STRATOSPHERIC OZONE CONSERVATION BY ELECTRON ATTACHMENT 
TO CHLORINE ATOMS — THE NEGATIVE-ION CHEMISTRY

D. D.-M. Ho, K. T. Tsang†, A. Y. Wong,* and R. J. Siverson*

Lawrence Livermore National Laboratory
University of California
Livermore, California 94550 U.S.A.

†Science Applications International Corporation
McLean, Virginia 22103 U.S.A.

*Department of Physics
University of California
Los Angeles, California 90024 U.S.A.

ABSTRACT

Creating low-energy electrons in the stratosphere by photoelectric emission
has the beneficial effect of suppressing ozone destruction by Cl. This is because
Cl is converted to Cl\(^-\), which is less reactive. Critical to the success of this
scheme is the ability to attach most of the electrons to Cl\(^-\) and its hydrates
Cl\(^-\)(H\(_2\)O). We found that this attachment efficiency is rather high. This is
remarkable given the fact that the electron affinity of Cl\(^-\) is less than that of
NO\(_3\)\(^-\). Photodetachment of NO\(_3\)\(^-\) is the key factor that leads to this high
efficiency. Computer calculations show that ozone increases with electron
injection, and most of the electrons end up attaching to Cl\(^-\)(H\(_2\)O). We also
point out that 40 km, the altitude at which most of the ozone destruction
occurs, is also the optimum altitude for injecting photoelectric electrons.
I. INTRODUCTION

Chlorine atoms released from photodissociation of chlorofluorocarbons (CFCs) are recognized as the major anthropogenic cause of stratospheric ozone depletion.\textsuperscript{1–3} Recently, Wong et al.\textsuperscript{4} suggested to suppress this ozone depletion process by converting neutral chlorine atoms, with their strong electron affinity, to its negative ions Cl\textsuperscript{−}. This is because the reaction Cl\textsuperscript{−} + O\textsubscript{3} \rightarrow ClO\textsuperscript{−} + O\textsubscript{2} is not as energetically favorable as the reaction Cl + O\textsubscript{3} \rightarrow ClO + O\textsubscript{2}.

Once formed, Cl\textsuperscript{−} is not likely to lose its negative charge by collisions with background neutrals with thermal energy because the electron affinity of Cl\textsuperscript{−} is 3.7 eV. Creating Cl\textsuperscript{−} has the further advantage that Cl\textsuperscript{−} forms hydrates – Cl\textsuperscript{−}(H\textsubscript{2}O)\textsubscript{n}. Hydration is due to the charge-dipole electrostatic interaction. The Cl\textsuperscript{−}(H\textsubscript{2}O)\textsubscript{n} has relatively long lifetime and can therefore serve as a "reservoir" that traps the reactive chlorine atoms. This long lifetime arises for two reasons. First, the recombination rate of the Cl\textsuperscript{−}(H\textsubscript{2}O)\textsubscript{n} with positively charged hydrates is lower than that of the Cl\textsuperscript{−} with positively charged ions and this has been demonstrated in a recent experiment.\textsuperscript{5} Second, hydration also increases the electron affinity of Cl\textsuperscript{−} by the order of 1 eV per water molecule for small n (Ref. 6), and this makes it even harder for the electrons to escape from the hydrates. The long lifetime of this negatively charged hydrate also offers the possibility that they can be drifted upward and away from the stratosphere by naturally occurring vertical (downward-pointing) electric fields—the so called fair-weather electric field.\textsuperscript{4}

The electrons required to convert Cl to Cl\textsuperscript{−} can be obtained from radio-frequency breakdown of background neutral gases by high-power microwaves transmitted from ground-based antennas.\textsuperscript{4,7,8} Alternatively, low-energy electrons can be generated by photoelectric emission from high-flying balloons with surfaces coated with photoelectric material. The balloons can remain charge neutral by releasing tiny water droplets that carry positive charges.\textsuperscript{5}

