Ozone Destruction by Chlorine: The Impracticality of Mitigation Through Ion Chemistry

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The feasibility of using negative ion chemistry to mitigate stratospheric ozone depletion by chlorine-containing radicals, as proposed recently, is addressed here. Previous in situ measurements of the negative ion composition of the stratosphere show that chlorine-containing ions represent only a small fraction of total ions. New measurements of the negative ion temporal evolution in the stratosphere show that the fractional abundance of chlorine-containing ions is never greater than 1 percent at any time in the ion evolution. On the basis of these and other arguments, using negative ion chemistry to mitigate ozone depletion by chlorine-containing compounds is not feasible.

In the last several years, Wong and colleagues (*1–4*) have proposed a scheme for alleviating ozone (O_3) destruction that is attributable to Cl-containing compounds. The method involves introducing electrons into the stratosphere and allowing them to evolve into negative ions containing Cl, mainly as Cl^- and its hydrates. This process would inactivate the Cl and ClO radicals and reduce the extent of O_3 destruction attributable to the catalytic cycle involving these Cl-containing radicals. Proposals have been made either to produce the electrons continuously and bind the Cl in a steady-state fashion or to collect the Cl^- ions and thereby remove the Cl from the atmosphere. Recently, this scheme has received considerable attention (*5, 6*).

Here, we point out several serious flaws in this proposed method to alleviate stratospheric O_3 destruction by Cl-containing species through negative ion chemistry. These flaws are sufficiently serious that the proposed method does not appear feasible. Our main arguments are based on previously published data on the ion chemistry and composition of the atmosphere as well as on new in situ measurements of the chemical evolution of negative ions in the stratosphere. Our approach was to use these data to show that only small amounts of Cl-containing negative ions are formed at any stage of the ion evolution and at any altitude in the stratosphere, contrary to claims that 50 to 90% of the negative ionization can form Cl^- (*3*). We discuss some of the possible errors in the model used to support the claims that large fractions of the negative ionization end up as Cl^- and its hydrates. Finally, several other arguments concerning the impracticability of the scheme are given.

The contention that it is possible to convert large amounts of atmospheric Cl-containing neutral species into Cl-containing negative ions contradicts reported data on in situ negative ion composition measurements in the stratosphere. The ion chemistry of the lower atmosphere has been reviewed thoroughly (*7–11*), and only those aspects related to the issue in question will be discussed in detail here. Arnold and co-workers (*12, 13*) have published data that show that there are essentially no negative ions containing Cl over the altitude range from 15 to 40.8 km. Above 30 km, negative ions containing Cl^- represent less than 1% of all ambient negative ions. A small fraction of ions have HCl ligands (*12*); however, this small amount does not decrease the amount of active Cl because HCl is already an inactive form of chlorine—that is, a reservoir species. The only published indication of negative ions containing Cl at a level >1% occurs in the data of Arijs *et al.* (*14*), which use measurements from 45 km. However, these researchers question their own data as to the identity of the ions, and the concentrations measured are such that Cl-containing ions are still in the minority. In any case, 45 km is well above the O_3 layer and is an altitude where tying up Cl as negative ions could have at most a small effect on the total O_3 column. It would also be impractical to collect Cl-containing negative ions at this height because (i) only a small fraction of the total Cl is at this altitude due to the low atmospheric density and (ii) only very large balloons (10^6 m^3) with restricted payloads can reach this altitude.

The in situ data clearly show that the terminal ions do not contain large amounts of Cl. In the stratosphere, terminal ions have lifetimes on the order of 100 to 1000 s (*15*). This is in stark contrast to the predictions by Tsang *et al.* (*3*) that state that between 50 and 90% of all ionization ends up as Cl^- at reaction times greater than about 10 to 100 s. Possible reasons for this disagreement are discussed below.

More recently, Wong *et al.* (*1*) proposed that one may collect Cl^- ions on a time scale after ion creation that is less than the time required to transfer charges into the more stable species. This proposal assumes either that Cl-containing ions are important sometime in the ion evolution or that a mass filter must be used, rendering the process very inefficient. They hypothesize this method of reducing O_3 destruction by Cl radicals even though the method is in conflict with their own model results, which do not show Cl-containing ions to be important until near the end of the ion evolution.

