

FARADAY RESEARCH ARTICLE

Atmospheric Lifetime, Its Application and Its Determination: CFC-substitutes as a Case Study

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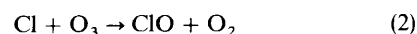
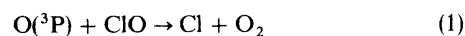
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The concept of atmospheric lifetime, its application in atmospheric chemistry, and its use in defining environmental acceptability indices such as the ozone depletion potential and the global warming potential are described. The determination of the atmospheric lifetime from laboratory measured chemical kinetic and photochemical parameters is highlighted. A brief description of the laboratory methods used to determine kinetic parameters and the difficulties encountered in measuring them are given. In all these descriptions and discussions, chlorofluorocarbons (CFCs) and their substitutes are used as examples. The environmental acceptability of the currently proposed CFC substitutes, the hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) are discussed. Lastly, the question is raised: Should atmospheric lifetime be used as an index of acceptability?

CFCs were hailed as the most stable and non-toxic compounds ever produced by mankind. Thomas Midgley of General Motors Corp., the inventor of CFCs, demonstrated their non-toxicity by inhaling them at public lectures. Their thermal stability, inertness, and non-toxicity made CFCs good replacements for the corrosive and toxic NH_3 and SO_2 used previously in refrigerators. A multitude of other uses, ranging from aerosol propellants to solvents, were found for CFCs, and they became ubiquitous in western society. Now, they are considered necessities in most parts of the world.

The introduction of CFCs came in an era when it was generally believed that human emissions could not adversely affect the Earth's atmosphere. Even though local pollution problems such as the London fog and Los Angeles smog were known to be human induced, the global impacts of anthropogenic emissions were generally neglected. This is understandable, since even the large emissions of CFCs (*e.g.* ca. 4×10^8 kg of CFCl_3 was released in 1990) for decades would lead to a negligible abundance in the atmosphere, at most a few parts per billion (mole fraction of 10^{-9})! During the last two decades, many major developments have changed the perceived safety of human-produced chemicals. It is now general knowledge that CFC emissions are detrimental to stratospheric ozone, which sustains life on Earth by filtering short wavelength radiation from the Sun. Stolarski and Cicerone¹ and Wofsy and McElroy² were the first to propose that chlorine could destroy ozone catalytically in the stratosphere. Measurements by Lovelock in the 1970s³ established the ubiquity of CFCs in the atmosphere. This pioneering work prompted Rowland and Molina⁴ to suggest that, because of their inertness, CFCs could transport chlorine to the stratosphere and promote ozone depletion. The CFCs are inert in the troposphere and are lost only by photolysis and reaction with $\text{O}(^1\text{D})$ in the stratosphere. It is the catalytic nature of ozone destruction by chlorine that causes small CFC abundances to have large effects on the ozone destruction rate.

The specific reactions proposed in the early 1970s for the chlorine catalysed destruction of ozone



are now known to be contributing less than cycles involving the $\text{ClO} + \text{ClO}$ and $\text{ClO} + \text{BrO}$ reactions to polar ozone loss⁵ and, possibly, to mid-latitude ozone decline.⁶ However, the inherent connection between CFCs and stratospheric ozone loss has withstood extensive scientific scrutiny. The discovery of the Antarctic ozone hole, though not cited in the scientific basis for the Montreal Protocol in 1985, catapulted controls on CFC emissions. The Montreal Protocol⁷ was an international treaty signed in Montreal, Canada, under United Nations auspices which curtailed production of CFCs because of their deleterious effect on the ozone layer. Now, such controls have become international agreements with quite strident phase-out schedules and acceptability standards. Amazingly, it appears that countries are coming into compliance even faster than mandated by the protocols and their amendments.

In response to the phase-out of CFCs, substitutes for many applications are needed. (It appears that medical applications of CFCs may continue.) The current emphasis is to design chemicals to work in existing devices with minimal changes, mostly for economic reasons. The prime candidates for replacing the CFCs are the HCFCs and HFCs. HCFCs and HFCs are promising replacement compounds because they are compatible with the existing technology, and are more environmentally friendly than CFCs, since they are degraded efficiently in the lower atmosphere, unlike the CFCs. The HCFCs and HFCs contain hydrogen atoms which make them vulnerable to attack by the OH radical in the lower atmosphere. The CFCs, their uses, and the potential replacement compounds are shown in Table 1. It is already accepted that all HCFCs are transitional rather than permanent, substitutes, because they also contain chlorine and hence have finite potential to destroy stratospheric ozone. The accept-

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Table 1 CFC applications and potential replacement compounds

CFC compound	application	replacement compound
CFC-11 (CFCl ₃)	insulation blowing agent	HCFC-123 (CHCl ₂ CF ₃) HCFC-141b (CH ₃ CCl ₂ F)
CFC-12 (CF ₂ Cl ₂)	household, commercial, and automotive refrigerant, and polystyrene extrusion agent	HCFC-22 (CHClF ₂) HCFC-142b (CH ₃ CF ₂ Cl) HFC-134a (CH ₂ FCF ₃) HFC-32 (CH ₂ F ₂) HFC-152a (CH ₃ CHF ₂) HCFC-123 (CHCl ₂ CF ₃) HCFC-124 (CF ₃ CHFCl)
CFC-113 (CF ₂ ClCCl ₂ F)	solvent for cleaning and drying electronics and metal	HCFC-123 (CHCl ₂ CF ₃) HCFC-141b (CH ₃ CCl ₂ F) HCFC-225ca/cb (CF ₃ CF ₂ CHCl ₂ /CHClF ₂ CClF ₂)
R502 [CFC-115 (CF ₃ CF ₂ Cl)/HCFC-22 (CHClF ₂) azeotrope]	commercial refrigerant	HCFC-22 (CHClF ₂) HFC-134a (CH ₂ FCF ₃) HFC-32 (CH ₂ F ₂)

The numbering system used to designate the chemicals containing carbon, hydrogen, fluorine, and chlorine was apparently developed by chemists at du Pont Co. as a code. This code, though decipherable, causes a lot of problems to chemists, and in that respect, the du Pont chemists succeeded! The code is as follows: The molecular formula may be obtained by adding 90 to the halocarbon number; the first digit gives the number of carbon atoms, the second digit the number of hydrogen atoms, and the last digit gives the number of fluorine atoms. The number of chlorine atoms is determined by subtracting the sum of the first three digits from 90. For example, HCFC-141b is C₁H₄Cl₂F₁.

toluene

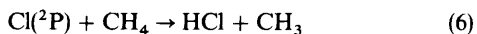
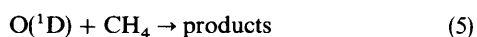
[²H₈]toluene

xylene

phenol

benzene

vibrational mode



The major loss process for CH_4 in the atmosphere is the reaction with the hydroxyl radical [reaction (4)]. Reactions (5) and (6) and soil uptake make minor, but non-negligible, contributions to the methane loss. The atmospheric lifetime of methane is the reciprocal of the sum of the first-order loss rate coefficients due to all these processes [eqn. (II)]. Of course, the reactions (5) and (6) are weighted suitably to take into account that they occur only in the stratosphere.