A key factor that determines the feasibility of the scheme is the attachment efficiency of the electrons to Cl\textsuperscript{−} and Cl\textsuperscript{−}(H\textsubscript{2}O)\textsubscript{n} [the attachment efficiency is defined as the ratio of the final densities of Cl\textsuperscript{−} and Cl\textsuperscript{−}(H\textsubscript{2}O)\textsubscript{n} to the initial electron density]. Tsang et al.\textsuperscript{7} mention that this efficiency is rather high for the electrons generated by photoelectric emission. In this paper, we examine the chemical processes that lead to the high attachment efficiency in more detail.
We discuss only the case in which electrons are generated from photoelectric emission. Calculations using a zero-dimensional (i.e. no transport) chemistry code show that the attachment efficiency can be as high as 80% and that most of the electrons end up attached to Cl\(^{-}\) (H\(_2\)O). This result is remarkable given the fact that Cl\(^{-}\) has a lower electron affinity than that of NO\(_3^{-}\) (3.7 eV vs 4.0 eV). Calculations also show that the concentration of O\(_3\) increases as the chlorine atoms in Cl, ClO, and HCl are being converted to Cl\(^{-}\) and Cl\(^{-}\) (H\(_2\)O).

In Section II, the computer modelling of the chemistry and the method to obtain equilibrium densities are explained. The electron to negative ion cascade and recycling processes, the important reactions that affect the final Cl\(^{-}\) (H\(_2\)O) density, and the diurnal effect are discussed in Section III. The results are summarized in Section IV.

II. COMPUTER MODELLING OF STRATOSPHERIC CHEMISTRY

The zero-dimensional chemistry code used here was developed by Zinn and Sutherland of the Los Alamos National Laboratory.\(^9\) The code solves a set of coupled first-order nonlinear differential equations that describe the temporal evolution of the concentrations of various species that are specified in the input. The reaction rates contained in these equations are obtained from a library file that contains about 10\(^4\) reactions. These include ionization and recombination, attachment and detachment, charge transfer, association and dissociation, excitation and de-excitation, atomic interchange and rearrangement, and water cluster negative- and positive-ion kinetics. In the input, one specifies the initial density of the species, electron and neutral temperatures, column densities, and the solar zenith angle. The code used here does not have diurnal effect, i.e., the solar radiation is always present in the calculation unless one turns it off manually.

In our model calculation, we choose the altitude to be 40 km and the solar zenith angle to be 45°. This altitude is chosen mainly because the ozone destruction by chlorine is concentrated between 37 to 40 km outside the polar regions.\(^10\) It also turns out that this is about the optimum altitude for electron

\(^*\)The time limit for submitting this paper to the workshop proceedings prevented us from checking all the reaction rates used in the calculations to the desired level of precision. Therefore, the conclusions reported here are subject to change.
injection for two reasons. First, 40 km represents roughly the maximum altitude that can be reached by high-flying balloons. Second, as shown in the following section, photodetachment of NO$_3^-$ is critical for obtaining high electron attachment efficiency. However, the rate of NO$_3^-$ photodetachment decreases with altitude because solar radiation and thus the rate of generating photoelectric electrons also decreases. Hence, both the electron attachment efficiency and the number of electrons generated decreases as we go to lower altitudes.

Sixty-one species, as listed in Table I, are used in our computer calculation and approximately 850 reactions are involved. The majority of these reactions have only slight impact on the concentrations of the species of interest. The electron temperature and the background neutral temperatures are set at 1000K and 270K, respectively. To begin the computer simulation, we first attempt to obtain an equilibrium among all the 61 species. This equilibrium is defined as a change of 1% or less in the concentration of all the species (except for N$_2$O, CO, and CH$_3$O$_2$, which have less than 3% changes) after 10$^5$ seconds (~28 hr). Equilibrium up to this time is sufficient for our purpose because; first, as shown in the following section, initially injected electrons reach equilibrium with Cl$^-$, Cl$^-$ (H$_2$O), and NO$_3^-$ in about 10$^4$ sec; second, various atmospheric transport processes will probably change the chemical composition after 10$^5$ sec and furthermore, the code does not have a diurnal effect so the equilibrium densities change after the first twelve hours in any case.

We begin the process of finding an equilibrium condition, without electron injection, by inputting the number densities from tabulated values$^{11}$ of the species that are listed in Table I into the computer code and allowing the code to run its course. [For the case without electron injection, the densities of the negative ions always remain very small and essentially do not affect the equilibrium neutral densities. In the input, therefore, we just set the initial densities of negative ions to some arbitrary small numbers, e.g., O(10$^{-2}$ cm$^{-3}$).] We then re-run the code by changing the input densities to that given by the code at 10$^5$ sec. This process is repeated until no species density changes by more than 3% after 10$^5$ sec. Both NO$_3$ and N$_2$O$_3$ settle to values several orders of magnitude lower than their tabulated values, but the concentration of these species are inconsequential to the results of this study. Also note that there are no positive ions in the input. This is because we assume that all the positive
charges are carried by tiny water droplets. These positively charged droplets then form clusters by attracting neutral water molecules around them.

