_2O_5 is, according to current models, the major form of NO_x under winter conditions. Several reactions that may be responsible for transforming wintertime NO_2 into HNO_3 have been identified. Future work will assess the impact of these added reactions on stratospheric chemistry.

A comprehensive comparison between 2-D theory (which includes the effects of latitudinal, seasonal, and diurnal insolation and a complete set of photochemical reactions with NASA (1982) recommended rates) and a wide range of atmospheric measurements at different latitudes, altitudes, and seasons shows agreement within a factor of 2, generally, but there are several notable discrepancies. For instance, current models tend to predict too much CFC-11 and CFC-12 (particularly CFC-11) around 30 km at mid-latitudes. This discrepancy may result from an underestimation of solar flux at 200-220 nm by current models. There is recent evidence that the O_2 cross sections in this spectral region (the Herzberg continuum) are lower than previously estimated. When these smaller cross sections are incorporated in the model, the principal results are: (1) improved agreement between measured and calculated CFC-11 and 12 profiles, (2) shorter lifetimes for CFC-11 and 12, and (3) smaller calculated steady state ozone depletion from the effect of CFCs alone (3.2% vs. the 4.5% calculated using 1982 chemistry and the old O_2 cross sections).

The aforesaid 2-D model has been used to identify certain shortcomings of the current 1-D models. For example, one error arises due to the inability of 1-D models to account for the latitudinal gradient of species concentration and photolysis rates in the lifetime calculation. Preliminary results indicate that transport in two dimensions leads to a shorter calculated residence time as compared with 1-D model calculations. This finding clearly illustrates that the calculated photolysis lifetime depends on the latitudinal variations of both gas concentrations and photolysis rates, as well as their correlations.

Incorporating the revised rate constants (NASA Panel, 1982) into the 1-D model leads to the principal findings that the calculated ClO at around 40 km is in improved agreement with observations and that the steady state ozone depletion due to CFCs alone is revised downward to 4.5% from the 6.1% calculated using 1981 rates. These ozone depletion numbers are based on releases of CFCs alone and do not reflect the effect of coupled perturbations due to anticipated increased emissions of CH_4, CO_2, N_2O, and NO_x.

The calculated extent of change in total column ozone by the year 2010 for selected scenarios is listed in the following table.

Scenario	Percentage Change Total Column Ozone by year 2010
CFC constant[a]	-1.5
CFC growth[b]	-1.8
CFC constant[a] + NO_x[c] + 0.2%-yr^{-1} N_2O + 0.55%-yr^{-1} CO_2 + 1.2%-yr^{-1} CH_4	+1.2
CFC growth[b] + NO_x[c] + 0.2%-yr^{-1} N_2O + 0.55% yr^{-1} CO_2 + 1.2%-yr^{-1} CH_4	+0.9

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[a] constant emission at 1980 levels

[b] 3%-yr^{-1} growth from 1980 to 2000 followed by constant emissions at the 2000 level

[c] increases based on U.S. Department of Transportation estimates

From these calculations it is apparent that even by the year 2010 there is little difference in the extent of ozone change between calculations for constant and for growth scenarios for CFCs. Use of a scenario that couples increasing CH_4, NO_x, N_2O, and CO_2 emissions with CFC emissions leads to a slight increase in the calculated amount of ozone in contrast to the small decrease calculated when only CFC emissions are included in the model. Time dependent calculations of stratospheric ozone profiles have also been made with the model incorporating coupled perturbations.

After it was suggested that the reaction of NaOH with HCl could be an important sink for stratospheric chlorine, the role of sodium in stratospheric chemistry was examined. The impact of sodium species on the stratospheric chlorine budget was found to be limited by the availability of sodium in the stratosphere, where the mixing ratio of total sodium is not expected to be larger than 0.1 ppbv. Recent revisions in the rates for the photolysis of NaCl and NaOH have led to renewed assessment of the importance of sodium and related chemistry. It has been found that the reactions $O(^3P)$ + NaO_2 and NaO + H_2O must be fast in order to explain the observed profiles for some sodium species. Modeling results suggest that sodium could have some importance to HO_x chemistry.

