

CHAPTER 12

Atmospheric Degradation of Halocarbon Substitutes

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CHAPTER 12

ATMOSPHERIC DEGRADATION OF HALOCARBON SUBSTITUTES

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SCIENTIFIC SUMMARY

The substitutes for long-lived halocarbons have been selected on the basis of either their susceptibility to oxidation in the lower part of the atmosphere and minimization of their transport to the stratosphere, or by absence of chlorine or bromine from the molecules. It has been assumed that the atmospheric degradation of the substitutes leads to products that do not cause ozone loss. Further, it is assumed that the degradation products have no other deleterious environmental effects.

These assumptions are examined in this chapter by assessing three aspects of chlorofluorocarbon (CFC) and halon substitutes: the factors that control their atmospheric lifetimes, the processes by which they are degraded in the atmosphere, and the nature of their degradation products. The main findings are:

- If a substance containing Cl, Br, or I decomposes in the stratosphere, it will lead to ozone destruction. Use of hydrochlorofluorocarbons (HCFCs) and other CFC substitutes containing Cl, Br, or I, which have short tropospheric lifetimes, will reduce the input of ozone-destroying substances to the stratosphere, leading to reduced ozone loss.
- None of the proposed CFC substitutes that are degraded in the troposphere will lead to significant ozone loss in the stratosphere via their degradation products.
- It is known that atomic fluorine itself is not an efficient catalyst for ozone loss and it is concluded that the F-containing fragments from the substitutes (such as CF_3O_x) also do not destroy ozone.
- Trifluoroacetic acid, formed in the degradation of certain HCFCs and hydrofluorocarbons (HFCs), will partition into the aqueous environment where biological, rather than physico-chemical, removal processes may be effective.
- The amount of long-lived greenhouse gases formed in the atmospheric degradation of HCFCs and HFCs appears to be insignificant.
- Certain classes of compounds, some of which have already been released to the atmosphere, such as perfluorocarbons, have extremely long atmospheric lifetimes and large global warming potentials.

12.1 BACKGROUND

Chlorofluorocarbons (CFCs) and halons deplete stratospheric ozone because of their long atmospheric lifetimes, allowing them to be transported to the stratosphere where they release chlorine and bromine, resulting in catalytic destruction of ozone. The substitute molecules have been selected on the basis of either their shorter tropospheric lifetime due to their susceptibility to oxidation in the lower part of the atmosphere and minimization of their transport to the stratosphere or, in some cases, by absence of chlorine or bromine from the molecules. It has been assumed that the atmospheric degradation of the substitutes leads to products that have lifetimes shorter than transport times for delivery of chlorine or bromine to the stratosphere. Further, it is assumed that the degradation products have no other deleterious environmental effects.

The purpose of this chapter of the 1994 WMO/UNEP assessment is scientific evaluation of the above assumptions concerning the substitute molecules. The following lead questions will be addressed:

- 1) Is significant ozone-destroying halogen released in the stratosphere from the substitute molecules themselves?
- 2) Is significant ozone-destroying halogen transported into the stratosphere from the degradation products formed in the troposphere?
- 3) Are ozone-depleting catalysts other than Cl or Br released in the stratosphere?
- 4) Are there any products formed that have other potential environmental impacts?

These questions are answered by examining three aspects of CFC and halon substitutes: the factors that control their atmospheric lifetimes, the processes by which they are degraded in the atmosphere, and the nature and behavior of their degradation products.

The atmospheric lifetime is the critical parameter required for the calculation of the Ozone Depletion Potential (ODP) and Global Warming Potential (GWP) of the substitutes, as discussed in Chapter 13 of this document. For the most part, these lifetimes are calculated from models using laboratory data. The accuracy of the calculated lifetimes, ODPs, and GWPs reflects the uncertainties in the laboratory data and in the models, *i.e.*, the treatment of transport, heterogeneous chemistry, etc. Here, the hydrofluorocarbons (HFCs) and hydrochloro-

fluorocarbons (HCFCs), the largest classes of replacements proposed to date, are treated first. Then, other replacements, which do not fall into one single category, are discussed.