We report here data on the evolution of negative ions as a function of time measured in situ at 33 km. The data were obtained with a balloon-borne mass spectrometer (of the Max Planck Institut für Kernphysik, Heidelberg) at 33 km attached to a flow tube equipped with a discharge ion source at one end and a variable-speed blower at the other. Reaction time was varied by changing the blower speed. An instrument similar to this has been described in detail elsewhere (*16*). The main difference in our apparatus was in the use of a blower to control the velocity in the flow tube.

The fractional abundance of negative ions as a function of time after ion creation as measured on the balloon platform at an altitude of 33 km is shown in Fig. 1. We measured the ion residence time by pulsing the ion source and measuring the arrival time of the pulse at the ion sampling plate. For simplicity, ions were grouped into several classes, including one that contained all possible Cl-containing ions. The Cl-containing ions include Cl^-, $Cl^-(H_2O)$, and $Cl^-(H_2O)_2$. At all times from 18 ms to almost 0.3 s, Cl-containing ions represented no more than 0.5% of all ions. The largest abundance was observed at the shortest times, and the data showed that Cl^- and its hydrates reacted away over the course of tens of milliseconds. Extrapolating to zero time on this semilogarithmic plot indicates that Cl^- will never be present in >1% of all ions. High-resolution data taken at 18 ms show that roughly half of the ions at that time have CO_3^- cores. Eventually, NO_3^- core ions become by far the dominant species. In any case, Cl-containing ions are formed in very small numbers. Ambient ion spectra were recorded on the same flight and also show no Cl-containing ions.

The in situ data show that it is not possible to form large amounts of Cl-containing negative ions in the stratosphere,

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either under steady-state conditions or early in the reaction sequence. Essentially all of the ambient negative ions have either NO_3^- or HSO_4^- cores; the latter are important only at altitudes >30 km and are derived from the former ions by reactions with H_2SO_4 (*17*). Thus, essentially all negative ions in the stratosphere either have NO_3^- cores or are formed from them. NO_3^- core ions are formed from virtually all of the nitrogen oxides and their acids reacting with ions produced earlier in the reaction scheme, mainly CO_3^- (*8, 10*). Our data show that CO_3^-, formed from CO_2 and O_n^- ions ($n = 1$ to 5), was produced very rapidly.

Except for causing a faster ion-ion recombination rate and therefore a shorter lifetime of the ions, increasing the amount of ionization does little to change the ion chemistry until essentially all of the nitrogen oxides are tied up in the form of ions. Therefore, only at a point where the ionization density approaches the concentration of all of the nitrogen oxides do Cl-containing ions have a chance to be important in the reaction scheme. The ionization densities required to tie up the nitrogen oxides as ions are on the order of 10^9 ions cm^{-3}. This density is very large and is many orders of magnitude greater than that found in the natural ionosphere. One consequence of this large ion density would be very short ion-ion recombination lifetimes (~0.1 s), and ion production rates of 10^{10} ions cm^{-3} s^{-1} would be required to sustain this level of ionization. This is an incredibly high density to sustain over any sort of global scale, considering that it requires at least 15 eV to produce one ion pair.

On the basis of a zero-dimensional computer model, Tsang *et al.* (*3*) and Ho *et al.* (*4*) have predicted that Cl^- and its hydrates will comprise 50 to 90% of all ions at long times ($t > 10$ to 100 s). Our ambient data show that this prediction cannot be correct at any stage in the ion temporal evolution. At an altitude of 45 km, the model predicts that the Cl^- core ion concentration increases because NO_3^- photodetaches rapidly and Cl^- does not. The model does not predict high concentrations of Cl^- at night or at lower altitudes where the O_3 concentration is high. The assumption that NO_3^- photodetaches rapidly and Cl^- does not is in error, at least for 266-nm light. At that wavelength, Cl^- photodetaches at a rate at least 3 and probably 10 times faster than does NO_3^- (*18*). In fact, photodetachment of NO_3^- was almost missed in these experiments because of the low signal levels. The energy threshold for photodetachment of Cl^- is also lower because of its lower detachment energy (*19*), and it is reasonable to assume that the Cl^- photodetachment cross section is greater than that for NO_3^- over the entire wavelength regime pertinent to the atmosphere. The atmospheric data on ion composition discussed above support this assumption. The model (*3, 4*) predicts that Cl^- core ions are the most abundant ions at evolution times on the order of 10 to 100 s and longer and therefore predicts that Cl^- core ions are the terminal ions in the stratosphere. This result contradicts the published data on the ambient ion concentration referred to above.

