

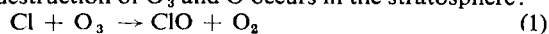
Stratospheric sink for chlorofluoromethanes: chlorine atom-catalysed destruction of ozone

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Chlorofluoromethanes are being added to the environment in steadily increasing amounts. These compounds are chemically inert and may remain in the atmosphere for 40–150 years, and concentrations can be expected to reach 10 to 30 times present levels. Photodissociation of the chlorofluoromethanes in the stratosphere produces significant amounts of chlorine atoms, and leads to the destruction of atmospheric ozone.

HALOGENATED aliphatic hydrocarbons have been added to the natural environment in steadily increasing amounts over several decades as a consequence of their growing use, chiefly as aerosol propellants and as refrigerants^{1,2}. Two chlorofluoromethanes, CF₂Cl₂ and CFCl₃, have been detected throughout the troposphere in amounts (about 10 and 6 parts per 10¹¹ by volume, respectively) roughly corresponding to the integrated world industrial production to date^{3–5,31}. The chemical inertness and high volatility which make these materials suitable for technological use also mean that they remain in the atmosphere for a long time. There are no obvious rapid sinks for their removal, and they may be useful as inert tracers of atmospheric motions^{4–6}. We have attempted to calculate the probable sinks and lifetimes for these molecules. The most important sink for atmospheric CFCl₃ and CF₂Cl₂ seems to be stratospheric photolytic dissociation to CFCl₂ + Cl and to CF₂Cl + Cl, respectively, at altitudes of 20–40 km. Each of the reactions creates two odd-electron species—one Cl atom and one free radical. The dissociated chlorofluoromethanes can be traced to their ultimate sinks. An extensive catalytic chain reaction leading to the net destruction of O₃ and O occurs in the stratosphere:



This has important chemical consequences. Under most conditions in the Earth's atmospheric ozone layer, (2) is the slower of the reactions because there is a much lower concentration of O than of O₃. The odd chlorine chain (Cl, ClO) can be compared with the odd nitrogen chain (NO, NO₂) which is believed to be intimately involved in the regulation of the present level of O₃ in the atmosphere^{7–10}. At stratospheric temperatures, ClO reacts with O six times faster than NO₂ reacts with O (refs 11, 12). Consequently, the Cl–ClO chain can be considerably more efficient than the NO–NO₂ chain in the catalytic conversion of O₃ + O → 2O₂ per unit time per reacting chain¹³.

Photolytic sink

Both CFCl₃ and CF₂Cl₂ absorb radiation in the far ultraviolet¹⁴, and stratospheric photolysis will occur mainly in the 'window' at 1,750–2,200 Å between the more intense absorptions of the Schumann–Runge regions of O₂ and the Hartley bands of O₃. We have extended measurements of absorption coefficients for the chlorofluoromethanes to cover the range 2,000–2,270 Å. Calculations of the rate of photolysis of molecules at a given altitude at these wavelengths is complicated by the intense narrow band structure in the Schumann–Runge region, and the

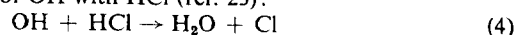
effective rates of vertical diffusion of molecules at these altitudes are also subject to substantial uncertainties. Vertical mixing is frequently modelled through the use of 'eddy' diffusion coefficients^{10,15–18}, which are presumably relatively insensitive to the molecular weight of the diffusing species. Calculated using a time independent one-dimensional vertical diffusion model with eddy diffusion coefficients of magnitude $K \sim (3 \times 10^3) - 10^4 \text{ cm}^2 \text{ s}^{-1}$ at altitudes 20–40 km (refs 10, 15–18), the atmospheric lifetimes of CFCl₃ and CF₂Cl₂ fall into the range of 40–150 yr. The time required for approach toward a steady state is thus measured in decades, and the concentrations of chlorofluoromethanes in the atmosphere can be expected to reach saturation values of 10–30 times the present levels, assuming constant injection at current rates, and no other major sinks. (The atmospheric content is now equivalent to about five years world production at current rates.) Lifetimes in excess of > 10 and > 30 yr can already be estimated from the known industrial production rates and atmospheric concentrations^{3,5}, and so the stratospheric photochemical sink will be important even if other sinks are discovered.