12.2 ATMOSPHERIC LIFETIMES OF HFCs AND HCFCs

The atmospheric lifetimes of all the HFCs and HCFCs are determined by the sum of their loss rates in the troposphere and in the stratosphere. The processes responsible for their losses in these two regions are slightly different and, hence, are discussed separately.

12.2.1 Tropospheric Loss Processes

The major fraction of the removal of HFCs and HCFCs occurs in the troposphere. Their reactions with the hydroxyl (OH) radical have been identified as the predominant tropospheric loss pathways. Reactions of HFCs and HCFCs, which are saturated hydrocarbons, with tropospheric oxidants such as NO₃ (Haahr *et al.*, 1991) and O₃ (Atkinson and Carter, 1984) are very slow and, hence, unimportant. Physical removal (*i.e.*, dry and wet deposition) of these compounds is negligibly slow (WMO, 1990).

The evaluated rate coefficients for the reaction of OH with the HFCs and HCFCs considered here are those recommended by the National Aeronautics and Space Administration (NASA) Panel (DeMore *et al.*, 1992). This Panel has reviewed the changes in the data base since the last evaluation. None of the changes affects significantly the calculated lifetimes and ODPs. References have been given where new data have been used.

In addition to their reaction with OH, these molecules may be removed from the troposphere via reaction with chlorine atoms (Cl). The rate coefficients for the reactions of Cl with a variety of HFCs and HCFCs have been measured and found to be of the same order of magnitude as the rate coefficients for their OH reactions (DeMore *et al.*, 1992; Atkinson, *et al.*, 1992; Tuazon *et al.*, 1992; Wallington and Hurley, 1992; Sawerysyn *et al.*, 1992; Warren and Ravishankara, 1993; Thompson, 1993). Because the global tropospheric concentration of Cl is likely to be less than 1% of that of OH, the only effect of Cl atom reactions is the small reduction of atmospheric lifetimes; the products of reaction are similar

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to those from OH reactions. The contributions of Cl reactions would be at most a few percent of those due to OH reactions. Loss by Cl atom reaction will only reduce the lifetimes in the atmosphere and the products of the reactions are similar to those from the OH reactions.

12.2.2 Stratospheric Loss Processes

In addition to the reactions of OH free radicals, the HFCs may be removed from the stratosphere by their reaction with O(¹D) atoms. In the case of HCFCs and brominated compounds, ultraviolet (UV) photolysis can also be important. The sum of the rates of these three processes, *i.e.*, OH reaction, O(¹D) reaction, and UV photolysis, determines where and how rapidly these molecules release ozone-depleting species in the stratosphere. In addition, the removal in the stratosphere also contributes to the overall lifetimes of these compounds.

The rate coefficients for the reaction of O(¹D) with the HFCs and HCFCs have been evaluated by the NASA and International Union of Pure and Applied Chemistry (IUPAC) Panels (DeMore *et al.*, 1992; Atkinson *et al.*, 1992). Inclusion of these reactions is unlikely to substantially reduce the calculated atmospheric lifetimes of these species. The UV absorption cross sections needed for these calculations have been reviewed previously (WMO, 1990; Kaye *et al.*, 1994) and there are no new data that need to be considered here. In general, HCFCs must have at least two Cl atoms for photolytic removal in the stratosphere to be competitive with OH reaction. The reactions of O(¹D) are important only for species with lifetimes longer than a few decades, *i.e.*, for molecules such as HFC-23.

12.3 ATMOSPHERIC LIFETIMES OF OTHER CFC AND HALON SUBSTITUTES

In addition to the HFCs and HCFCs, many other substitutes for CFCs have been considered for use and evaluated for their environmental acceptability. They include the fluoroethers, perfluorocarbons (PFCs), sulfur hexafluoride (SF₆), and trifluoromethyl iodide (CF₃I). The PFCs and SF₆ are very long-lived species with strong infrared absorption characteristics. Thus they can be efficient greenhouse gases. On the other hand CF₃I is very short-lived. Yet, iodine in the stratosphere can be even more efficient than bromine in destroying ozone and hence is of concern.

