ATMOSPHERIC CHEMISTRY

Mesospheric Mysteries

Paul Crutzen

Although the atmospheric layer between altitudes of about 45 and 85 km (upper stratosphere and mesosphere) contains only about 1% of all atmospheric ozone, knowledge of the photochemical processes that determine its concentration is still of considerable interest. Absorption of solar ultraviolet radiation by ozone is the main source of energy in this layer and is thus responsible for driving its general circulation. Furthermore, the cloud-free upper stratosphere and mesosphere will be most affected by human activities: Temperature decreases of about 10°C are expected owing to a doubling of the atmospheric carbon dioxide content. In comparison, the estimated corresponding climate warming at Earth's surface varies from 1° to 3.5°C (*1*) for a doubling of the atmosphere CO_2 concentration, the uncertainty being mainly due to uncertain cloud feedbacks.

Although the chemistry of the upper stratosphere and mesosphere is quite simple, with chemical ozone loss reactions being dominated by HO_x catalysis, numerous studies (*2*, *3*) have failed to find the expected agreement between odd oxygen (that is, O and O_3) production and destruction. On page 1967 of this issue, Summers *et al.* (*4*) propose a solution to this discrepancy. Noting the close spatial coincidence in the measured maxima of OH radical concentrations by the MAHRSI spectrograph (*5*) and the recently revised water vapor mixing ratios by the HALOE instrument, these authors propose that a balance between odd oxygen loss and production can be achieved if major changes are introduced in some chemical reaction rate constants, leading to a diminished role of HO_x catalysis.

Between 45 and 70 km, the production of odd oxygen by the photodissociation of O_2 by a photon of frequency ν

$$O_2 + h\nu \rightarrow 2O \qquad (1)$$

where h is Planck's constant, is mainly balanced by catalytic destruction reactions between HO_x radicals and atomic oxygen atoms

$$O + OH \rightarrow H + O_2 \qquad (2)$$
$$O + HO_2 \rightarrow OH + O_2 \qquad (3)$$

Below 70 km, the HO_x radicals are primarily produced by the reaction

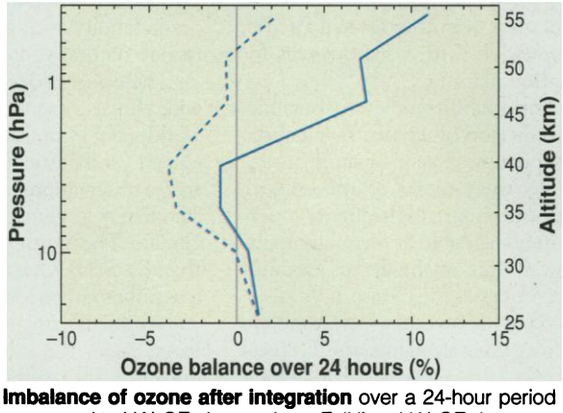
$$O(^1D) + H_2O \rightarrow 2OH \qquad (4)$$

with the $O(^1D)$ atoms coming from the photolysis of ozone at wavelengths shorter than about 325 nm. At higher altitudes, direct photolysis of H_2O, especially by absorption of Lyman α radiation

$$H_2O + h\nu \rightarrow H + OH \qquad (5)$$

becomes more important.

Because of rapid reactions from about 30 to 70 km, a close agreement should exist between odd oxygen production by reaction 1 and destruction by various catalytic cycles. Most studies in the past have indeed reached such a conclusion for the stratosphere up to about 45 km altitude in which other ozone destruction reactions, more complex than reactions 2 and 3, involving NO_x and ClO_x as additional catalysts, play major roles. Paradoxically, in the chemically simpler domain between 45 and 70 km, major deviations from balance have been noted in different studies reaching widely different conclusions. For instance, whereas Crutzen *et al.* (*3*) found a surplus in odd oxygen production, other studies (*2*) found a deficiency. The main reason for the different conclusions reached by these and other studies is probably the use of different observational data sets.



Imbalance of ozone after integration over a 24-hour period compared to HALOE observations. Full line: HALOE data, version 17 and no reaction pathways from ClO to HCl (*3*); dashed line: HALOE data, version 18 and a branching ratio of 5% for $ClO + OH \rightarrow HCl + O_2$ (*9*) and 3% for $ClO + HO_2 \rightarrow O_3$ (*10*).

Summers *et al.* (*4*) provide additional information that, if correct, implies the need for major revisions in our understanding of upper atmospheric chemistry. The authors note a remarkable spatial coincidence between maxima in measured OH concentrations and in the revised water vapor mixing ratios recently measured by the HALOE instrument in the 65- to 70-km region. Using the CRISTA spectrographic observations of ozone on the same space shuttle, the authors found that good correspondence between odd oxygen production and destruction rates can be obtained if some critical rate constants in the HO_x chemistry are revised in such a way that the impact of HO_x catalysis on ozone destruction is substantially reduced. This agreement can be achieved by a major downward revision in the rate constant for reaction 3 or an increase in the main HO_x destruction reaction

$$OH + HO_2 \rightarrow H_2O + O_2 \qquad (6)$$

The revised HALOE H_2O observations also relate to another currently debated issue. If the HALOE H_2O measurements in the 65- to 70-km region showing maximum volume mixing ratios of about 8 parts per million by volume (ppmv) are correct, then they violate the expected maximum value of about 6.5 ppmv for the H_2O mixing ratio, which follows from the oxidation of CH_4 to twice as much H_2O (*6*). The HALOE observations would give credence to the hypothesis of an extraterrestrial source of H_2O from small icy comets (*7*).