There are two additional points to note: (1) The lifetime for a species may be a strong function of location in the atmosphere and (2) the average lifetime is weighted by the spatial variation of the species in the atmosphere. Therefore, the movement of the species between the different regions of the atmosphere can be a major factor in determining the lifetime. The transport rate is usually calculated by using numerical models which are 'calibrated' to fit observed tracer fields. Since mixing in the troposphere is fast (approximately a few months for complete mixing within the Northern and Southern hemispheres and a couple of years for inter-hemispheric mixing) and the majority of the atmosphere is in the troposphere, a small local removal rate in this region can be very effective in removing a species from the atmosphere. Conversely, a rapid removal mechanism in the mesosphere may represent an inefficient sink because there is very little mass in that part of the atmosphere, and transport to and from this region is slow. When removal by processes such as soil uptake or ocean dissolution are to be included, the modelling becomes more complex. It is important to remember that most atmospheric lifetimes are calculated and what we call 'chemical lifetime' can be determined by the rate of physical transport.

The rate of change of concentration of a species with time in the atmosphere, dC/dt , is given by

$$\frac{dC}{dt} = P - L \quad (\text{III})$$

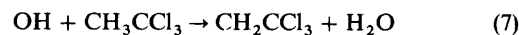
where P and L are the production and loss rates, respectively. Generally, the production rate does not depend on the concentration of the species in the atmosphere, while the loss rate is, usually, proportional to its concentration. (It could be proportional to the n th power of concentration where $n \neq 1$! Here, we will not consider such cases.) Thus,

$$\frac{dC}{dt} = P - k[C] = P - \frac{1}{\tau} [C] \quad (\text{IV})$$

Eqn. (IV) provides a way of obtaining lifetimes from measurements of atmospheric concentrations and estimates of the source strengths. Methyl chloroform (CH_3CCl_3 , MCF) is a good example of an atmospheric species for which eqn. (IV) can be used to estimate its atmospheric lifetime.

MCF is a human-made compound which has no natural sources. The rate of MCF release into the atmosphere (in reality, production) can be estimated from data supplied by the manufacturers.⁸ Further, because of long-term field measurement programmes such as the ALE-GAGE project,⁹ the spatial and temporal variation of the atmospheric abundance of MCF is known. Thus, we know P and dC/dt . Since MCF production is recent and the production rate is changing with time, dC/dt is not zero, *i.e.* the system has not reached steady state. The 1992 (the latest year for which data are available) input into the atmosphere was *ca.* 6×10^8 kg,¹⁰ *i.e.* *ca.* 25 pptv† addition for that year. The current atmo-

spheric abundance is *ca.* 200 pptv and it has been increasing at a rate of *ca.* 5 pptv per year during the past decade. Thus, the increase per year is quite small compared to the abundance in the atmosphere. The atmospheric lifetime of MCF has been calculated by Prinn *et al.* to be 5.7 years⁹ based on the known input into the atmosphere and the abundances and increases measured during the ALE-GAGE project. A similar, but less accurate, lifetime can be calculated by equating the production rate to the loss rate. The major atmospheric-loss process for MCF is the reaction with OH radicals,



Since we know that the lifetime of MCF is 5.7 years, we can relate it to an 'average' atmospheric OH concentration,

$$\frac{1}{\tau} = \frac{1}{5.7 \text{ years}} = k' = k_{\text{OH}+\text{MCF}} [\text{OH}]_{\text{ave}} \quad (\text{V})$$

This leads to a global weighted-averaged OH concentration of *ca.* $9 \times 10^5 \text{ cm}^{-3}$ using our recently measured value of $k_7 = (1.75 \pm 0.34) \times 10^{-12} \exp[(1550 \pm 60)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.¹¹ This analysis is a simplification because a non-negligible fraction of MCF is removed *via* oceanic uptake.¹² It is interesting to note that production of CH_3CCl_3 is banned under the London amendment to the Montreal Protocol starting in 1996. After this time, the CH_3CCl_3 concentration should reach a maximum and then decay exponentially. This period will provide an opportunity to further test our understanding of the processes that control the lifetime of MCF (and, by analogy, other similar compounds).

The OH concentration derived from eqn. (V) is the effective concentration that removes MCF from the atmosphere. It would not be applicable to another molecule whose rate coefficient for reaction with OH has a very different temperature dependence. In this case, the differences in the activation energies can be taken into account and a new 'effective' OH concentration deduced.⁹ For the HFCs and HCFCs, where OH abstracts an H atom from a C—H bond, the activation energies are similar to that for the OH + MCF reaction, and the OH concentration derived from eqn. (V) is appropriate for the lifetime calculations. If the activation energies are much larger than for reaction (7), the removal will take place lower in the troposphere (*i.e.* at warmer temperatures) and be shifted further into the tropics. In contrast, if the OH reaction has no activation energy, more of the troposphere will be available for the removal. However, reactions with small activation barriers are almost always very fast. In this case the atmospheric lifetime is determined by the OH concentration in the area where the compounds are released and globally averaged removal rates based on MCF data are inappropriate.

Uses of Atmospheric Lifetimes

The atmospheric lifetime determines the abundance and rate of growth of a species in the atmosphere for a given emission. Fig. 1 shows the atmospheric abundances, as a function of time, of two species with different atmospheric lifetimes but with the same emission rates (in moles rather than by weight). The abundance of the species with a longer lifetime increases in the atmosphere faster and reaches a higher level for a fixed emission time. Also, it takes longer for this species to reach steady state, as indicated by the time taken for the solid line to flatten out. If the emissions were cut off at a given time, $t = 1$, the atmospheric abundance of both species would decrease exponentially. The concentration of the species with

† 1 pptv = 1 part per trillion (10^{-12}) by volume.

