

ATMOSPHERIC CHLORINE AND STRATOSPHERIC OZONE*

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The total tropospheric concentration of organochlorine compounds in remote locations is approximately 3×10^{-9} mol Cl (mol air) $^{-1}$ in 1981. The five most abundant of these species are CH_3Cl , CCl_4 , CCl_3F , CCl_2F_2 and CH_3CCl_3 ; each contributes $(0.4 - 0.7) \times 10^{-9}$ mol Cl (mol air) $^{-1}$ to the total. Other contributors include C_2Cl_4 , C_2HCl_3 , $\text{CCl}_2\text{FCClF}_2$, $\text{CClF}_2\text{CClF}_2$, CHCl_3 , CH_2Cl_2 and CHClF_2 . The fractional contribution from inorganic species is minor except in the immediate vicinity of their sources (*e.g.* in sea spray near the ocean). All these organic compounds except CH_3Cl have as their primary and usually sole source the activities of man. Methyl chloride is believed to originate largely from Cl^- substitution into methyl iodide formed by biological processes in the ocean. The most important physicochemical processes which either decompose molecules or remove them from the atmosphere include (a) solar photodissociation, (b) reaction with chemical species induced by solar processes, such as $\text{O}(^1\text{D})$ atoms and OH radicals, and (c) wet and dry deposition (*e.g.* HCl dissolved in rain). The deposition processes are at most of minor importance for highly volatile water-insoluble organochlorine compounds, and their atmospheric sinks are almost entirely linked to solar photochemistry. The presence of O_3 in the stratosphere (about 3×10^{-7} mole fraction for the entire atmosphere) with strong UV absorption peaking near 260 nm effectively prevents the arrival in the troposphere of any radiation with $\lambda < 290$ nm. Below 200 nm the stratospheric absorption screen is continued by molecular O_2 . Chemical species can therefore be divided into two distinct categories relative to solar photodissociation through their absorption spectra in the UV. Molecules with appreciable cross sections in the visible or in the near UV beyond 295 nm are exposed throughout the troposphere to intense solar fluxes and consequently have short atmospheric lifetimes in daylight (*e.g.* Cl_2 has a lifetime of less than 1 h). However, molecules with no absorption in the visible or in the UV for $\lambda > 295$ nm are essentially protected from solar photodissociation at all altitudes in the troposphere and lower stratosphere. Photodissociation can only become significant for most of these molecules at altitudes for which much of the O_3 is below them; typically these altitudes begin at 20 - 25 km for wavelengths in the range 195 - 220 nm. Since only 3% of the atmosphere lies above 25 km the atmospheric lifetimes of these molecules stretch into many decades if solar photodissociation is the dominant removal process.

None of the saturated chlorine-containing compounds has any absorption in the range 295 - 600 nm, and direct photolysis in the troposphere is negligible for them. An exception is the molecule CBrClF_2 whose absorption spectrum is

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extended by the bromine atom (10^{-24} cm² at 320 nm) and which has an estimated tropospheric lifetime of 7 years. Molecules such as CClF₃ and CF₄ whose UV absorption occurs only for $\lambda < 195$ nm have estimated atmospheric lifetimes against solar photolysis exceeding 10^3 years; the most important stratospheric reaction process for CClF₃ is attack by O(¹D) atoms. All molecules are exposed to rapidly increasing UV intensities above 20 km, and those with appreciable cross sections in the 195 - 220 nm region have lifetimes which decrease rapidly with increasing altitude. For example, the average photochemical lifetime for CCl₂F₂ is about 30 years at 20 km, 1 year at 30 km and 1.5 months at 40 km; the lifetimes for CCl₃F are less at each altitude by about a factor of 10. The overall atmospheric lifetime for these compounds is determined in part by meteorological processes, *i.e.* by the rapidity with which previously unexposed molecules are transported upward into the regions of intense UV radiation. The estimated atmospheric lifetimes against solar photodissociation for typical chlorofluorocarbons are from 40 to several hundred years.