These positively charged clusters have low recombination rates with negatively charged hydrates.\(^5\) Furthermore, the densities of these clusters are small (By equating the forces of electrical repulsion within the water droplet to the surface tension force, it can be shown that a droplet with 10 µm radius can carry an electric charge of approximately \(10^{-12}\) C.\(^5\) This corresponds to an electron density of \(6 \times 10^6\) cm\(^{-3}\,), and thus their collision frequencies with negative ions are low. Consequently, we can ignore the positively charged water clusters in our input.

To confirm that the chemistry code correctly models the catalytic destruction cycle of ozone by chlorine atoms, the Cl and ClO concentrations in the equilibrium concentration are decreased by one order of magnitude while decreasing the HCl concentration by two orders of magnitude. This results in a substantial increase in ozone concentration, as shown in Fig. 1. Alternatively, the Cl and ClO concentrations are increased by one order of magnitude and this results in a decrease in ozone concentration as shown in Fig. 1. These results

---

Table I. Relevant atmospheric species contained in the chemistry code. The symbol "W" stands for \(\text{H}_2\text{O}\).

<table>
<thead>
<tr>
<th>(\text{N}_2)</th>
<th>(\text{O}_2)</th>
<th>(\text{O}_3)</th>
<th>(\text{CO}_2)</th>
<th>(\text{CO})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CH}_4)</td>
<td>(\text{CH}_3)</td>
<td>(\text{H}_2)</td>
<td>(\text{H}_2\text{O})</td>
<td>(\text{H}_2\text{O}_2)</td>
</tr>
<tr>
<td>(\text{H})</td>
<td>(\text{OH})</td>
<td>(\text{HO}_3)</td>
<td>(\text{N})</td>
<td>(\text{N}(2\text{D}))</td>
</tr>
<tr>
<td>(\text{N}_2,(\text{A}^3\Sigma_u^+))</td>
<td>(\text{NO})</td>
<td>(\text{N}_2\text{O})</td>
<td>(\text{NO}_2)</td>
<td>(\text{NO}_3)</td>
</tr>
<tr>
<td>(\text{N}_2\text{O}_5)</td>
<td>(\text{O})</td>
<td>(\text{O}(1\text{D}))</td>
<td>(\text{O}(1\text{S}))</td>
<td>(\text{O}_2,(\text{a}^1\Delta_g))</td>
</tr>
<tr>
<td>(\text{O}_2,(\text{b}^1\Sigma_g^+))</td>
<td>(\text{Cl})</td>
<td>(\text{Cl}_2)</td>
<td>(\text{ClO})</td>
<td>(\text{HCl})</td>
</tr>
<tr>
<td>(\text{HCl})</td>
<td>(\text{CH}_3\text{O}_2)</td>
<td>(\text{CH}_3\text{O})</td>
<td>(\text{CH}_2\text{O})</td>
<td>(\text{CHO})</td>
</tr>
<tr>
<td>(\text{ClONO}_2)</td>
<td>(\text{OH}^-)</td>
<td>(\text{O}^-)</td>
<td>(\text{O}_2^-)</td>
<td>(\text{O}_3^-)</td>
</tr>
<tr>
<td>(\text{O}_4^-)</td>
<td>(\text{CO}_3^-)</td>
<td>(\text{CO}_4^-)</td>
<td>(\text{NO}_2^-)</td>
<td>(\text{NO}_3^-)</td>
</tr>
<tr>
<td>(\text{Cl}^-)</td>
<td>(\text{ClO}^-)</td>
<td>(\text{WO}^-)</td>
<td>(\text{WO}_2^-)</td>
<td>(\text{W}_2\text{O}_2^-)</td>
</tr>
<tr>
<td>(\text{WO}_3^-)</td>
<td>(\text{W}_2\text{O}_3^-)</td>
<td>(\text{WCO}_3^-)</td>
<td>(\text{W}_2\text{CO}_3^-)</td>
<td>(\text{WCO}_4^-)</td>
</tr>
<tr>
<td>(\text{WNO}_2^-)</td>
<td>(\text{W}_2\text{NO}_2^-)</td>
<td>(\text{WNO}_3^-)</td>
<td>(\text{W}_2\text{NO}_3^-)</td>
<td>(\text{WCl}^-)</td>
</tr>
</tbody>
</table>

---
thus confirms that the code does model the catalytic ozone destruction cycle by chlorine.