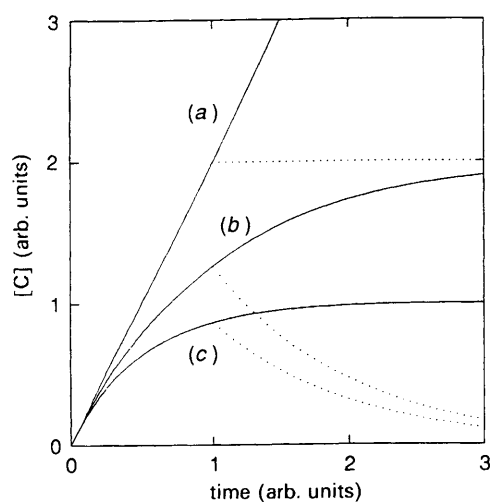


Fig. 1 Comparison of the temporal variation of the atmospheric concentration of three species with the same emission rates but different removal rates. A compound with no loss (a) accumulates the fastest and maintains a constant concentration when emissions are stopped (time = 1). Species with significant loss processes [(b) and (c)] accumulate more slowly. The compound with the highest loss rate (c) accumulates the slowest, approaches a smaller steady-state concentration and decays faster (dotted lines) when the emissions are stopped.

the longer lifetime decreases more slowly than the one with the shorter lifetime. Therefore, if the emission of a species into the atmosphere is curtailed, it will take the atmosphere longer to get back to its original state if the lifetime is longer. This is why it will take a couple of centuries for the atmospheric abundances of CFCs to decrease to the pre-CFC values when emissions of CFCs are stopped in or around 1995. The pre-ozone hole level of chlorine was *ca.* 2 ppbv† and current levels are about 3.9 ppbv. Therefore, even after the cessation of CFC emissions, the ozone hole will persist for nearly 60 years. If the currently proposed CFC substitutes had been used in place of the CFCs, we would not have accumulated 2 ppbv of chlorine in the atmosphere and, hence, would not have the ozone hole today! (The emission of CH_3Cl from oceans is the only significant natural source of atmospheric chlorine, *i.e.* pre-CFC source of stratosphere chlorine, and presently, the contribution of CH_3Cl to the total current chlorine budget is *ca.* 15%.)

Two indices used commonly to express the potential for atmospheric perturbation are ODP and GWP. Both these indices depend on the lifetimes of the reference molecule and the molecule under consideration. These indices are used for societal judgement of the environmental acceptability of human-made chemicals; therefore, a high premium is placed on the accuracy of these parameters.

the mechanism for the destruction of all the CFCs considered was photolysis in the stratosphere. However, now the ODP concept has been extended to include molecules which have very different loss processes. For example, the HFCs and HCFCs are removed mostly in the troposphere *via* reaction with OH, while the reference compound, CFCl_3 , is destroyed in the stratosphere. In this case, the systematic errors in the calculated rates of loss processes are not cancelled by taking the ratio of the projected ozone losses, because the compounds have dissimilar removal pathways. However, because the ODP index is easy to use and provides a reasonable measure of the relative merits of various substitutes, the ODP is still a widely used index. In fact, the Montreal Protocol and the US Clean Air Act use ODP to judge acceptability.

There are several problems with the definition of ODP. The first problem arises because the ODP is a function of time. Usually, the ODP is defined as the steady-state value which is the depletion potential when concentrations of both X and CFCl_3 have reached steady state. Before steady state, the ODP changes with time because species with different lifetimes accumulate at different rates. The shorter-lived substitutes reach steady state faster and their short-time ODP is higher than the steady-state ODP. Therefore, the ODP must be defined for a specific time horizon. Another problem is how ΔO_3 is estimated. Model calculations underestimate the changes in O_3 levels that have been measured by satellite and ground-based instruments during the past decade. Often it is assumed that ratioing the changes in O_3 used in the definition ODP should minimize this error. This is not always the case. Solomon *et al.*¹⁵ have defined a more realistic ODP which is based on observations of ozone losses and vertical profiles of X and/or compounds with similar loss processes. This approach, termed the semi-empirical approach, greatly offsets the errors which result from the atmospheric loss for molecule X being different from that for CFCl_3 . In both approaches one needs the atmospheric lifetime of molecule X and CFCl_3 to calculate the ODP. The semi-empirical method is more accurate because the rates of transport of molecules in the stratosphere are derived from observed vertical profiles, rather than by calculation. Thus, this method bypasses the calculation of transport rates, which are a major source of error.

In addition to the ODP, the chlorine loading potential (CLP) is used to gauge the impact of chlorine-containing compounds on stratospheric ozone:

$$\text{CLP} = \frac{(\tau_X n_X / \text{molecular weight of X})}{(\tau_{\text{CFCl}_3} n_{\text{CFCl}_3} / \text{molecular weight of CFCl}_3)} \quad (\text{IX})$$

where τ_X is the atmospheric lifetime of species X and n_X is the number of Cl atoms in species X ($n_{\text{CFCl}_3} = 3$). The CLP is a measure of the maximum amount of chlorine in a molecule that could reach the stratosphere, relative to CFC-11. There-

ciency of a compound relative to CO₂. The halocarbon global warming potential (HGWP) expresses the greenhouse efficiency relative to CFC-11 (CFCl₃)

$$\text{HGWP} = \frac{(\tau_X \text{ d}F_X / \text{molecular weight of X})}{(\tau_{\text{CFCl}_3} \text{ d}F_{\text{CFCl}_3} / \text{molecular weight of CFCl}_3)} \quad (\text{X})$$

where $\text{d}F$ is the radiative forcing, the IR energy absorbed by unit concentration (usually 1 ppbv) of the molecule in W m^{-2} . The GWP of CFC-11 (CFCl₃) is *ca.* 1400 for an infinite time horizon. The time horizon issue is rather complicated and one should read the IPCC documents¹⁶ for the discussions of the time horizons and lifetime of CO₂. We highlight the HGWP for two reasons: (1) In replacing a CFC with a substitute, what matters is the effectiveness of the substitute relative to the CFC. (2) The GWP is not as well defined as HGWP because the 'lifetime' of CO₂ is uncertain owing to various CO₂ recycling processes involving the atmosphere, biosphere and the oceans.

Note that the above indices compare the lifetimes of species which have different pathways for their removal. The reference compound for the ODP, CFC-11, is removed *via* stratospheric photolysis while the reference compound for GWP, CO₂, is taken up by the biosphere and oceans. The compounds whose ODP and GWP are being defined may be removed by chemical reactions, photolysis, or other physical processes in the troposphere or the stratosphere. For example, Halon 1211 (CF₂ClBr), is removed *via* tropospheric photolysis, HFCs *via* OH reaction and COS by plant uptake. Thus, comparisons of lifetimes of species with completely different loss mechanisms are required to estimate their effects on the atmosphere.

Determination of Lifetimes

In the preceding section, we noted the importance of knowing atmospheric lifetimes for evaluating the environmental indices, ODP, CLP, and HGWP. How can one determine these atmospheric lifetimes? One method is to use atmospheric observations and estimates of source strengths, as described earlier for MCF, although this story is rather

unusual. Many important atmospheric species have natural sources and their emission rates are not well understood. A current need is to estimate the lifetimes of chemicals which have not yet been introduced into the atmosphere. In this case, one must evaluate the rates for all the possible atmospheric-loss processes and calculate the lifetime with numerical models. Central to this approach is the appreciation that the calculated lifetimes may have systematic errors, since the calculated lifetimes are no better than the input data. However, if two molecules are removed by the same process, their relative lifetimes should be determined quite accurately by this method. This situation applies to HCFCs and HFCs, the two classes of chemicals which are forerunners as replacements for CFCs, because they, like MCF, are also removed mostly *via* OH reactions. Thus, the lifetimes of HFCs and HCFCs are as good as that of MCF if the rate constants are accurate.