The rate coefficients for reactions of OH and O(¹D) reaction with the fluoroethers have not so far been reported. The H-containing fluoroethers are expected to have reactivity with OH comparable to the HFCs, and therefore their lifetimes will be similar due to tropospheric degradation. The ether functional group does not make photolysis an important loss process.

The major loss process for the PFCs, other than CF₄ and C₂F₆, appears to be their photolysis in the upper stratosphere and the mesosphere by the Lyman- α (121.6 nm) radiation (Cicerone, 1979; Ravishankara *et al.*, 1993). The absorption cross sections at this wavelength, needed for this evaluation, are given by Ravishankara *et al.* (1993). Reaction with O(¹D) atoms has been shown to be unimportant as a loss process for the PFCs. In the case of some PFCs, such as the perfluorocyclobutane, their reactions with ions in the ionosphere may also contribute (Morris *et al.*, 1994).

CF₄ and C₂F₆ are already present in the atmosphere as by-products of aluminum production. Their loss processes through reaction with atmospheric ions are slower than the heavier PFCs, giving lifetimes in excess of 300,000 years. The ion-molecule reactions are the only identified loss processes for CF₄ and C₂F₆; however, their breakdown in air used in combustion could shorten the lifetimes of CF₄ and C₂F₆ to 50,000 years and 10,000 years, respectively (Morris *et al.*, 1994).

Another long-lived compound is SF₆, for which the major loss processes appear to be Lyman- α photolysis and electron attachment. Since it is not clear if SF₆ is removed in the latter process, the estimated lifetime of 600 years is a lower limit.

CF₃I has been considered as a substitute for halons and CFCs. The major atmospheric loss process for this molecule, as with all organic-iodine compounds, appears to be photolysis in the troposphere (Solomon *et al.*, 1994). This process leads to an average atmospheric lifetime of only a few days. Other loss processes, such as reaction with OH, are unlikely to compete with the photolytic removal of CF₃I and can only marginally decrease the lifetime, even if they are very rapid.

The chemistry of iodine in the troposphere has been described by Chameides and Davis (1980), Jenkin *et al.* (1985), and more recently by Jenkin (1993), who made use of the expanded kinetic data base that has been evaluated by the IUPAC panel (Atkinson *et al.*, 1992). Recently Solomon *et al.* (1994) have considered the

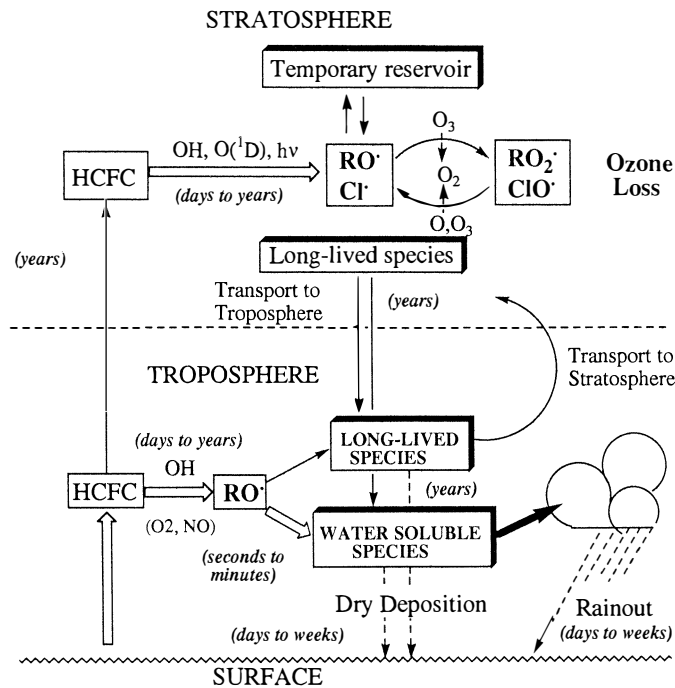


Figure 12-1. Atmospheric degradation of HCFCs, HFCs, and other CFC substitutes. The time scales for the different processes involving transport and chemistry are given in italics.

impact of iodine compared to chlorine and bromine on stratospheric ozone. They show that iodine is likely to be at least as effective as bromine for ozone destruction, and they note that several key chemical processes relating to iodine-catalyzed ozone destruction, notably $\text{IO} + \text{ClO}$, $\text{IO} + \text{BrO}$ and $\text{IO} + \text{O}_3$, have not yet been quantified in laboratory studies. These factors are taken into account in calculating the ODP for CF_3I in Chapter 13.