To study the effect of electron injection, we re-run the code with initial electron density of $7.35 \times 10^6 \text{ cm}^{-3}$. The temporal evolution of Cl, ClO, and HCl are shown in Figs. 2, 3, and 4, respectively. They show that the concentrations of these species decrease with respect to the case without electron injection and reach an equilibrium at about $2 \times 10^4 \text{ sec}$. As a result of chlorine decrease, ozone increases by about 0.4% after 12 hr as shown in Fig. 1. This number increases to 0.6% if the initial electron density is raised by a factor of 4. We should be able to raise this number even further by continuous emitting electrons over a longer period of time. The reason that there is only a 0.4% increase in ozone in spite of a 30% reduction in Cl after 12 hr is because the rate coefficient for $\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$ at 270K is in the order of $10^{-11} \text{ cm}^3/\text{sec}$.

The reason that the Cl, ClO, and HCl densities decrease is because the chlorine in these species are being converted to Cl$^-$ and Cl$^-$ (H$_2$O). Figure 5 shows that 14% of the initial electrons are being attached to Cl$^-$ and Cl$^-$ (H$_2$O) at $10^3 \text{ sec}$ and increases to 87% at $10^4 \text{ sec}$. [Note that 84% of the electrons are attached to Cl$^-$ (H$_2$O) because Cl$^-$ (H$_2$O) has higher electron affinity than Cl$^-$.]
Figure 2. Cl concentration vs time.

Figure 3. ClO concentration vs time.
Thus, the process of attaching electrons to Cl$^{-}$ and Cl$^{-}$ (H$_2$O) is an efficient process. In the following section, we examine the electron cascade and recycling processes in more detail and make an attempt to explain why the attachment efficiency is so high.

III. ELECTRON TO NEGATIVE ION CASCADE AND RECYCLING PROCESSES

Most of the electrons first attach to O$^-$ and O$_2^-$ (with electron affinities of 1.43 eV and 0.45 eV, respectively). This is because atomic and molecular oxygen are the only major atmospheric constituents (N$_2$, O$_2$, CO$_2$) that have positive electron affinities (electron affinities for N$_2$ and CO$_2$ are -1.9 eV and -1.5 eV, respectively). The major reactions that lead to O$^-$ and O$_2^-$ formations are

\[
e + O_2 + M \rightarrow O_2^- + M , \\
O_2^- + O \rightarrow O^- + O_2 , \\
e + O_3 \rightarrow O^- + O_2 .
\]
Figure 5. Negative Ion Concentrations vs. Time.

Electrons can then go from $O^-$ and $O_2^-$ to $O_3^-$ and $O_4^-$ via three-body processes

$$O^- + O_2 + M \rightarrow O_3^- + M,$$

$$O_2^- + O_2 + M \rightarrow O_4^- + M.$$  \hfill (4)

Note that the electron affinities for $O_3^-$ and $O_4^-$ are 2.1 eV and 2.0 eV, respectively. Figure 5 shows that the densities of $O^-$ and $O_2^-$ peak at about $10^{-3}$ sec. (Not shown in this figure are $O_3^-$ and $O_4^-$. They are of much lower density than $O^-$ and $O_2^-$, but also peak at about the same time).
The negatively charged oxides (O\(^-\), O\(_3\)\(^-\), O\(_3\)\(^-\), and O\(_4\)\(^-\)) then react with CO\(_2\) and form negative carbonates through the reactions

\[
\begin{align*}
O^- + CO_2 + M & \rightarrow CO_3^- + M , \\
O_3^- + CO_2 & \rightarrow CO_3^- + O_2 , \\
O_4^- + CO_2 & \rightarrow CO_4^- + O_2 .
\end{align*}
\]