Evaluation of the Environmental Impact of HCFs and HCFCs

The criteria for the environmental acceptability of a molecule are its ODP and GWP. The Montreal Protocol restricts the production of CFCs with ODPs greater than 0.2. However, there is no international agreement on the acceptability of a greenhouse gas, although, there is a voluntary move to avoid the use of potent greenhouse gases as CFC substitutes. It is very likely that there will be future regulations on greenhouse gases using GWPs as the indices of acceptability. As noted above, the primary quantity required to calculate ODPs and GWPs is the atmosphere lifetime.

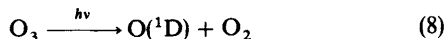
The lifetimes of HCFCs and HFCs are determined by the rates of the important removal processes [eqn. (II)]. The common reactive species responsible for the removal of chemicals from the atmosphere are given in Table 2. In order to evaluate the atmospheric lifetime, one must know the rate coefficients for all the important loss processes. Many times, a number of gas-phase reactions can be eliminated by analogies and thermodynamic arguments. For example, in the case of HFCs and HCFCs, it is safe to assume that their reactions with ozone and NO₂ are not important, since the analogous reactions between these oxidants and saturated hydrocarbons are slow. It is also likely that hydroxyl radicals do react with

Table 2 Oxidants in the lower atmosphere and their abundance

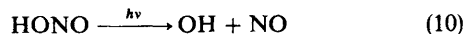
molecule	approximate abundance		origin
	troposphere	stratosphere	
O ₂	0.2	0.2	biological activity
O ₃	< 1.5 ppmv	< 5 ppmv	O ₂ or NO ₂ photolysis followed by O + O ₂ reaction
NO ₂	a few ppbv	a few ppbv	oxidation of NO and direct emission in troposphere N ₂ O degradation in stratosphere
NO	< ppbv	< ppbv	direct emission in troposphere. N ₂ O degradation in stratosphere
NO ₃	< ppbv	< ppbv	reaction of NO ₂ with O ₃
Cl	a few pptv?	< pptv	heterogeneous reactions in troposphere CFCs, CH ₃ Cl, <i>etc.</i> in stratosphere
halogens and halogen oxides	??	< 2 ppbv (ClO) < 20 pptv (BrO)	??
O(³ P)	< pptv	< pptv	photolysis of O ₃ or NO ₂
OH	< 10 ⁷ cm ⁻³ averaged	< 10 ⁸ cm ⁻³ averaged	reaction of O(¹ D) with H ₂ O, other small sources
O(¹ D)		< 10 ³ cm ⁻³	photolysis of O ₃ or O ₂
light	λ > 290 nm	185 < λ < 2120 nm and λ > 290 nm	Sun

The abundances are approximate diurnal averages.

HCFCs and HFCs since they react efficiently with saturated hydrocarbons. Indeed, OH reactions are expected to be the most important atmospheric-loss process for HFCs and HCFCs. In the troposphere and stratosphere, OH is produced mostly *via* the sequence:



Processes such as the photolysis of HONO,



are believed to be minor contributors to the production of OH.

Loss of HFCs and HCFCs by heterogeneous processes may be ruled out as a major mechanism because the halocarbons are very weakly soluble in water. Photolysis is also negligible in the troposphere because of poor overlap between the absorption spectra of the HFC and HCFC compounds and the solar radiation reaching the troposphere.

In the stratosphere, reactions of HFCs and HCFCs with OH are still important. The reaction with O(¹D), which is not important in the troposphere owing to the extremely low concentration of the electronically excited atom, is potentially important in the stratosphere. O(¹D) is produced mainly by ozone photolysis [reaction (8)] with minor contributions from O₂ photolysis. In the stratosphere, the concentrations of O(¹D) are greatly enhanced because of its increased rate of production *via* O₃ photolysis (due to the enhanced UV levels and higher O₃ concentrations) and a reduced rate of quenching, due to the lower total pressure. Even in the stratosphere, the O(¹D) concentrations are small (<10³ molecule cm⁻³). Reactions with the more abundant O(³P) appear to be too slow to be important; these reactions are endothermic or nearly thermoneutral. UV photolysis may be a significant sink for halocarbons containing the Cl chromophore, since radiation between 180 and 220 nm is available in the middle stratosphere. HFCs do not absorb radiation with wavelengths longer than *ca.* 180 nm, and photolysis of HFCs is negligible in the troposphere and the stratosphere. To evaluate the lifetime and fate of the CFC replacement compounds in the stratosphere, their UV absorption cross-sections, dissociation quantum yields, and rate coefficients for reaction with O(¹D) and OH are needed.

Measurements of OH Rate Constants

Since OH reaction is the dominant loss process for HCFCs and HFCs in both the troposphere and the stratosphere, the rate coefficients for these processes have been studied extensively. Many studies of CFC-substitutes have employed the discharge flow technique in which OH radicals are generated *via* reactions of atoms, produced in a high-energy discharge, with molecules (*e.g.* H + NO₂ → OH + NO or F + H₂O → HF + OH). The change in the OH concentration with reaction time is determined by varying the contact distance between the OH and the HFC or HCFC reactant in a flow-tube reactor. The OH radical is detected at the exit of the reactor with a wide variety of methods, including laser magnetic resonance (LMR) spectroscopy (the NOAA group, see for example ref. 17); resonance fluorescence (RF) (Jeong and Kaufman,¹⁸ Wayne and co-workers,¹⁹ Clyne and Holt²⁰); electron paramagnetic resonance (Orkin and Khama-ganor²¹); and laser-induced fluorescence (LIF) (Nelson *et al.*²²). The OH kinetics have also been studied with several variants of the flash photolysis technique, in which the OH radicals are generated photolytically in a short pulse of light from either a flash lamp or a laser, and the radicals are moni-

tored as a function of time by using fast optical techniques, including LIF (NOAA group¹⁷), resonance absorption (Paraskevopolous and co-workers²³), and RF (Kurylo and co-workers²⁴ and LeBras and co-workers²⁵). A related technique in which the OH radicals are produced by pulsed radiolysis and monitored *vs.* time by absorption, has also been employed in ref. 26.

The OH + HFC and HCFC kinetics have also been studied by monitoring the disappearance of the HFC or HCFC species in the presence of OH, relative to the loss of another compound for which the OH rate constant is well known. This approach has two advantages: (1) The decay of the compound of interest is monitored directly, so that impurities in the HFC sample do not influence the measurement and (2) if measured relative to CH₃CCl₃, the ratio is what is needed for lifetime calculations and, hence, can be more accurate than individual rate constant measurements. However, care must be exercised to ensure that reactive species other than OH are not present. Several studies of the OH + HFC and HCFC kinetics have been carried out with this technique (Huder and DeMore²⁷ and Sidebottom and co-workers²⁶). The studies of DeMore and co-workers are particularly noteworthy because they systematically measured rate coefficients as functions of temperature for a large array of HFCs and HCFCs relative to different reference compounds, including MCF.