ATMOSPHERIC CHEMISTRY

The CMA FPP program to elucidate stratospheric chemistry centers on species and reactions likely to affect the interactions between chlorine containing species and ozone.

1) HO_x Reactions

The family of HO_x reactions continues to be a major source of uncertainty in stratospheric chemistry, principally because of the difficulty of producing and monitoring the HO_2 radical.

A flash photolysis resonance fluorescence technique has been used to measure the rate constant for the reaction

$$OH + H_2O_2 \text{ --------> } H_2O + HO_2$$

over the temperature range 250 - 370 ^oK. The rate equation is in good agreement with other recent studies, and this study has revealed problems in pre-1980 studies due to secondary reactions producing OH.

Steady state photolysis and isotope exchange experiments produced no evidence for adduct formation in the reaction

$$OH + HO_2 \text{ ---------> } H_2O + O_2$$

Further studies have been funded for 1983 to define better reaction rate values.

There are still conflicting reports on the pressure dependence of the crucial disproportionation reaction of HO_2. A new high intensity vacuum-UV flash photolysis apparatus with sufficient sensitivity to detect HO_2 will be used for further study of the effects of pressure and water vapor on the reaction rate. Another study, involving an improved, well-defined source of HO_2 radicals, indicates no pressure dependence over the range of 1 to 7 torr. These laser magnetic resonance studies continue in 1983, with emphasis on the reaction's temperature dependence. An LMR system for the direct observation of HO_2 will be used to investigate several reactions of this critical species.

2) NO_x Reactions

Although the kinetic data for this cycle are generally considered reliable, there is a significant discrepancy between certain atmospheric measurements and calculated concentrations for NO_x species. It is not clear whether the disagreement is due to measurement problems or incorrect assumptions about the chemistry of the NO_x cycle.

The LMR technique has been successfully applied for monitoring HO_2 in its reaction with NO. Attempts to define the rate equation for the reaction of NO with O_3 have led to the development of a new method for determining activation energies over small temperature intervals.

The reaction leading to the formation of peroxynitric acid has been studied during 1982, and this study will continue into 1983. Of particular interest are the low pressure parameters of the reaction and their temperature dependence. Other investigations of this reaction will also be undertaken during 1983 and will employ both LMR and resonance fluorescence techniques.

Discrepancies between the observed and calculated distributions of nitrogen oxides and nitric acid in the stratosphere have been difficult to explain. The techniques of resonance fluorescence and diode laser spectroscopy will be used to analyze the products of the reaction between OH and NO_2 in an attempt to resolve this problem.

The photochemistry and kinetics of reactions involving NO_3 are being studied. To date the absorption cross section for NO_3 has been measured in the 570 to 730 nm range, and preliminary kinetics studies have been carried out on a number of reactions. The generation of NO_3 from the reaction between OH and HNO_3 has been studied by several workers, but no firm agreement has been achieved on the pressure and temperature dependence of the process.

3) ClO_x Reactions

ClO_x reactions have received considerable attention from CMA-FPP-funded investigators. In contrast to the NO_x cycle, most of the important rate constants have been reliably measured, and, generally speaking, research work has divided into either fully defining temperature and pressure dependences or investigating areas of potentially new chemistry, e.g., sodium metal involvement.

Several notable contributions have been made to the understanding of ClO_x reactions, particularly those involving ClO. Preliminary measurements during 1982 on the ClO + OH reaction gave results in conflict with earlier measurements and could reflect a lack of knowledge on the product split between HO_2 + Cl and HCl + O_2. The question will be addressed in the program of work being funded for 1983. Another study indicates that $ClONO_2$ is formed by ClO + NO_2 + M at a rate consistent with the disappearance rate of ClO, implying that no isomers are formed. Other ongoing work has addressed the question of HOCl chemistry and the importance of ClO_3 in the chlorine cycle. Work on HOCl continues during 1983, but no further work on ClO_3 is planned, because alternative chemistry of O atoms can explain previous anomalous results.