The most important atmospherically active chemical species in so far as chlorinated molecules are concerned are O(¹D) atoms in the upper stratosphere and OH radicals throughout both stratosphere and troposphere. The primary source for O(¹D) atoms is the photolysis of O₃ for $\lambda < 314$ nm, and the primary source for tropospheric OH is the reaction of O(¹D) with H₂O vapor. The average concentration of OH is of the order of 10^6 cm⁻³ throughout the 0 - 50 km altitude range, while the O(¹D) concentration increases approximately from 10^{-3} cm⁻³ at ground level to 10^2 cm⁻³ in the upper stratosphere. Even though O(¹D) reaction rates are usually very rapid (about 10^{-10} cm³ molecule⁻¹ s⁻¹) with molecules containing even one chlorine atom, the lifetimes toward reaction with it are still about 10^8 s (3 years) in the upper stratosphere. A typical OH abstraction rate constant of 10^{-14} cm³ molecule⁻¹ s⁻¹ also corresponds to a lifetime of about 10^8 s (several years). Molecules such as CH₃CCl₃ which do react with tropospheric OH are nevertheless able to accumulate there to some extent because of its atmospheric lifetime of about 7 years. Chlorinated olefins normally react with OH radicals at rates in the 10^{-12} - 10^{-13} cm³ molecule⁻¹ s⁻¹ range and have atmospheric lifetimes of only a few weeks. Species such as CCl₂=CCl₂ and CHCl=CCl₂ therefore show widely variable concentrations dependent both on season and on the recent trajectory of the air mass being measured.

The vertical mixing of the atmosphere occurs through large-scale mass transport and volatile organic compounds are carried into the stratosphere at rates independent of molecular weight. After photodissociation the various molecular fragments continue to diffuse both upward and downward, still in bulk motions. In the steady state the mole fraction of chlorine is constant at all altitudes through the troposphere and stratosphere even though the chemical form of the chlorine can undergo substantial alteration during the mixing process. The stratospheric mixing ratio of chlorine is thus closely correlated with the mixing ratio observed in the well-mixed upper troposphere, and an increase in tropospheric concentration of chlorine is followed within a few years by an increase in the various levels of the stratosphere. However, the real atmosphere is not yet in a steady state with respect to the mole fraction of chlorine because such a large fraction of the current tropospheric chlorine content has been introduced into it within the past

two decades in the form of anthropogenic organochlorine compounds. The upward mixing and photodissociation of these newly added components is still in progress, with near-equilibrium lagging 10 to 20 years behind the tropospheric conditions. Cryogenic trapping experiments for total chlorine content in the lower stratosphere have shown a mixing ratio of about 3×10^{-9} for chlorine, indicating that the major molecular species containing chlorine in the troposphere have already been detected.

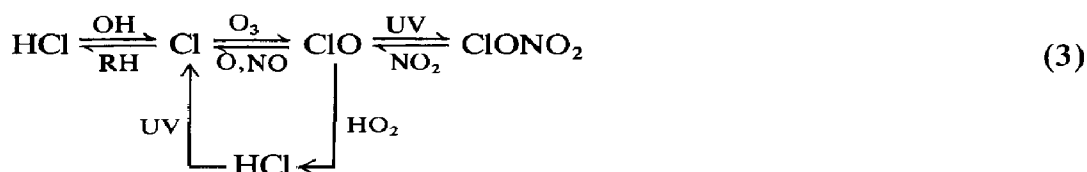
The initial photodecomposition of CCl_2F_2 releases one chlorine atom, and the subsequent reactions of the CClF_2 radical release the other chlorine atom and eventually the fluorine atoms as well. The observation in the stratosphere of HF with no other known tropospheric fluorine source than the chlorofluorocarbon compounds is clear evidence that these molecules are being photodissociated in the stratosphere. The most probable reaction for atomic chlorine throughout the stratosphere is removal of an oxygen atom from O_3 :



In the upper stratosphere above 30 km this reaction is normally followed by



and the net reaction for eqn. (1) plus eqn. (2) is the conversion of the two "odd-oxygen" species back into O_2 . After about 10^3 such cycles, requiring about 10^3 min, chlorine is diverted into the form of HCl by reaction with CH_4 , CH_2O , H_2 or HO_2 . Reaction with OH can then again release chlorine from the HCl. The combination of ClO with NO_2 and HO_2 can lead to the formation of ClONO_2 and HOCl respectively. Both of these molecules are photolyzed by solar UV with $\lambda > 300$ nm, returning the chlorine atoms again to the ClO_x chain of eqn. (1) plus (2). The more important of these stratospheric chemical transformations are summarized in the following equations:



The distribution of chlorine among these species at each altitude can be calculated if the appropriate reaction rate constants and UV absorption cross sections are known for stratospheric temperatures (210 - 280 K) together with the appropriate solar fluxes and molecular concentrations. In practice, much of this information is available, but important gaps exist (e.g. measured OH concentrations at altitudes of 20 - 30 km). In addition, conflicting laboratory data (the rate constant for OH with HO_2 , important for the concentrations of both these species) and puzzling chemical mechanisms (possible isomerism among the reaction products of $\text{ClO} + \text{NO}_2$) provide substantial current error bars on some of the measured laboratory quantities.