We have measured OH rate constants for a wide range of proposed CFC-substitute compounds by employing the discharge-flow (DF) and pulsed-photolysis techniques.^{17,28-30} In this section we describe briefly our experimental apparatus and methodology; the apparatus and methodology used by many other investigators are very similar. The principles of rate constant measurement with the discharge-flow technique have been described by Howard.³¹ A schematic diagram of our flow-tube apparatus is shown in Fig. 2. A laser magnetic resonance (LMR) spectrometer moni-

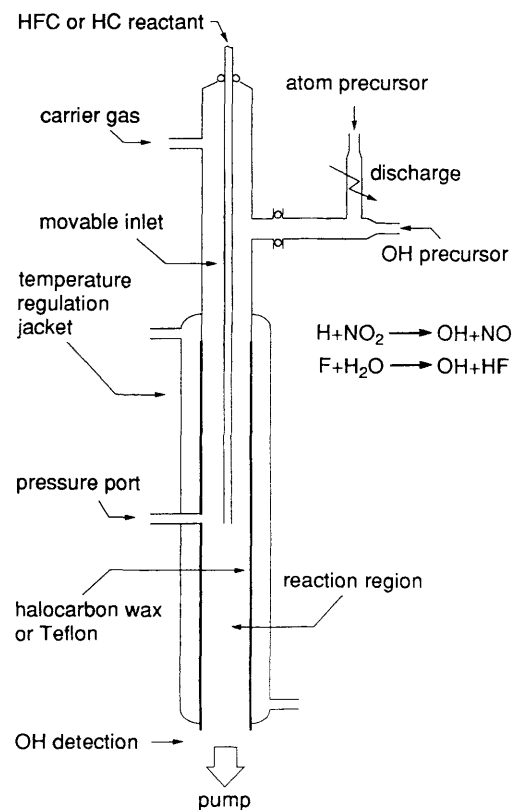


Fig. 2 Schematic diagram of the discharge flow apparatus used in the NOAA laboratory

itors the effluent of a Pyrex flow tube 100 cm long and with an internal diameter of 2.5 cm. OH radicals are generated in a small side-arm reactor *via* the reaction of NO₂ with H atoms or H₂O with F atoms. The atomic species are produced by the dissociation of molecular hydrogen or CF₄ in a microwave plasma. The OH radicals enter the flow tube about 10 cm upstream from the 50 cm long reaction region. The HFC or HCFC reactant is added through a movable injector to the centre of the flow tube with a small flow of an inert carrier gas, typically He. The bulk of the flow in the reactor is the inert carrier gas, which is introduced *via* ports upstream from the radical source. Reaction between OH and the reactant occurs over a variable distance of about 10 to 50 cm. The total gas flow rate through the flow tube is *ca.* 10 STP cm³ s⁻¹ (STP = 273 K and 760 Torr) at a total pressure of 1 to 2 Torr, giving linear flow velocities of 500–2000 cm s⁻¹ and reaction times ranging from 5 to 100 ms. The walls of the flow tube and injector are coated with halocarbon wax or fitted with a Teflon sleeve to reduce the loss of radicals and inhibit heterogeneous chemistry. The temperature of the reactor is controlled by flowing thermostatted fluid through a jacket surrounding the reactor.

The flash photolysis–laser-induced fluorescence (FP–LIF) apparatus is illustrated in Fig. 3. OH radicals are produced in a small Pyrex reactor by the pulsed UV photolysis of various precursors. Photolysis light sources (precursor and wavelength) include Xe flash lamps (H₂O between 165–190 nm, HNO₃, H₂O₂, *etc.*), excimer laser (O₃–H₂O mixture at 248 nm; HNO₃ and H₂O₂ at 248 nm; HONO at 351 nm), and harmonics of the Nd : YAG laser (O₃–H₂O mixture at 266 nm; HNO₃ and H₂O₂ at 266 nm; HONO at 355 nm). The rapid photolytic production of OH initiates the chemistry, and the OH concentration is monitored *vs.* time by the laser-induced fluorescence of OH following excitation of the A²Σ(v' = 1) ← X²Π(v'' = 0) transition at *ca.* 282 nm with a pulsed laser. The laser-induced fluorescence signal provides a sensitive and rapid detection scheme for real-time monitoring of the OH concentration. The temporal profile of OH is mapped out by averaging the fluorescence signal for a range of delay times between the photolytic production of OH and its LIF interrogation.

The DF–LMR and FP–LIF techniques are complementary, well tested kinetic methods. The DF method offers the advantage of isolated OH source chemistry, although heterogeneous chemistry on the walls of the reactor is a potential problem. The LMR detection offers excellent sensitivity. The FP–LIF method is not complicated by heterogeneous processes since the radical detection volume is isolated from the

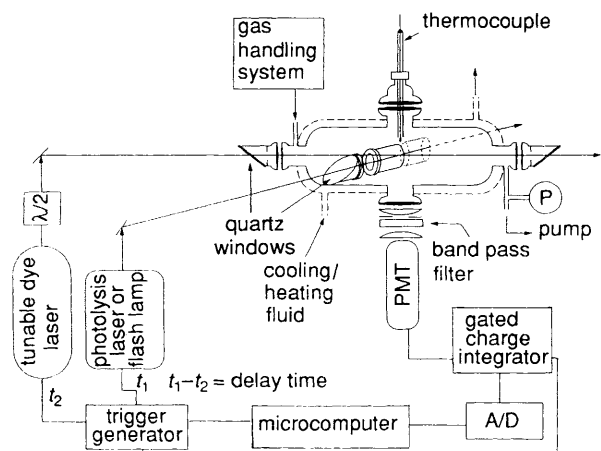


Fig. 3 Schematic diagram of the pulsed-photolysis–laser-induced fluorescence apparatus used in the NOAA laboratory

walls of the reactor and diffusion times are long compared to reaction time. However, this technique requires *in situ* photolytic production of the radicals and reactions of photo-products with the OH radicals is a major concern in these systems. The use of lasers and multiple precursors has greatly enhanced the applicability of this method. In our laboratory, multiple OH source schemes have been employed to examine possible secondary chemistry associated with the OH production method. In particular, use of HONO photolysis at 351 or 355 nm avoided photodissociation of the HCFCs. In both the DF and FP techniques, the OH concentration is monitored as a direct function of time or some parameter related to time (*e.g.* distance in a constant velocity flow). This type of measurement may be complicated by the presence of reactive impurities in the excess reactant sample and care must be taken to ensure that the samples are not contaminated in the system. The FP–LIF technique does offer very good sensitivity coupled with excellent time resolution. This allows one to maximize [X]/[OH]₀, where X refers to the stable excess reactant, by working with small radical concentrations and large reactant concentrations. The large [X] facilitates the measurement of its concentration which directly influences the accuracy of the measured rate constant. A potential drawback to this approach is that large concentrations of pure reactant samples are required. Recirculation of the reactants is a possible method to minimize sample use. However, production of reactive species has to be minimized and measured.