The electron affinities for CO\(_3^-\) and CO\(_4^-\) are 2.69 eV and 3.25 eV, respectively, and electrons thus cascade from species with lower electron affinities to those with higher electron affinities. Figure 5 shows that CO\(_4^-\) peaks at about 10\(^{-2}\) sec; CO\(_3^-\) has a flat peak between 10\(^{-1}\) and 1 sec. At about 10\(^{-2}\) sec, electron density has dropped almost four orders of magnitude from its initial value, and most of the electrons are attached to the negative carbonates. Note that CO\(_4^-\) can be destroyed by the process

\[
CO_4^- + O_3 \rightarrow O_3^- + O_2 + CO_2 ,
\]

and the O\(_3^-\) formed can in turn go through reaction (7) and form CO\(_3^-\).

The Cl\(^-\) can now be generated from the reactions that involve negative carbonates.

\[
\begin{align*}
CO_3^- + ClO & \rightarrow Cl^- + CO_2 + O_2 , \\
CO_4^- + HCl & \rightarrow Cl^- + HO_2 + CO_2 .
\end{align*}
\]

The electrons again cascade to species with high electron affinity. Alternatively, Cl\(^-\) can also be obtained from the two step reaction with NO\(_2^-\) serving as the intermediate species:

\[
\begin{align*}
\cases{CO_3^- + NO \rightarrow NO_2^- + CO_2 , \\
or \\
O^- + NO_2 \rightarrow NO_2^- + O_2 ,}
\]

\[
NO_2^- + HCl \rightarrow Cl^- + HNO_2 .
\]
Electron affinity for NO$_2^-$ is 2.27 eV. Negative chlorine ions then form hydrates from the reaction

$$\text{Cl}^- + (\text{H}_2\text{O})_n + \text{M} \rightarrow \text{Cl}^- (\text{H}_2\text{O})_n + \text{M}.$$ \hspace{1cm} (15)

We have used only $n = 1$ in our calculation.

Instead of attaching to Cl$^-$, some electrons end up attaching to NO$_3^-$ through the reactions

$$\text{CO}_3^- + \text{NO}_2 \rightarrow \text{NO}_3^- + \text{CO}_2,$$ \hspace{1cm} (16)

$$\text{NO}_2^- + \text{O}_3 \rightarrow \text{NO}_3^- + \text{O}_2.$$ \hspace{1cm} (17)

Electrons again cascade to species with higher electron affinity. This is the general trend of the electron cascade process. Reaction (12) violates this general rule, but this reaction is slower than reaction (16). Hydration of NO$_3^-$ then follows from the reaction

$$\text{NO}_3^- + \text{H}_2\text{O} + \text{M} \rightarrow \text{NO}_3^-(\text{H}_2\text{O}) + \text{M}.$$ \hspace{1cm} (18)

Our calculations included NO$_3^-$ (H$_2$O)$_n$ with $n$ up to 2.

Figure 5 shows that NO$_3^-$ peaks between 10 and $10^3$ sec. This is because lifetime of NO$_3^-$ is limited by photodetachment,

$$\text{NO}_3^- + \text{hv} \rightarrow \text{e} + \text{NO} + \text{O}_2.$$ \hspace{1cm} (19)

This process is critical in obtaining high electron attachment efficiency. Since NO$_3^-$ has a higher electron affinity than Cl$^-$, one might expect that most of the electrons will eventually attach to NO$_3^-$. Reaction (19) prevents this from happening because electrons released by this reaction can repeat the cascade process described above. In recycling the process, some electrons end up attaching to Cl$^-$ (H$_2$O) and some end up attaching to NO$_3^-$ (H$_2$O). However, the destruction rate of NO$_3^-$ (H$_2$O) due to collisional dissociation,

$$\text{NO}_3^- (\text{H}_2\text{O}) + \text{M} \rightarrow \text{NO}_3^- + \text{H}_2\text{O} + \text{M},$$ \hspace{1cm} (20)
is higher than that of Cl\textsuperscript{-} (H\textsubscript{2}O),

\[ \text{Cl}^- (\text{H}_2\text{O}) + M \rightarrow \text{Cl}^- + \text{H}_2\text{O} + M \quad \text{(21)} \]

Consequently Cl\textsuperscript{-} (H\textsubscript{2}O) has a longer lifetime than NO\textsubscript{3}\textsuperscript{-} (H\textsubscript{2}O). Therefore, after recycling through the cascade process a number of times, most of the electrons end up attaching to Cl\textsuperscript{-} (H\textsubscript{2}O). Also note that charge exchange from Cl\textsuperscript{-} to NO\textsubscript{3}\textsuperscript{-} is probably not very important because of the closeness of their electron affinities; furthermore, the densities of these two species never go above $7 \times 10^6$ cm\textsuperscript{-3} in our calculation.