The data base needed for the calculation of the lifetimes of halons and their possible bromine-containing substitutes has been evaluated in the past assessments (WMO, 1990, 1992) and there are no significant changes in this data base.

12.4 ATMOSPHERIC DEGRADATION OF SUBSTITUTES

A general flow diagram of the degradation of the HFCs and HCFCs is shown in Figure 12-1, which shows the approximate time scales for various processes. A key question is: Could the degradation products of the substitutes generate species that can destroy ozone in the

stratosphere? If long-lived chlorine-containing species are produced, they can be transported into the stratosphere from the troposphere. In such a case, the assumption that degradation in the troposphere essentially stops transport of chlorine or bromine to the stratosphere would be erroneous. Similarly, if ozone-destroying radicals other than chlorine are released from degradation products, erroneous ODPs will result. If long-lived greenhouse gases are produced, their impact on climate forcing becomes an issue, with potential feedback to the ozone depletion problem.

Laboratory studies to elucidate the atmospheric degradation mechanisms and numerical atmospheric model calculations have been carried out. The laboratory studies include analysis of the end products in air and direct measurements of the rate coefficients and products for some of the key reactions. From these studies, it appears that the slowest step in the conversion of HFCs and HCFCs to their ultimate stable products (such as CO_2 , H_2O , HF , HCl , and in some cases, other products such as trifluoroacetic acid) is the initiation by reaction with OH . The time scale for this process ranges from

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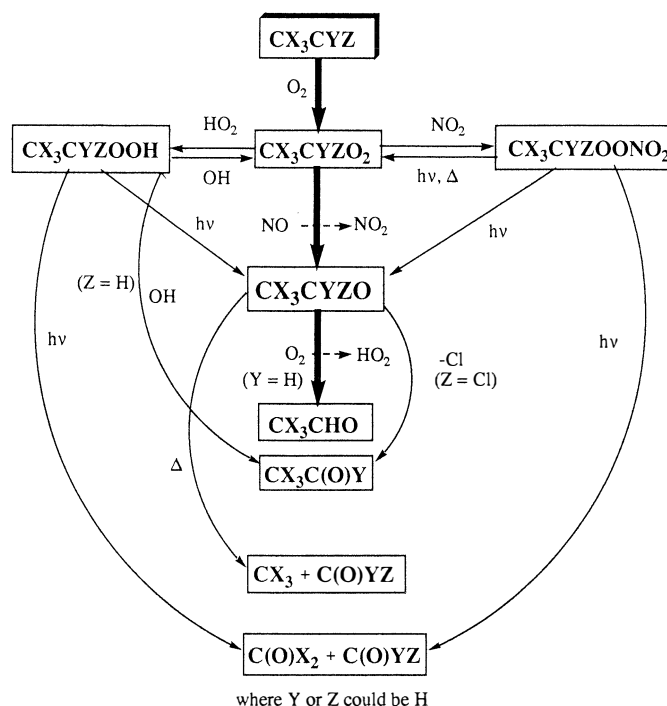


Figure 12-2. Generalized atmospheric degradation scheme for CX_3CYZ radicals. X, Y, and Z may be F, Cl, Br, or H, $h\nu$ indicates photolysis; Δ indicates thermal decomposition. Reactant species are indicated on arrows.