Evolution of the OH + HCFC-141b(CH₃CFCl₂) Rate Constant

As an example of the great effort expended to characterize the reactivity of the proposed CFC replacement compounds, we describe the measurements of the OH + HCFC-141b rate constant over the past six years. The HCFC-141b story is exemplary because of the wide range of experimental techniques which have been applied and the difficulties encountered in the measurement of a small OH rate constant.

The rate constant data for the OH + HCFC-141b reaction is summarized chronologically in Table 3, and shown in Fig. 4. The first measurements of the rate constant were reported

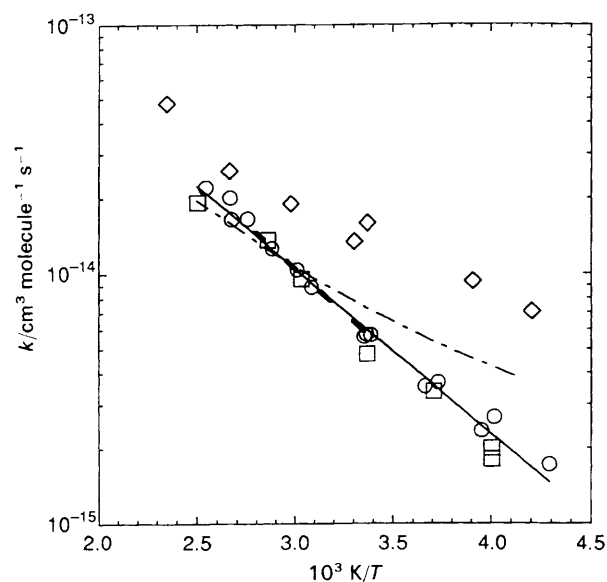


Fig. 4 Summary of the rate coefficients measured for the OH + HCFC-141b reaction as a function of temperature; (◇) ref. 19, (○) ref. 29, (□) ref. 34, (△) ref. 27. The solid line is a fit to the data of Talukdar *et al.*²⁹ and Zhang *et al.*³⁴

Table 3 Measured values of the rate coefficients for the reaction of OH with HCFC-141b

$k(298\text{ K})^a$	A^b	E/R (K)	T range (K)	method	ref.
16.3 ± 5.6	5.8	1100 ± 250	238–426	DF–RF	19
7.0 ± 1.2	3.6 ± 1.1	1140 ± 210	243–400	FP–RF	32
5.9 ± 0.5	14.7 ± 3.2	1640 ± 100	253–393	DF–LMR and FP–LIF	29
6.1	14.2 ± 6.0	1623 ± 293	250–400	FP–RF	34
5.9	14	1630	298–358	chamber	27

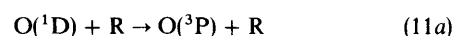
All quoted errors are those from the authors. ^a Rate coefficients in the units of $10^{-15}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$, $k(T) = A \exp(-E/RT)$. ^b In units of $10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$

by Brown *et al.*¹⁹ and Liu *et al.*³² who employed the DF–resonance fluorescence and the FP–resonance fluorescence techniques, respectively. Liu *et al.*³² noted an upward curvature in the Arrhenius plot of the $\ln k$ vs. $1/T$ at low temperature and reported a room-temperature rate constant which was one half the value reported by Brown *et al.* Early experiments in our laboratory reported similar curvature in the Arrhenius analysis.³³ This curvature has been attributed to the presence of CH_2CCl_2 as an impurity at the 1000 ppmv level in the CH_3CFCl_2 sample.²⁹ The $\text{OH} + \text{CH}_2\text{CCl}_2$ rate constant is large ($k_{298} \approx 1 \times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ at the pressures employed) and exhibits a slight negative temperature dependence. The $\text{OH} + \text{HCFC}$ and HFC rate constants are generally small and the reactions have large activation energies ($E/R = 1000\text{--}2000\text{ K}$). Therefore, at low temperatures the relative contribution of the impurity reaction to OH loss increases, leading to upward curvature in the Arrhenius plot. Gas chromatographic analysis of the HCFC-141b sample identified CH_2CCl_2 as an impurity, which is a starting material in the synthesis of HCFC-141b. Talukdar *et al.*²⁹ measured the $\text{OH} + \text{HCFC-141b}$ rate constant with highly purified HCFC-141b samples and obtained a slightly lower rate constant at room temperature and significantly reduced curvature in the Arrhenius plot. Careful studies of the dependence of the measured rate constant on the energy of the flash lamp used to photolyse H_2O ($\text{H}_2\text{O} + h\nu \rightarrow \text{OH} + \text{H}$) demonstrated that photolysis of the reactant CH_3CFCl_2 generated radicals which react with OH. Talukdar *et al.* avoided this complication by photolysing HONO at 355 nm to generate OH. A re-measurement of the rate constant by Zhang *et al.*³⁴ (same group as Liu *et al.*) in which the potential systematic problems, especially those involved with the reactions of OH with the photo-fragments of HCFC-141b, were carefully addressed, produced a result in very good agreement with the work of Talukdar *et al.* These results were confirmed by Huder and DeMore²⁷ who used a relative rate technique. This is an important confirmation because the relative rate technique is not prone to interferences from impurities which plagued the early OH kinetic measurements. In the relative technique, OH is generated by the continuous photolysis of ozone at 254 nm in the presence of water [$\text{O}_3 + h\nu \rightarrow \text{O}(^1\text{D}) + \text{O}_2$; $\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH}$], and the loss of the HCFC is monitored relative to the loss of CH_4 and CH_3CCl_3 for which the OH rate constants are well established. This technique is complementary to the OH-monitoring methods because the decay of the HCFC reactant is analysed directly, and the presence of impurities should not influence the measurement. The Wayne group³⁵ has since carefully analysed their system and deduced that the problem associated with their earlier measurements was due to heterogeneous reactions. They confirm that the lower rate constants measured by Talukdar *et al.*, Zhang *et al.*, and Huder and DeMore are the more accurate values. This historical accounting shows why measurement of these rates coefficients is very time-consuming and how different systematic errors

lead to erroneous results. It has probably taken more than ten person-years of effort to establish this rate coefficient! Of course, such efforts are justified because of the policy implications of the results.

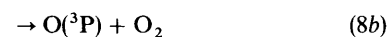
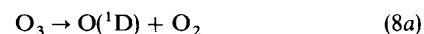
Measurement of $\text{O}(^1\text{D})$ Rate Constants

The $\text{O}(^1\text{D})$ reactions proceed by several channels.