4) Chemistry Workshop

Workshops on Stratospheric Chemistry, held in March of 1982, and January of 1983, brought together a number of internationally recognized scientists to discuss progress and future directions in this field. Reports on these workshops are available from CMA.

ATMOSPHERIC OBSERVATIONS

A major exercise begun in 1982 is the Balloon Intercomparison Campaign co-funded by NASA, CMA FPP, CEC, and other national bodies from Belgium, Canada, France, Italy, Japan, the United Kingdom, and the United States. The purpose of this campaign is to improve knowledge of the accuracy of individual experimental techniques by conducting measurements of the same trace species in the same air mass at the same time. Complementing the balloon observations were ground based measurements at the Kitt Peak National Observatory and at the Holloman Air Force Base and observations from an aircraft flown by the National Center for Atmospheric Research.

A second series of measurements, scheduled to take place in May, 1983, in conjunction with observations in support of the NASA Climate Program, will complete one of the most extensive and well characterized field measurement campaigns ever undertaken.

A continuation of the data reduction from the SIBEX balloon campaign was funded in 1982 to enable a more complete assignment of spectral lines. The conclusions are due for publication shortly.

Funding of field measurements by the CMA FPP in 1983 includes a flight of the newly developed reel up/reel down technique incorporating a new generation of instrumentation for in-situ detection of ClO and related species.

Microwave measurements from Mauna Kea have been successfully used for the determination of the ClO vertical profile and the diurnal variation of ClO, and for the detection of HO_2. The FPP continues to fund IR spectroscopy from mountain sites in the USA and Europe. Significant developments are anticipated from the continuing analysis of the historical solar spectral record at Kitt Peak Observatory. Some evidence for the presence of temporary reservoirs, so far undetected in the stratosphere, has been provided by balloon-borne IR spectrometers. In 1983, the CMA FPP is funding latitudinal surveys of trace species using ground-based IR spectroscopy.

Work continues on the intercomparison of conventional Umkehr measurements with IR and microwave techniques for the determination of ozone profiles. This research has assumed special importance in view of the problem of correcting Umkehr measurements for the effects of stratospheric aerosols.

The CMA FPP has funded some measurements in the troposphere, including the Atmospheric Lifetime Experiment (ALE) and investigations of possible sinks for CFCs (e.g., in heterogeneously assisted processes). See separate section on ALE.

Laboratory studies are essential for quantitative understanding of field measurements, and the CMA FPP has funded both the development of techniques and the accurate measurement of the temperature and pressure dependences of spectral features, e.g, tunable diode laser spectroscopy of the vibrational-rotational bands of HO_2. Of particular interest in 1983 will be a balloon flight of a copper vapor laser spectrometer for simultaneous measurement of a series of radical species in the HO_x cycle.

OZONE TREND ANALYSIS AND OZONE DATA

The CMA-FPP-funded groups at the University of Wisconsin and Princeton University have continued their studies on the analysis of stratospheric ozone data for evidence of ozone changes. Nimbus 4 satellite and Dobson ground-based ozone data have been extensively analyzed in terms of changes in total ozone (the amount in a column of air) and in ozone at different altitude levels (i.e., profile zone).

No evidence of an ozone depletion has been detected in total ozone from 36 ground stations over the period 1970-1980. The trend has been slightly positive (viz., less than 0.5% per decade), with trend detection thresholds in the range from ±1.0% to ±1.3%. (The detection threshold is that level above which a change both would be judged statistically significant at the 95% confidence level and could not be reasonably explained by natural variation alone.)