We have checked the importance of reaction (19), which leads to the high attachment efficiency of electron to Cl\textsuperscript{-} (H\textsubscript{2}O), by two methods. We re-run the code both by turning reaction (19) off and also re-run the code by switching the radiation source off. Both cases show that all the electrons end up attaching to NO\textsubscript{3}\textsuperscript{-} because it has the highest electron affinity. This thus confirm our argument.

We have also studied the case for injecting electrons at 45 km. The electron attachment efficiency is now above 95\% at the end of the day (12 hr sunlight). This efficiency is higher than the 40 km case because of stronger solar radiation at higher altitude.

The photodissociation of Cl\textsuperscript{-} also has not been included in the calculation. This is because the Cl\textsuperscript{-} photodissociation cross section, calculated by D. A. Liberman using the time dependent local density approximation (TDLDA),\textsuperscript{12} has a peak at about 750Å while no radiation below 2000Å can reach 40 km and radiation above 3000Å is not energetically enough to cause photodissociation of Cl\textsuperscript{-}. The Cl\textsuperscript{-} photodissociation cross section between 2000Å to 3000Å is away from the peak and has low value. The photodissociation and photodetachment cross section of Cl\textsuperscript{-} and O\textsubscript{3}\textsuperscript{-} should be checked carefully in future studies.

The reactions described above are shown in Fig. 6. The hydrates of negative oxides and carbonates are not shown because their densities are low. In any case, the hydration rates of these species do not affect the qualitative nature of the electron cascade process. For example, if we turn off the dominant destruction reaction for O\textsubscript{2}\textsuperscript{-} (H\textsubscript{2}O),
Figure 6. Stratospheric negative ion chemical pathways.

\[ O_2^-(H_2O) + CO_2 \rightarrow CO_4^- + H_2O \] \hspace{1cm} (22)

the final Cl\(^-\) (H\(_2\)O) concentration decreases by only about 1%. If, instead, we turn off the dominant reaction for CO\(_3^-\) (H\(_2\)O),

\[ CO_3^-(H_2O) + M \rightarrow CO_3^- + H_2O + M \] \hspace{1cm} (23)

the final Cl\(^-\) (H\(_2\)O) concentration decreases by about 20%. These arguments show that uncertainties in the formation and destruction rates for O\(_2^-\) and CO\(_3^-\) hydrates do not have a strong effect on the electron attachment efficiency. The reason is that the short lifetimes of the negative oxides and carbonates do not provide sufficient time for hydration. Thus, it is almost certain that most electrons can pass the oxide and carbonate stages in the cascade process.

In contrast, if we turn off the dominant destruction reaction, Reaction (20), for NO\(_3^-\) (H\(_2\)O), most of the electrons eventually attach to NO\(_3^-\) and NO\(_3^-\) (H\(_2\)O) and greatly reduce the electron attachment efficiency to Cl\(^-\) (H\(_2\)O). It is
therefore important to conduct more precise measurements on the NO$_3^-$ (H$_2$O) formation and destruction rates.

It is also important to have precision measurements of the Cl$^-$ (H$_2$O)$_n$ formation and destruction rates. Note that in our present calculation, only Cl$^-$ (H$_2$O)$_n$ with $n = 1$ is included. With the inclusion of $n$ greater than one in our future studies, we expect that the total concentration of $\sum_n$ Cl (H$_2$O)$_n$ will increase.

The second dominant destruction reaction for Cl$^-$ (H$_2$O) is due to photodissociation,

$$\text{Cl}^-(\text{H}_2\text{O}) + \text{hv} \rightarrow \text{CO}^- + \text{H}_2\text{O}.$$ (24)

In the computer calculation discussed so far, this reaction has not been included. If we set the rate for this reaction equal to that of NO$_3^-$ (H$_2$O), then the final Cl$^-$ (H$_2$O) density drops by about 7%. If we set the rate equal to that of O$_2^-$ (H$_2$O), which is about one order of magnitude higher than that of NO$_3^-$ (H$_2$O), then the final Cl$^-$ (H$_2$O) concentration drops about by 35%. Thus, uncertainty in the Cl$^-$ (H$_2$O) photodissociation rate does not qualitatively change the result.