It is too early to judge with confidence the proposition by Summers *et al.* (*4*). Further modeling efforts will be of little use, except for model intercomparisons. To resolve the "ozone deficiency" and extraterrestrial H_2O source issues, major emphasis should be given to a reanalysis of the rate constants of reactions 2, 3, and 6 and to measurements and an intercomparison of measurements of H_2O and O_3 in the upper stratosphere and mesosphere.

Our own experience has shown how sensitive the odd-oxygen budget analysis is to the rate constants and the ozone and water vapor profiles. Whereas in an earlier paper (*3*) we found a surplus in odd oxygen production above 40 km, now using updated central values for HALOE observations and rate constants for the reactions $ClO + OH \rightarrow HCl + O_2$ (*8*) and $ClO + HO_2 \rightarrow HCl + O_3$ (*9*), we reach much better results up to about 55 km (see figure) (*10*). It is hoped that the recently completed flight of MAHRSI and CRISTA

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The author is at the Max Planck Institute for Chemistry, D-6500 Mainz, Germany. E-mail: air@mpch-mainz.mpg.de

with improved instrumentation will give more information on this potentially highly interesting, but also still highly uncertain, story.

References and Notes

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NOTA BENE: CLIMATE

Seasonal Climate Prediction

Weather prediction is generally restricted to a time scale of about 2 weeks, a limit imposed by the intrinsic variability of the atmosphere (*1*). However, because of the coupling between the atmosphere and the more slowly varying oceans, climate prediction over longer time scales of seasons, years or even decades may be possible (*2*). In recent years, climate researchers have made major advances in seasonal prediction, especially in the tropical Pacific. At a recent meeting of the World Climate Research Program (WCRP) (*3*) in Geneva, the successful prediction of the 1997–98 El Niño–Southern Oscillation (ENSO) event was hailed as a significant step in understanding and predicting climate. ENSO, a major interannual climate fluctuation in the tropical Pacific, is known to affect climate worldwide, with consequences for agriculture and energy-consumption planning.

A number of factors made the ENSO prediction possible. Because of their persistence, prediction of eastern tropical sea surface temperatures (SSTs) is possible a year or more in advance (*4*), allowing, in principle, the forecast of atmospheric conditions. However, such forecasts require high-quality observational data that are immediately available and equally high-quality prediction models based on state-of-the-art understanding of oceanic and atmospheric processes.

After the catastrophic 1982–83 ENSO event, which came as a surprise to researchers and the affected nations alike, the Tropical Oceans and Global Atmosphere (TOGA) program (*5*, *6*), which was already in the planning stages, got another boost. TOGA aimed to establish an observational and modeling infrastructure to allow seasonal prediction. At the time, observational coverage was inadequate, data were analyzed and transmitted too slowly and were not internally consistent, and the models were inappropriate. Within TOGA the existing observational network was expanded into an integrated observing system of moored buoys, drifting buoys, tide gauge systems, and volunteer observing ships. These data are delivered rapidly to prediction models and are used in conjunction with satellite data. The program aimed to improve understanding of the climate processes themselves and how they were represented in the models (*5*).

Coupled atmosphere-ocean general circulation models (CGCMs) were first applied to ENSO prediction in the mid-1980s (*7*). These early predictions were able to forecast a warming event in 1987 but predicted it to occur 3 months earlier than it did; moreover, spatial details of the event could not be forecast accurately. Today's models, such as the CGCM at COLA (Center for Ocean-Atmosphere Studies), have shown in "hindcast" simulations that not only could details of earlier ENSO events have been predicted for the tropical Pacific but so could their effect on extratropical atmospheric circulation, affecting, for example, the Indian Monsoon and North American climate (*8*). For 1997–98, the models predicted a warm ENSO event 6 months before the SSTs began to show the typical ENSO features (*9*). Such prediction allows affected countries such as Peru and Australia to take measures against floods and droughts and to adjust agricultural policy accordingly.

Since the TOGA program was officially brought to a close in 1994, the International Research Institute (IRI) (*10*) has been set up to continue and expand routine climate monitoring and accurate climate prediction in close collaboration between observation and modeling. Other programs such as CLIVAR (Study of Climate Predictability and Variability), another WCRP program (*11*), aim to take climate prediction further. Future projects aim to provide more detailed regional prediction and to assess decadal predictability of climate, as well as climate change and its attribution to natural variability versus human influences.

These are major challenges on the way to an operational worldwide climate observing and prediction system. Other regions of the world suffer from insufficient observation; for example, the Indian Ocean (and particularly the southern Indian Ocean) has a very sparse observational network, and major gaps exist in the understanding of its climate and variability and their influence on world climate. The North Atlantic Oscillation (*12*), which is less regular than ENSO but has a major influence on climate in mid-latitudes and as far south as Morocco, is also monitored much less intensively and is presently not understood or predicted nearly as well as ENSO. In addition, the interactions between these large-scale climate features are not well understood (*13*). Future developments depend crucially on an extended, sustained worldwide observation system that covers both terrestrial and oceanic areas.

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–Julia Uppenbrink