Our calculation of photodissociation rates is modelled after those of Kockarts¹⁹ and Brinkmann²⁰, and is globally averaged for diurnal and zenith angle effects. The photodissociation rates at an altitude of 30 km are estimated to be $3 \times 10^{-7} \text{ s}^{-1}$ for CFCl₃ and $3 \times 10^{-8} \text{ s}^{-1}$ for CF₂Cl₂, decreasing for each by about a factor of 10⁻² at 20 km. The appropriate solar ultraviolet intensities at an altitude of 30 km may be uncertain by a factor of 2 or 3 (ref. 21) and we have therefore calculated lifetimes for photodissociation rates differing from the above by factors of 3 or more. The competition between photodissociation and upward diffusion reduces the relative concentration of chlorofluoromethane at higher altitudes and the concentrations should be very low above 50 km. The peak rate of destruction, and formation of Cl atoms, occurs at 25–35 km, in the region of high ozone concentration. The rates of formation of Cl atoms at different altitudes, and the chlorofluoromethane atmospheric lifetimes are sensitive to the assumed eddy diffusion coefficients, as well as to the photodissociation rates.

The major chain processes in the stratosphere involving species with odd numbers of electrons belong to the H (H, OH, HO₂), N (NO, NO₂), and Cl (Cl, ClO) series. (ClO₂ is rapidly decomposed and its concentration is negligible relative to Cl plus ClO.) These odd-electron chains can only be terminated by interaction with one another, although other reactions can convert one series to another. At most altitudes, the first reaction for converting the Cl–ClO odd-electron chain to an even-electron species containing chlorine is the abstraction of H from CH₄, which transfers the odd-electron character to the CH₃ radical:



At stratospheric temperatures the rate constant for Cl atoms²², for (3) is about 10⁻³ times as fast as (1) and the O₃/CH₄ concentration ratio can make the rate of (3) less than that of (1) by another factor of 10. The Cl atom chain can be renewed by the reaction of OH with HCl (ref. 23):

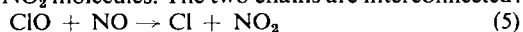


Ultraviolet dissociation by absorption in the range 1,750–2,200 Å can also occur at the higher altitudes. The reaction rate

of (4) in the stratosphere depends on the concentration of OH, which is known only roughly. In our estimates, termination of the Cl-CIO chain results from downward diffusion of the longer lived species in the chain (CIO, HCl) and eventual removal by tropospheric processes. The rate of termination thus also depends on diffusion processes and estimates will vary with the choice of eddy diffusion coefficients.

Possible terminations involving the Cl series with itself (for example, $\text{Cl} + \text{ClO} \rightarrow \text{Cl}_2\text{O}$) or with one of the others (for example, $\text{Cl} + \text{NO} \rightarrow \text{NOCl}$) normally lead to molecules with appreciable absorption coefficients at longer wavelengths, which are very rapidly dissociated again by the much more intense solar fluxes available there. Thus, even if a molecule which temporarily terminates two chains is formed, at least one of which involves the Cl series, the terminating molecule is rapidly photolysed and both chains are regenerated again.

Under most stratospheric conditions, the slow reactions in both the Cl-CIO and NO-NO₂ chains occur between O atoms and ClO and NO₂ molecules. The two chains are interconnected:



The rate of this reaction in the stratosphere is frequently comparable to that of reaction (2). The overall effect is complex and depends on the relative concentrations of ClO_x, NO_x, O₃, O and OH. Reaction (1) is so rapid that the ClO/Cl ratio is usually > 10, even when Cl is produced by both reaction (2) and reaction (5), so that the overall rate of reaction (2) is not directly affected by the occurrence of reaction (5). As soon as Cl is produced, however, HCl can form by reactions (1) or (3), resulting in the temporary termination of the Cl atom chain. Whether or not the chain is then restarted depends primarily on the concentration of OH. There are substantial ranges of stratospheric altitudes in which neither reaction (3) nor reaction (5) seriously impedes the chain process of reactions (1) and (2).