Ho and co-workers (*3, 4*) also state that "charge exchange from Cl^- to NO_3^- is probably not very important because of the closeness of their electron affinities." The term "charge exchange" is used there to mean any process that changes Cl^- to NO_3^-. In the same way, the term "electron attachment to Cl" is used to mean any process that forms Cl^-—that is, not only direct electron attachment to Cl, which would be exceedingly inefficient. There are actually a number of processes that can convert Cl^- to NO_3^-; these include the reactions of Cl^- with $ClONO_2$ (*20*), HNO_3 (*21*), N_2O_5 (*22*), and probably NO_3 (*23*). These processes become more important with decreasing altitude because of the higher concentrations of the molecules involved. Another flaw in this model is not including data for H_2SO_4, which is known to be important in the upper stratosphere (*12, 13*). Correcting these deficiencies may be sufficient to alter the output so that this model predicts the observed results.

Besides these scientific problems, there are also practical problems with the scheme proposed by Wong and colleagues (*1–4*) to alleviate O_3 depletion through negative ion chemistry that seem very difficult to overcome. It is beyond the scope of this report to explore these in detail, but we will discuss some of the more obvious ones. To produce a free electron in the stratosphere, an ion pair must be formed. In the atmosphere, this process requires at least 15 eV per electron because the corresponding positive ions would be mainly N_2^+ (*19*). A more realistic energy requirement is on the order of 35 eV per ion pair (*24*). One version of the scheme would include sheets of metals of low work function (that is, that require little energy to expel electrons) to generate the negative ions. This still requires production of positive ions to prevent charging of the sheets. Any reduction in the amount of energy needed to form a negative ion will scale directly in the following calculations. In order to deplete the Cl population, one must tie up or collect a large amount of the Cl-containing molecules. There are roughly 4 × 10^{34} Cl-containing molecules in the stratosphere alone and roughly seven times that amount in the entire atmosphere. This estimate is based on a total Cl mixing ratio of 2.5 parts per billion by volume. Assuming that the ionization process takes 35 eV per ion pair and that 1% of the ions end up containing Cl, removing the Cl-containing molecules in the stratosphere alone requires 2.2 × 10^{19} J. This energy translates into 700,000 MW during a 1-year period. [For comparison, the peak electric power consumption in the continental United States in December 1988 was 650,000 MW (*25*).] This power must be supplied by either an airplane or a balloon payload.