weeks, for the shortest-lived substitutes, to hundreds of years for the long-lived ones. In some cases, such as with CF_4 and C_2F_6 , where the normal degradation processes are inoperative, lifetimes are even longer, while CF_3I is removed by photolysis in a time scale of a few days. The subsequent chemistry that leads to breakdown is very rapid. However, the formation of shorter-lived, but potentially important atmospheric species needs to be considered. The overall degradation of all the HFCs and HCFCs and CF_3I appears to go through the formation of the haloalkoxy (RO) radical. There are two special reasons for the importance of the RO radical formation. It can potentially lead to destruction of ozone in the stratosphere, via reactions of species such as CF_3O and $FC(O)O$, and in addition RO can lead to the formation of semi-stable species that are sufficiently long-lived to be transported into the stratosphere. If such a species contains an ozone-destroying Cl atom (or CF_3 group), the Ozone Depletion Potentials of the starting HCFCs or HFCs would be larger than that calculated by ignoring this transport. In addition, the reactions of

the RO radical lead to the formation of water-soluble end products. Finally, it has been hypothesized that reactions of oxygen with CF_3O and $FC(O)O$ could potentially lead to destruction of O_3 in the stratosphere.

The “broad-brush” picture of the degradation, shown in Figure 12-1, will be discussed in detail in the following sections. This picture shows where in the degradation scheme the above questions arise. Research carried out during the past few years has addressed these issues and is discussed below.

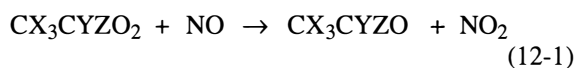
12.5 GAS PHASE DEGRADATION CHEMISTRY OF SUBSTITUTES

In the atmosphere, photolysis or OH radical reaction (H-atom abstraction from a haloalkane, or OH radical addition to a haloalkene) leads to the formation of haloalkyl peroxy radicals (WMO, 1990, 1992). The general degradation scheme, after formation of the haloalkyl radical, is shown in Figure 12-2 and is applicable to both the troposphere and stratosphere, and leads to the

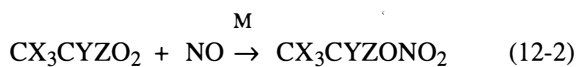
formation of the carbonyls $C(O)X_2$, $C(O)XY$, CX_3CHO , and $CX_3C(O)Y$ from the $CX_3C(Y)Z$ radical. There are differences between the degradation of the carbonyls in the troposphere and stratosphere caused by (a) the importance of physical loss processes of carbonyls in the troposphere and (b) increased intensity of short-wavelength UV radiation in the stratosphere, leading to increased importance of photolysis of carbonyl compounds in the stratosphere.

12.5.1 Reaction with NO

Rate constants for the reactions of a number of haloalkyl peroxy radicals with NO have been measured (Wallington and Nielsen, 1991; Peeters and Pultau, 1994; Atkinson *et al.*, 1992; Sehested *et al.*, 1993). The reactions are expected to produce NO_2 and the haloalkoxy radical, RO:



and, to date, there is no evidence for the formation of the nitrates via the pathway:



In any case, photolysis of the haloalkyl nitrates is expected to occur with a close to unit quantum yield by breakage of the O- NO_2 bond (Atkinson *et al.*, 1992) to produce the haloalkoxy radical, RO.

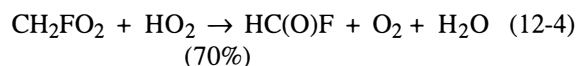
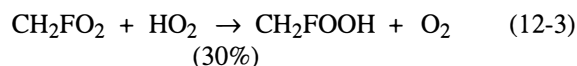
12.5.2 Reaction with NO_2

The reactions of haloalkyl peroxy radicals with NO_2 have been evaluated by Atkinson *et al.*, (1992). These reactions lead to the formation of peroxy nitrates $CX_3CYZOONO_2$.

12.5.3 Reaction with HO_2 Radicals

Rate constants for reaction with the HO_2 radical have been measured for $CF_2ClCH_2O_2$ and CF_3CHFO_2 radicals (Hayman, 1993), and a product study has been conducted for the CH_2FO_2 radical reaction (Wallington *et al.*, 1994a). The two measured rate constants are similar to those determined for the methyl and ethyl peroxy radicals. However, Wallington *et al.* (1994a) have

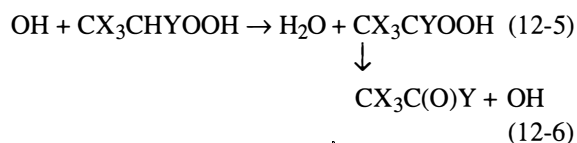
shown that the HO_2 radical reaction with CH_2FO_2 proceeds by two channels at room temperature:



As shown in Figure 12-2, this second reaction channel bypasses the intermediate formation of the haloalkoxy radical, but forms the same carbonyl product.