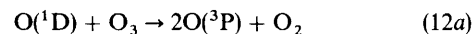


Channel (a) represents physical quenching of the electronic energy of the excited atom. It is assumed that the electronic energy released by the quenching process (*ca.* 45 kcal mol⁻¹) does not fragment the reactant. Channel (b) represents all reactive channels where bonds are broken and/or formed. In order to evaluate the importance of the $\text{O}(^1\text{D})$ reaction in the atmospheric degradation of the replacement compounds, the rate constant for the reactive channel (b) is needed.

The rate constants for the reactive channel in the $\text{O}(^1\text{D})$ reaction with the replacement compounds have been measured by several investigators using different techniques.^{36–39} In our laboratory, we have used the pulsed photolysis–time-resolved vacuum UV atomic resonance fluorescence technique.⁴⁰ Electronically excited O atoms are produced by the pulsed excimer laser photolysis of ozone at 248 and 308 nm.



The quantum yield for $\text{O}(^1\text{D})$ production is 0.9 at 248 and 0.7 and 308 nm.⁴¹ The temporal evolution of the ground-state oxygen atom is monitored by resonance fluorescence excited by a cw atomic fluorescence lamp at *ca.* 130 nm. The kinetics of reaction (11) are studied by monitoring the evolution of the ground-state O atom [$\text{O}(^3\text{P})$] produced in the quenching process and by the reaction of $\text{O}(^1\text{D})$ with O_3



The rate constant of the reactive channels (11b) of the $\text{O}(^1\text{D}) + \text{HCFC}$ and HFC reactions are determined by measuring the total rate constant for the loss of $\text{O}(^1\text{D})$ and the yield for the quenching step (11a). The rate constant for the total loss of the reactant is extracted from the temporal evolution of the $\text{O}(^3\text{P})$ product. The yield for the quenching channel is determined by comparing the $\text{O}(^3\text{P})$ resonance fluorescence signal in the presence of the reactant and in the presence of a very efficient non-reactive quencher (N_2) which converts all of the $\text{O}(^1\text{D})$ to $\text{O}(^3\text{P})$. The details of the data analysis are presented by Warren and Ravishankara.⁴²

The $\text{O}(^1\text{D})$ reactions with HCFCs are fast [$k_{11} = (0.9\text{--}2.6) \times 10^{-10}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$] and proceeded predominantly via reaction [channel (11b) yield = 70–80%].⁴² The HFC

reactions are also efficient [$k_{11} = (0.5-2.0) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$] but proceed predominantly *via* quenching of the O(¹D) [channel (11b) yield < 50%].⁴² Preliminary experiments in our laboratory also indicate that the yield of OH in the O(¹D) + HCFC and HFC reactions is small. Therefore, formation of ClO when possible, and insertion into the C—C bond appear to be significant.

Measurement of UV Absorption Cross-sections

The CFC substitutes which contain only carbon, hydrogen, and fluorine (HFCs) absorb strongly only in the VUV region of the spectrum and photolysis is not an important atmospheric removal mechanism for these compounds. The HCFCs, which contain the chlorine chromophore, usually have significant absorption in the ultraviolet region. Compounds with more chlorine atoms have larger absorption cross-sections at $\lambda > 180 \text{ nm}$, and compounds with more Cl atoms per C atom have absorption spectra that are further red shifted. Photolysis can be an effective atmospheric loss process for an HCFC molecule if it absorbs in the wavelength region above 290 nm with cross-sections greater than *ca.* $10^{-23} \text{ cm}^2 \text{ molecule}^{-1}$. These weak absorption cross-sections, which decrease monotonically with increasing wavelength, usually decrease with decreasing temperature. Therefore, for atmospheric purposes, the temperature dependences of the cross-sections need to be determined accurately. Cross-section measurements have been carried out for the HCFCs and HFCs by a large number of groups. Details of the measurement methodology can be found in papers from our group,⁴³ Molina *et al.*,⁴⁴ Simon and co-workers,⁴⁵ and NIST.⁴⁶ In practice, there are difficulties encountered in measuring small cross-sections. Possible problems include the presence of impurities, condensation on windows, variation in the refractive index matching between the cell window and the gas and lack of precision in measuring small absorptions. Readers are referred to the articles mentioned above for further details.

Other Atmospheric Reactions

In addition to photolysis and the reactions with species such as OH and O(¹D), several other atmospheric-loss processes, including reactions with halogen atoms, NO₃, and halogen oxides, should be considered. The reactions of NO₃ with HCFCs and HFCs have been found to be extremely slow⁴⁷ and are probably not important in either the troposphere or the stratosphere. The halogen oxides are also unlikely to be reactive with the rather strongly bound HFCs and HCFCs. Below, we discuss the possible roles of Cl atom reactions and Lyman- α photolysis.

Reactions of Cl Atoms

Reactions with Cl atoms in the troposphere and lower stratosphere have been largely ignored as a removal process for HFCs and HCFCs because there are no well established sources of Cl in the troposphere, unlike the case of the OH radical. However, it has been postulated that significant concentrations of chlorine atoms may be present in the troposphere due to the liberation of photo-labile NOCl from the heterogeneous reaction of N₂O₅ with NaCl in sea salt aerosols⁴⁸ and other processes.⁴⁹ Some Cl atoms may also be produced by the reaction of OH with HCl in the troposphere.^{50,51} In this case, if Cl atoms react rapidly with HCFCs, the lifetimes of HCFCs would be lower than the current estimates. To assess this possibility, the rate coefficients for the reactions of Cl atoms with HFCs and HCFCs

have been measured.^{42,52-55} These studies show that the reactivity of Cl with the partially halogenated ethanes is similar to that of OH radicals. In the troposphere, where most of the HCFCs are degraded, the concentrations of Cl atoms must be at least 10 times smaller than that of the OH radical. This assertion comes from detailed analyses of the methane budget and vertical profiles of some organic compounds and is too complex to recount here. Therefore, the reactions of the HFCs and HCFCs with Cl cannot compete with the OH reactions in the troposphere. If Cl atom concentrations in the marine boundary layer are comparable to OH due to high sea salt aerosol concentrations, the atmospheric lifetimes of the HFCs and HCFCs would still not be greatly affected by Cl atom reactions, because of the small volume of the marine boundary layer compared to the rest of the troposphere. The concentrations of Cl atoms in the stratosphere ($\leq 10^5 \text{ cm}^{-3}$) could be larger than in the troposphere. However, HCFCs with two chlorine atoms on the same carbon atom are mostly destroyed *via* photolysis in the stratosphere. Other HCFCs react with OH. We conclude that the reactions of HCFCs with Cl are not an important loss process for HCFCs in the atmosphere. It is possible that the Cl atom reactions contribute to the degradation of some HFCs in the stratosphere because of the slow HFC photolysis rates. However, it is unlikely to be more important than their reactions with OH. It is interesting to note, however, that in the future the stratosphere concentrations of Cl should decrease with the elimination of CFCs.