A variety of experimental techniques has been applied to the determination of the concentrations of these chlorine species in the stratosphere. Good

evidence exists for HCl, ClO and chlorine atoms, while an upper limit can be placed on ClONO₂ concentrations. Among the more prominent measurement techniques are (a) the collection of air in an evacuated flask, with laboratory analysis by gas chromatography (CCl₃F, CCl₂F₂, CH₃Cl etc.), (b) IR spectroscopy from a balloon-borne instrument pointed toward the setting sun (HCl, CCl₃F, CCl₂F₂, ClONO₂), (c) atomic resonance fluorescence (Cl, ClO after reaction with injected NO to form Cl), (d) aircraft- and balloon-borne filters (HCl) and (e) ground and balloon-based millimeter wave emission spectroscopy (ClO).

In the upper stratosphere the time constants for interconversion among these species (chiefly Cl, ClO and HCl) are small enough for the knowledge of the *in situ* solar flux to be sufficient for calculation, since the concentrations are essentially in a photochemical steady state. In the lower stratosphere more complex molecules are shielded against rapid photodissociation by the integrated O₃ concentration above them, and the time constants for reaction for some of these species can be fairly large (e.g. the storage of NO_x as HNO₃). At these altitudes the solar flux and other conditions affecting the chlorine chemical distribution need to be averaged over the previous week or month. In this situation, the observed chemistry becomes intertwined with the meteorological history of the air parcel, and much greater variability is expected and found in measured concentrations. Within these limitations, the observed concentrations of chlorinated species in the stratosphere are in general agreement with calculations based on laboratory knowledge of chlorine chemistry and atmospheric knowledge of the other interacting species. However, the chemical calculations for altitudes between 15 and 30 km imply the presence at those altitudes of several molecular species formed by free-radical chain termination reactions (ClONO₂, HOCl, H₂O₂, N₂O₅, HO₂NO₂) for which essentially no atmospheric measurements exist. All these are subject to solar photolysis for $\lambda > 300$ nm and consequently they have lifetimes in the range of hours and are expected to exist only in trace quantities. Nevertheless, measurements of some of these species would be very helpful in confirming the details of the stratospheric chemical interactions in the 15 - 30 km region. Considerable differences can still exist in present comparisons of the actual atmosphere with chemically consistent numerical models of the atmosphere. Models calibrated on the current atmosphere can then be extended into predictions of the future, utilizing various hypothesized estimates of future changes in the atmospheric concentrations of some of the anthropogenic species. Such models of the future atmosphere show about 10% less stratospheric O₃ for the steady state with the current release rates of molecules such as CCl₃F, CCl₂F₂ and CH₃CCl₃. These models also consistently show much heavier percentage losses of O₃ (about 40%) for the altitude (40 km) at which the effect of the ClO_x chain is expected to maximize. Contemporary O₃ changes are estimated to be about one-tenth of these steady state values when calculated for the change in the chlorine concentration alone. The model predictions become much more complicated when possible trends with time in other anthropogenic gases (CO₂, NO_x from the present jet aircraft fleet, N₂O etc.) are included.

The growth in tropospheric concentrations of CCl₂F₂, CCl₃F and CH₃CCl₃ is quite marked, with increases by factors of 2.5, 3 and 4 respectively during the 1970s. Molecules existing for decades in the troposphere are exposed to many

possible minor removal pathways, but no important tropospheric sink for either CCl_2F_2 or CCl_3F has been identified. (Even well-identified tropospheric sinks are not necessarily particularly rapid, as illustrated by the 10 year average atmospheric lifetime for nuclear-bomb-produced $^{14}\text{CO}_2$ whose known sinks include both photosynthesis and dissolution in the ocean to form HCO_3^- and CO_3^{2-} .) Comparisons of the amounts of these chlorofluorocarbons actually observed in the atmosphere with release data estimated from production figures shows no evidence for any "missing" material such as would be expected if some undetected tropospheric process were removing them. Observation of the rate of change of these concentrations over the past few years also suggests that no important unidentified removal process is affecting either CCl_3F or CCl_2F_2 . About one-half of the CH_3CCl_3 estimated to have been released to the atmosphere is still there; most of the remainder has been decomposed by reaction with tropospheric OH. The very rapid increase in atmospheric concentrations of CH_3CCl_3 during the 1970s reflects its accelerated production during that period, in contrast with CCl_3F and CCl_2F_2 whose yearly production has been roughly constant for the past 8 or 9 years.