12.5.4 Hydroperoxides

As discussed in WMO (1992), the hydroperoxides $CX_3CYZOOH$ are expected to undergo photolysis, reaction with the OH radical, and (in the troposphere) wet deposition. Photolysis leads to formation of the alkoxy radical CX_3CZYO plus OH or possibly to $X + CX_2CZYOOH$ for $X = Br$ and I . OH radical reaction will lead to reformation of the haloalkyl peroxy radical CX_3CYZO_2 . For hydroperoxides of the structure $CX_3CYZOOH$ with $Z = H$, OH reaction also yields $CX_3C(O)Y$:



To date, kinetic and photochemical data are only available for methyl hydroperoxide and *tert*-butyl hydroperoxide (OH reaction rate constant only) and, based on these limited data, the haloalkyl hydroperoxides are expected to have tropospheric lifetimes of a few days and hence a very low potential for transporting Cl or Br into the stratosphere.

The fate of $CX_3CYZOOH$ in aqueous solution needs to be investigated. In particular, any transformation to yield a long-lived species (for example CX_3H or CX_3Z), that is desorbed from solution back into the gas phase may be important.

12.5.5 Haloalkyl Peroxynitrates

As discussed in WMO (1992) and the IUPAC evaluation (Atkinson *et al.*, 1992), the haloalkyl peroxynitrates thermally decompose back to the peroxy radical and NO_2 (Figure 12-2). The thermal decomposition rates of

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the peroxy nitrates ROONO_2 , where $\text{R} = \text{CF}_2\text{Cl}$, CFCl_2 , CCl_3 , CF_2ClCH_2 , and CFCl_2CH_2 , have been measured (Köppenkaströp and Zabel, 1991; Kirchner *et al.*, 1991). The lifetimes due to thermal decomposition range from <1 s for the C_2 haloalkyl peroxy nitrates and 3-20 s for the C_1 haloalkyl peroxy nitrates at 298 K, to approximately 2 days for the C_2 haloalkyl peroxy nitrates and 0.1-1 year for the C_1 haloalkyl peroxy nitrates in the upper troposphere and lower stratosphere.

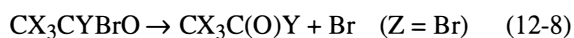
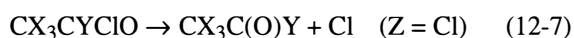
By analogy with CH_3OONO_2 (Atkinson *et al.*, 1992), the haloalkyl peroxy nitrates are also expected to undergo photolysis in the troposphere, with lifetimes of a few days, and transport of the haloalkyl peroxy nitrates to the stratosphere will be insignificant.

Hence, apart from those reaction paths noted above and shown in Figure 12-2, the tropospheric degradation reactions of the HCFCs and HFCs funnel through the formation of the haloalkoxy radical, and the tropospheric reactions of the RO radicals then determine tropospheric degradation products formed from the HCFCs and HFCs (WMO, 1990, 1992).

12.5.6 Reactions of Haloalkoxy Radicals

There are three potential reaction paths for the haloalkoxy radicals formed from the HCFCs, HFCs and halons:

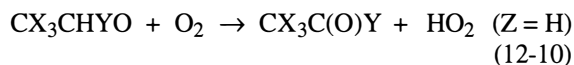
C-Cl or C-Br bond cleavage:



C-C bond cleavage:



H-atom abstraction:



The actual pathway followed and hence the particular carbonyl product formed depend on the nature of X, Y, and Z.