We also investigated the diurnal effect on the electron attachment efficiency. We use the values of the densities of the species listed on Table I, with initial electron injection, at the time when the code advanced the first 12 hr (the end of the day) as new initial values. We then turn off the radiation and let the code run its course. At the end of the second 12 hr (the end of the night), we notice that ozone decreases by about 0.7% at the end of the night from its peak value at the end of the day. This drop is because ozone is destroyed by the reaction

$$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 ,$$ (25)

and because the atomic-oxygen-producing processes such as

$$\text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O} ,$$ (26)

$$\text{O}_2 + \text{hv} \rightarrow \text{O} + \text{O} ,$$ (27)
are absent in the absence of solar radiation. Decrease in atomic oxygen thus reduces the rate of ozone production via

\[ O + O_2 + M \rightarrow O_3 + M \]  \hspace{1cm} (28)

Despite the decrease in ozone concentration, this concentration is still 0.4% higher than the corresponding case, without electron injection, at the end of the night. This demonstrates that electron injection raises the ozone concentration during both day and night.

But the reason that ozone density is still higher at night for the case with initial electron injection than without is probably that we start with a higher ozone density at the beginning of the night for the former case than for the later. Electrons, on the other hand, play a much smaller role in suppressing ozone destruction during the night than during the day. The reason is that the reactions

\[ \text{Cl}^- + \text{HNO}_3 \rightarrow \text{NO}_3^- + \text{HCl} \]  \hspace{1cm} (29)

and

\[ \text{Cl}^-(\text{H}_2\text{O}) + \text{HNO}_3 \rightarrow \text{NO}_3^-(\text{H}_2\text{O}) + \text{HCl} \]  \hspace{1cm} (30)

destroy most Cl\(^-\) and Cl\(^-\) (H\(_2\)O) during the night. Thus, in the absence of solar radiation, electrons migrate to the species with highest electron affinity.

Finally, note that the electron affinity of HSO\(_4^-\) is 4.5 eV, which is higher than that of any of the species mentioned here. However, the concentration of HSO\(_4^-\) is probably too low at 40 km to cause any significant effect on the result shown.

IV. SUMMARY

Zero-dimensional modelling of stratospheric chemistry shows that converting Cl to Cl\(^-\) and Cl\(^-\) (H\(_2\)O) by injecting low-energy electrons has the beneficial effect of suppressing ozone destruction. With an initial electron density of \(7.35 \times 10^6\) cm\(^{-3}\), ozone density increases by about 0.4% at the end of a
12 hr period. Critical to the success of suppressing ozone destruction is the ability to achieve high electron attachment efficiency to Cl\(^-\) and Cl\(^-\) (H\(_2\)O). Calculations show that this efficiency can be as high as 80% at 40 km with the presence of solar radiation and that most of the electrons end up attaching to Cl\(^-\) (H\(_2\)O) because it has a higher electron affinity than Cl\(^-\). This result is remarkable given the fact that Cl\(^-\) has lower electron affinity than of NO\(_3\)^-. Photodetachment of NO\(_3\)^- by solar radiation appears to play a critical role in achieving this high efficiency. The formation and destruction rates of Cl\(^-\) (H\(_2\)O) and NO\(_3\)^- (H\(_2\)O) have important effects on the final Cl\(^-\) (H\(_2\)O) density, and hence these rates as well as the photodissociation cross sections of both Cl\(^-\) and NO\(_3\)^- should be measured more precisely. In contrast, the formation and destruction rates of the hydrates of negative oxides and carbonates play only a minor role in affecting the final Cl\(^-\) (H\(_2\)O) density.

ACKNOWLEDGMENTS

We thank S. T. Brandon, P. S. Connell, D. A. Liberman, D. Y.-K. Lo, T. Miller, P. W. Murphy, and S. S. Prasad for discussion and help. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract No. W-405-Eng-48.

REFERENCES

5. A. Y. Wong, "Ion Dynamics and Ozone," this proceeding.


END

DATE FILMED

12/11/90