Lyman- α Photolysis

The perfluorocarbons (PFCs, C_xF_y) are an example where none of the traditional reactions (see Table 2) are effective loss processes.^{30,56} The PFCs do not react with OH, their interaction with O(¹D) proceeds mainly *via* quenching of O(¹D), they do not absorb radiation below *ca.* 130 nm, they are water insoluble and they are most probably biologically inactive. The most likely degradation path for these molecules is photolysis in the upper stratosphere and lower mesosphere by the weak Lyman- α radiation at 121.6 nm. Some of these molecules may also be lost *via* reactions with ions and thermal electrons in the mesosphere. For some of the perfluorinated compounds, *e.g.* CF₄ and C₂F₆, even Lyman- α photolysis is not a likely degradation pathway. Destruction in combustion systems is probably the most important loss mechanism for these compounds. Lyman- α photolysis may be a significant sink for the HFC-23, CHF₃, which is unreactive and has a long atmospheric lifetime of *ca.* 400 years (neglecting Lyman- α photolysis). If CHF₃ absorbs Lyman- α radiation strongly, its lifetime may be *ca.* 10% lower.

Estimation of Atmospheric Lifetimes

As mentioned at the outset, most atmospheric lifetimes are calculated by using numerical models which include atmospheric motions and chemistry. These calculations require accurate rate data for the major loss processes in addition to a thorough knowledge of the spatial and temporal distribution of the reactive species, solar flux, *etc.* In general, the spatial distributions of the reactive species are only known from modelling exercises and the temporal variations are averaged for lifetime calculations.

Without direct measurements of the concentrations of the reactive species which determine the lifetimes of compounds added to the atmosphere, it is difficult to assess the accuracy of the calculated lifetimes. Fortunately, the majority of the HFCs and HCFCs are removed by reactions with OH and

Table 4 Approximate atmospheric lifetimes, ozone depletion potentials, and global warming potentials for currently-considered CFC-substitutes

molecule	No. of Cl atoms	m /g mol ⁻¹	τ /years	ODP	GWP
CHClF ₂ (HCFC-22)	1	86	15	0.05	510
CH ₂ F ₂ (HFC-32)	0	52	6	0	180
CHF ₃ (HFC-23)	0	70	ca. 400	0	8000
CFCl ₃ (CFC-11)	3	136	66	1	1400
CF ₂ Cl ₂ (CFC-12)	2	120	104	0.9	4500
CH ₃ CCl ₃ (MCF)	3	132	6	0.15	34
CF ₃ CHFCl (HCFC-124)	1	136	8	0.02	150
CH ₃ CF ₂ Cl (HCFC-142b)	1	100	25	0.06	540
CF ₃ CHCl ₂ (HCFC-123)	2	152	1.7	0.01	30
CH ₃ CFCl ₂ (HCFC-141b)	2	116	13	0.13	150
CF ₃ CH ₂ F (HFC-134a)	0	104	18	0	420
CH ₃ CHF ₂ (HFC-152a)	0	68	2	0	50
CH ₃ CH ₂ F (HFC-161)	0	48	0.25	0	4

The lifetime (τ), ODP, and GWP values are approximate. Whenever possible, the quoted lifetimes are those calculated in our laboratory. The GWP values were either calculated using our IR data by Dr. Ramaswamy of NOAA's GFDL or were taken from IPCC.¹⁶ The ODP for HCFC-22 was taken from the AFEAS report.³³

the OH concentration field can be reasonably well defined because of the MCF data and model calculations, as discussed earlier. Note that model calculations can give good relative concentrations of OH in the atmosphere at various locations as functions of time and season. These values are placed on an absolute scale by the MCF lifetime data. In almost all lifetime calculations, the OH concentrations and their temporal and spatial variation, are calculated from measured or estimated abundances of the precursors and photon fluxes using 1-, 2-, or 3-D models. This OH field is then scaled to reproduce the lifetime of MCF (5.7 years). This method does not necessarily lead to the correct OH fields. However, as long as reaction with OH is the important loss process and the activation energies for the OH reactions with the substitute and MCF are approximately the same, the calculated lifetimes should be quite accurate. This is especially true for species with lifetimes longer than *ca.* 2 years. If the lifetime is less than 2 years, the species will not be well mixed in the troposphere. The point of injection then becomes important and one needs to know the spatial distribution of OH, and the MCF-determined OH field is not appropriate. The other factor that makes the MCF-determined OH field applicable to the HFCs and HCFCs is that the reactions of OH with these species have activation energies very similar to that with MCF.⁴¹ This ensures that the location of maximum degradation in the troposphere are the same for both MCF and the compound of interest, *i.e.* the tropical upper troposphere. Readers should refer to the papers by Prather and Spivakovsky⁵⁷ and Prinn *et al.*⁹ for further details on use of MCF-standardized OH concentration fields. It is also worth noting that the impact of species with lifetimes much smaller than 2 years is quite small on either the stratospheric ozone or global warming issues, except in some special cases.

The calculated lifetimes and ODPs of some of the CFC-substitutes are listed in Table 4. It is clear that species which have short atmospheric lifetimes also have small ODPs. A

future. In general, if the GWP of the substitute is not too much greater than that of CFC-11 (or the HGWP ~ 1), it will probably be deemed acceptable.

Should Atmospheric Lifetime be a Measure of Acceptability?

The majority of species emitted by natural processes into the atmosphere have lifetimes of less than a few years. The hydrocarbons emitted from trees, for example, live for a few hours or possibly a few days. Methane, which has significant natural sources, has an atmospheric lifetime of about 10 years. CO₂ and N₂O are exceptionally long-lived natural emissions which have lifetimes of nearly a century. The main sink for CO₂ is conversion into carbonates in the oceans while N₂O is removed primarily by photolysis in the stratosphere. All the natural species are short-lived compared to some of the compounds produced by humans. The most stable gases emitted by humans appear to be the perfluoro compounds. These molecules, which are very potent greenhouse gases, have atmospheric lifetimes of thousands of years. As mentioned earlier, the time it takes to cleanse the atmosphere increases proportionately with the atmospheric lifetime. Therefore, even though there may be no currently identified harm to the atmosphere due to the emissions of a very long-lived species, one cannot be certain that they are benign. When CFCs were invented and released into the atmosphere, their deleterious effects were not known. Fortunately, CFCs are relatively short lived, compared to PFCs, and it will take only about a century for CFCs to be removed from the atmosphere once their emissions are curtailed. The release of any very long-lived species in the atmosphere should be viewed with the greatest concern. The PFC lifetimes, though long on historical timescales, are short compared to the evolutionary timescales. Hence, life on Earth may not be able to adopt to the changes these emissions may cause. Thus, it seems prudent to ask if the long-lived molecules must be considered 'inert' and are thus benign.

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