12.5.7 Halogenated Carbonyl Compounds

Halogenated carbonyl compounds are produced from the atmospheric degradation of all halocarbons,

including CFCs, HCFCs, HFCs, halons, and the halogenated aldehyde intermediates. The carbonyls fall into the following categories:

Carbonyl halides	C(O)X_2	(X = F or Cl)
Formyl halides	HC(O)X	(X = F, Cl, or Br)
Acetyl halides	$\text{CX}_3\text{C(O)Y}$	(Y = F or Cl and X = H, F, Cl, or Br)
Organic acids	$\text{CX}_3\text{C(O)OH}$	(X = H, F, Cl, or Br)
Aldehydes	$\text{CX}_3\text{C(O)H}$	(X = H, F, Cl, or Br)

The fate of these carbonyl compounds is dependent on whether they are generated in the troposphere or in the stratosphere. Removal in the stratosphere is largely dominated by photolysis, whereas in the troposphere, physical removal and hydrolysis processes may be important relative to photolysis or reaction with the OH radical. Figure 12-2 and Table 12-1 show a summary of the products formed from the tropospheric degradation of HCFCs and HFCs. CF_3 radicals are also formed from several of the HCFCs and HFCs (Table 12-1), and their atmospheric chemistry is considered below.

12.5.8 Aldehydes

In the troposphere, the aldehydes, CX_3CHO , will react with OH radicals and undergo photolysis. The rate constants for the reaction with OH radicals have been determined (Scollard *et al.*, 1993; Atkinson, 1994) and lead to lifetimes in the troposphere of 4-25 days (Scollard *et al.*, 1993). While the absorption cross sections have been measured (Libuda *et al.*, 1991; Rattigan *et al.*, 1991, 1993), the photodissociation quantum yields are not available. Assuming unit quantum yields, the photolysis lifetimes of the halogenated aldehydes and CH_3CHO are calculated to be 1-7 hours. Thus, the aldehydes are likely to have short tropospheric lifetimes, of the order of a few hours to approximately one month, depending on the magnitude of the photodissociation quantum yields.

Assuming a photodissociation quantum yield significantly less than unity, similar to that for CH_3CHO , photolysis of the halogenated aldehydes is still expected to dominate as a tropospheric loss process, leading to C-C bond cleavage.

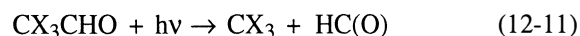


Table 12-1. Carbonyl products formed from the tropospheric degradation reactions of a series of HCFCs and HFCs. (Formation of CF₃ radicals is also noted.)

HCFC or HFC	Chemical Formula	Carbonyl and/or CF ₃	(a)
methyl chloroform	CH ₃ CCl ₃	CCl ₃ CHO	
chloroform	CHCl ₃	C(O)Cl ₂	
methylene chloride	CH ₂ Cl ₂	HC(O)Cl	
HCFC-22	CHF ₂ Cl	C(O)F ₂	
HCFC-123	CF ₃ CHCl ₂	CF ₃ C(O)Cl	
HCFC-124	CF ₃ CHFCl	CF ₃ C(O)F	
HCFC-141b	CFCl ₂ CH ₃	CFCl ₂ CHO	
HCFC-142b	CF ₂ ClCH ₃	CF ₂ ClCHO	
HCFC-225ca	CF ₃ CF ₂ CHCl ₂	CF ₃ CF ₂ C(O)Cl	
HCFC-225cb	CF ₂ ClCF ₂ CHFCl	CF ₂ ClCF ₂ C(O)F	(b)
methyl bromide	CH ₃ Br	HC(O)Br	
HFC-23	CHF ₃	CF ₃	
HFC-32	CH ₂ F ₂	C(O)F ₂	
HFC-125	CHF ₂ CF ₃	C(O)F ₂ + CF ₃	
HFC-134	CHF ₂ CHF ₂	C(O)F ₂	
HFC-134a	CH ₂ FCF ₃	CF ₃ C(O)F	(c)
		HC(O)F + CF ₃	(c)
HFC-143a	CH ₃ CF ₃	CF ₃ CHO	
HFC-152a	CH ₃ CHF ₂	CHF ₂ CHO	
		C(O)F ₂	
HFC-227ea	CF ₃ CHFCF ₃	CF ₃ C(O)F + CF ₃	

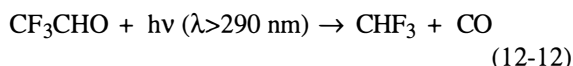
(a) From WMO (1990), Edney *et al.* (1991), Sato and Nakamura (1991), Hayman *et al.* (1991), Jemi-Alade *et al.* (1991), Scollard *et al.* (1991), Edney and Driscoll (1992), Wallington *et al.* (1992), Nielsen *et al.* (1992a, b), Tuazon and Atkinson (1993a, b, 1994), Shi *et al.* (1993), Hayman (1993), Meller *et al.* (1991, 1993), Zellner *et al.* (1991, 1993), Rattigan *et al.* (1994).