The initial photolytic reaction produces one Cl atom from each of the parent molecules, plus a CX₃ radical (X may be F or Cl). The detailed chemistry of CX₃ radicals in O₂ or air is not completely known, but in the laboratory a phosgene-type molecule, CX₂O, is rapidly produced and another X atom—probably Cl (or CIO)—is released from CFCl₂ or CF₂Cl^{24,25}. CX₂O may also photolyse in the atmosphere to give a third and fourth free halogen atom. Thus, each molecule of CFCl₃ initially photolysed probably leads to between two and three Cl atom chains, and CF₂Cl₂ probably produces two Cl atom chains when it is photolysed. Initial calculations suggest that F atom chains will be much shorter than Cl atom chains because the reaction of abstraction from CH₄ is much faster for F atoms²⁶, whereas the reaction between OH and HF is 17 kcalorie mol⁻¹ endothermic and will not occur in the stratosphere. We have not yet attempted to analyse the subsequent reaction paths of HF.

Production rates

The 1972 world production rates for CFCl₃ and CF₂Cl₂ are about 0.3 and 0.5 Mton yr⁻¹ respectively^{1,2,5}, and are steadily increasing (by 8.7% per year for total fluorocarbons in the United States from 1961–71) (ref. 1). We have not included any estimates for other chlorinated aliphatic hydrocarbons also found in the atmosphere, such as CCl₄ (refs 3 and 4), CHCl₃, C₂Cl₄ and C₂HCl₃ for which there is no evidence for long residence times in the atmosphere²⁷. If the stratospheric photolytic sink is the only major sink for CFCl₃ and CF₂Cl₂, then the 1972 production rates correspond at steady state to globally averaged destruction rates of about 0.8×10^7 and 1.5×10^7 molecules cm⁻² s⁻¹ and formation rates of Cl atoms of about 2×10^7 and 3×10^7 atoms cm⁻² s⁻¹, respectively. The total rate of production of 5×10^7 Cl atoms cm⁻² s⁻¹ from the two processes is of the order of the estimated natural flux of NO molecules ($2.5\text{--}15 \times 10^7$ NO molecules cm⁻² s⁻¹) involved in the natural ozone cycle⁹⁻¹², and of the 5×10^7 NO molecules cm⁻² s⁻¹ whose introduction around 25 km from strato-

spheric aviation is estimated would cause a 6% reduction in the total O₃ column¹⁰.

Photolysis of these chlorofluoromethanes does not occur in the troposphere because the molecules are transparent to wavelengths longer than 2,900 Å. In fact the measured absorption coefficients for CFCl₃ and CF₂Cl₂ are falling rapidly at wavelengths longer than 2,000 Å (ref. 14). The reaction between OH and CH₄ is believed to be important in the troposphere^{17,28}, but the corresponding Cl atom abstraction reaction (for example, $\text{OH} + \text{CFCl}_3 \rightarrow \text{HOCl} + \text{CFCl}_2$) is highly endothermic and is negligible under all atmospheric conditions. Neither CFCl₃ nor CF₂Cl₂ is very soluble in water, and they are not removed by rainout in the troposphere. Details of biological interactions of these molecules in the environment are very scarce because they do not occur naturally (except possibly in minute quantities from volcanic eruptions)²⁹, but rapid biological removal seems unlikely. The relative insolubility in water together with their chemical stability (especially toward hydrolysis)³⁰ indicates that these molecules will not be rapidly removed by dissolution in the ocean, and the few measurements made so far indicate equilibrium between the ocean surface and air, and therefore a major oceanic sink cannot be inferred³.

It seems quite clear that the atmosphere has only a finite capacity for absorbing Cl atoms produced in the stratosphere, and that important consequences may result. This capacity is probably not sufficient in steady state even for the present rate of introduction of chlorofluoromethanes. More accurate estimates of this absorptive capacity need to be made in the immediate future in order to ascertain the levels of possible onset of environmental problems.

As with most NO_x calculations, our calculations have been based entirely on reactions in the gas phase, and essentially nothing is known of possible heterogeneous reactions of Cl atoms with particulate matter in the stratosphere. One important corollary of these calculations is that the full impact of the photodissociation of CF₂Cl₂ and CFCl₃ is not immediately felt after their introduction at ground level because of the delay required for upward diffusion up to and above 25 km. If any Cl atom effect on atmospheric O₃ concentration were to be observed from this source, the effect could be expected to intensify for some time thereafter. A lengthy period (of the order of calculated atmospheric lifetimes) may thus be required for natural moderation, even if the amount of Cl introduced into the stratosphere is reduced in the future.

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