Furthermore, more than just the strato-

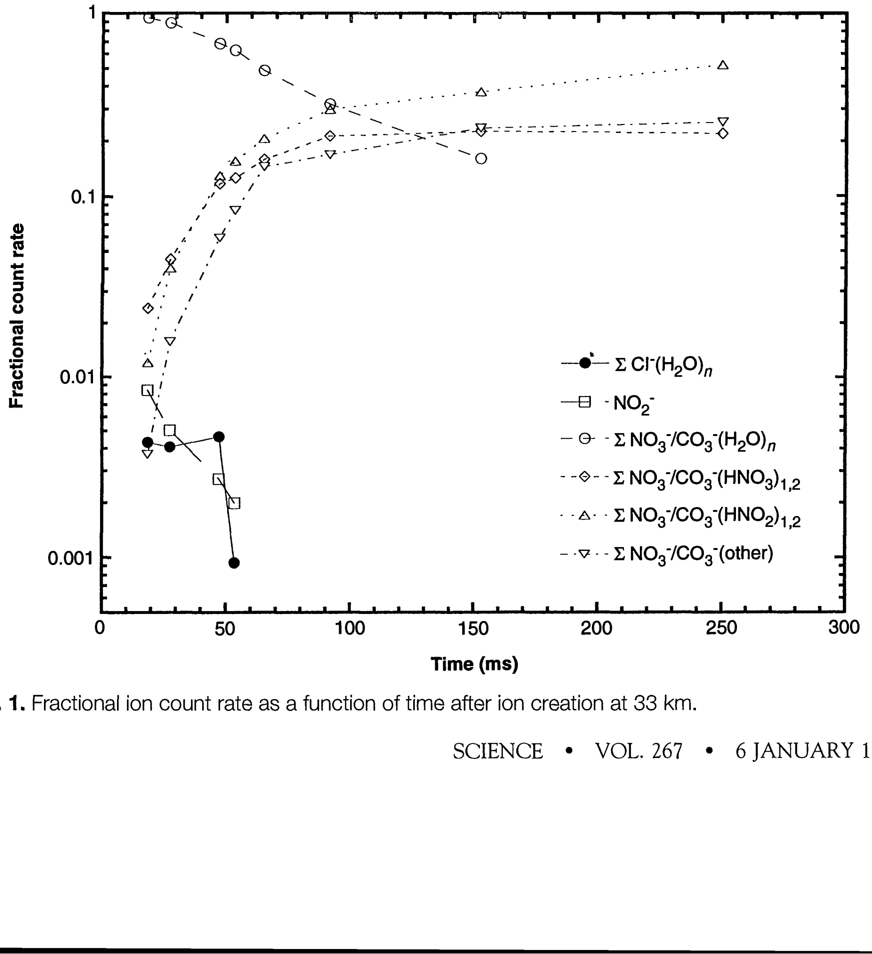

Fig. 1. Fractional ion count rate as a function of time after ion creation at 33 km.

sphere's Cl would have to be collected for a long-term effect. The conversion of power to ionization would be below unit efficiency, and the amount of Cl collected would be less than the number of Cl^- ions produced. In fact, Wong *et al.* (*1*) show that in a laboratory experiment the ionization density must be 20 times the density of Cl molecules in order for O_3 remediation to occur.

Weight is another problem if one is going to remove Cl from the stratosphere. The stratospheric Cl content is equal to 2.4×10^9 kg. Removing the Cl would require transporting at least this mass from the stratosphere to the ground. If the Cl were in any form other than Cl or Cl_2, transporting even more weight would be required. One of the proposed schemes (*6*) requires releasing positively charged water molecules to balance the release of negative charge. This scheme would require even more weight to be transported because many water molecules are needed per charge in a multiply charged droplet. Additionally, much of the water may evaporate in the atmosphere, thereby not only increasing the weight that must be transported but also humidifying the atmosphere.

Perhaps a simple way of looking at these weight and energy problems is to realize that in the remediation scheme, a large fraction of the world's total accumulated production of chlorofluorocarbons must either be tied up as negative ions or collected by processes performed on either airplanes or balloons. Another potential problem is that ionization in air often produces large quantities of radicals such as nitrogen oxides and OH. The amount of radical production is usually orders of magnitude greater than the amount of ion production. The production of such radicals would also increase the energy required, resulting in reduced efficiency of Cl^- production as well as seriously altering the neutral chemistry of the stratosphere.

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Use of a Sound-Based Vibratome by Leaf-Cutting Ants

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Leaf-cutting ants harvest fresh vegetation that they then use as food for symbiotic fungi. When cutting leaf fragments, the ants produce high-frequency vibrations with a specialized organ located on the gaster. This stridulation behavior is synchronized with movements of the mandible, generating complex vibrations of the mandibles. The high vibrational acceleration of the mandible (up to three times the gravitational force at peak acceleration at about 1000 hertz) appears to stiffen the material to be cut. An identical effect is achieved when soft material is sectioned with a vibratome. This hypothesis is supported by experiments simulating the cutting process with vibrating isolated mandibles: When tender leaves were cut, the vibration of the mandible reduced force fluctuations and thus permitted a smoother cut to be made.

Leaf-cutting ants harvest fragments of leaves on trees and bushes (*1*). During the cutting process, the ant anchors herself to the leaf edge by her hind legs and pivots around them while cutting with her mandibles arcs out of the leaves. The sizes of the harvested fragments depend on, among other parameters, the size of the forager, the quality of the leaf, and the harvesting situation of the colony (*2*). Depending on the size of the fragment being cut, an ant performs approximately 20 to 50 single bites for collecting a single piece of leaf.

It has been observed previously that leaf-cutting ants stridulate during the cutting process and that the produced sound, in the form of substrate-borne vibrational signals, attracts nest mates to the cutting site (*3*). Stridulation is produced when the ant moves her gaster up and down, so that a cuticular file located on the first gastric tergite is rubbed against a scraper situated on the postpetiole (*4*). These vibrations are conducted into the leaf through the ant's mandibles and legs (*3*). Because most of the energy is transmitted through the mandibles, we investigated whether these vibrations facilitate the cutting process in the manner of vibratomes (*5*), which are instruments frequently used for histological preparations. In order to obtain smooth and very thin sections of soft material, the cutting knife in a vibratome vibrates (*6*). The vibratome then accelerates and thereby stiffens the object to be cut. This has an effect similar to hardening the material by freezing or by chemical fixation.

In *Atta cephalotes*, the two mandibles play different roles during the cutting pro-

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