The present day ozone change estimate based on model calculations that incorporate effects due to CFCs, CO_2, CH_4, N_2O, and NO_x is +0.3%. When the uncertainties in the theoretical model predictions and ozone trend calculations are taken into consideration, there is no inconsistency between calculations and observations.

Analyses of Nimbus 4 satellite ozone data for the period 1970-77 suggest an instrument drift of -0.5%/year in total ozone and an apparent larger instrument drift in profile ozone in the region 38-48 km. A comparison of satellite and ground-based measurements supports the conclusion that the ground-based Dobson network provides globally representative trend estimates in the period of the 1970's for both total ozone and ozone vertical profiles. Satellite data analyses will continue when Nimbus 7 data tapes are available in a form suitable for trend analysis.

Both previously mentioned research groups found an effect in the early 1960's that correlated with the Russian nuclear tests in 1961 and 1962. A volcanic eruption (Agung) occurred at about the same time, making it difficult to interpret the cause of the 1962-63 perturbation in ozone. The inclusion of a calculated nuclear test effect and a solar cycle variation did not alter the conclusion that there was no change in total ozone during the 1970's.

Including meteorological data (e.g., temperature, pressure, and vorticity) in the ozone trend models leads to some reduction in the trend standard errors, but to little change in the actual trend values.

Both groups also detected no significant change in ozone in the period 1970-80 at the 40 km altitude level, based on analyses of Umkehr ozone data from 13 ground-based stations. However, preliminary analysis of data on atmospheric transmission of solar radiation measured at Mauna Loa, Hawaii, indicates that trend analysis of ozone concentrations in the region of 34-48 km may be affected by aerosol dust. A procedure that adequately accounts for these interfering effects of stratospheric aerosols is being sought.

A task group of NASA, NOAA, Atmospheric Environment Service (AES), and University of Wisconsin researchers has been set up by NASA to study the profile data from satellites Nimbus 4 and 7.

A joint project by the US EPA, NOAA, and the CMA FPP is underway at NOAA in Boulder to automate Umkehr ozone monitoring stations. The purpose is to have at least 6 strategically located Dobson stations automatically taking ozone profile measurements of very high quality on a regular basis (i.e., every day, weather permitting).

The CMA FPP has recently committed partial funding for a project to gather improved atmospheric transmission data to study aerosol effects on stratospheric ozone measurements. If NOAA can obtain the balance of the necessary funding, this project will enhance the quality of upper stratospheric ozone date as measured by ground-based stations.

ATMOSPHERIC LIFETIME EXPERIMENT (ALE)

The four original ALE monitoring stations have been in operation since 1978, and a fifth station located on the Oregon coast was added to the network in 1980. The ALE program monitors concentrations of CFCs 11 and 12, CCl_4, N_2O, and CH_3CCl_3. Preliminary results from three and one-half years of data indicate that any tropospheric sinks for CFC 11 or 12 must be very small in comparison to the photolytic processes in the stratosphere. Publication of results from the first three and one-half years of this program is in progress, and the full data base will be made available from the NASA library toward the end of 1983. CMA FPP funding of the stations' operations will cease in November, 1983, when sufficient data will have been collected for an accurate lifetime determination. The investigators are actively seeking supplemental funds to continue the global monitoring role of these stations.

PRODUCTION AND RELEASE OF CFC-11 and CFC-12

Production and sales data for CFC-11 and CFC-12 have been collected from CFC manufacturers on a worldwide basis and have been provided to the CCOL. These figures show that estimated world production of CFC-11 and 12 peaked in 1974, and that the 1981 production was 11% below the 1974 level. The world estimates include assumptions of continued increase in countries not directly reporting to the independent accountants used by the CMA FPP. Releases of CFCs are calculated from the production and sales figures and have also been provided. The basis for these calculations has been revised during the past year to reflect ongoing studies by the CMA FPP. A description of the revisions has also been included with the most recent calculations.