(b) ~1% yield of C(O)FCl also observed at room temperature and atmospheric pressure of air (Tuazon and Atkinson, 1994); C(O)F₂ also presumably formed as co-product with C(O)FCl.

(c) CF₃C(O)F and HC(O)F + CF₃ yields are a function of temperature and O₂ concentration (Wallington *et al.*, 1992; Tuazon and Atkinson, 1993a; Rattigan *et al.*, 1994).

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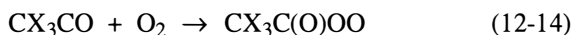
The quantum yield for formation of CHF₃ from CF₃CHO via



is too low to significantly enhance the GWP of the parent compound (Meller *et al.*, 1993).

The OH radical reactions proceed by H-atom abstraction to initiate a series of reactions such as shown in Figure 12-3.

The initially formed acyl radical, CX₃CO, has been shown to either thermally decompose or react with O₂ to form the acyl peroxy radical, CX₃C(O)OO (Barnes *et al.*, 1993; Tuazon and Atkinson, 1994):



There is a monotonic trend towards decomposition, at 298 K and atmospheric pressure of air, with increasing number of Cl atoms in the CCl_xF_{3-x}CO radical (Barnes *et al.*, 1993; Tuazon and Atkinson, 1994). Only for CF₃CO, CF₂ClCO, and CFCl₂CO is the O₂ addition reaction important under atmospheric conditions. This can lead to the formation of the peroxyacylnitrates (CF₃C(O)OONO₂ from HCFC-143a, CF₂ClC(O)OONO₂ from HCFC-142b, and CFCl₂C(O)OONO₂ from HCFC-141b) by adding to NO₂. The alternative reaction pathways with NO or HO₂ lead to loss of the acyl group through formation of RCO₂, which decomposes to R + CO₂.

12.5.9 Peroxyacyl Nitrates

By analogy with peroxyacetyl nitrate and methyl peroxyacetyl nitrate, the thermal decomposition lifetimes of the halogen-containing peroxyacyl nitrates are expected to be significantly longer than those for the haloalkyl peroxyacetyl nitrates, and this expectation is borne out by the data of Barnes *et al.* (1993). Thermal decomposition rates have been measured by Barnes *et al.* (1993) for RC(O)OONO₂, with R = CF₃, CF₂Cl, and CFCl₂.

The calculated thermal decomposition lifetimes of these peroxyacyl nitrates range from approximately 2-3 hours at 298 K (ground level) to 6000-7000 years in the upper troposphere (220 K). By analogy with peroxyacetyl nitrate (Atkinson *et al.*, 1992), photolysis is likely

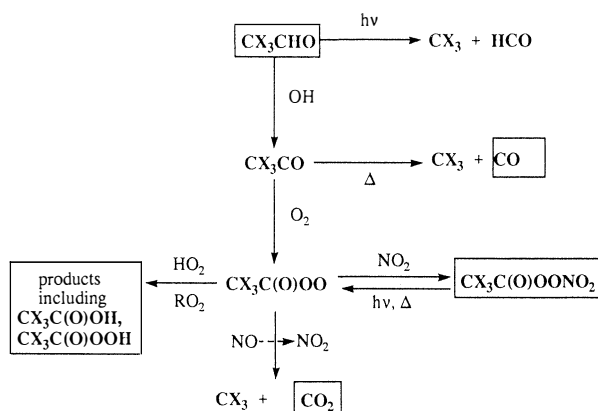


Figure 12-3. Oxidation of aldehydes formed from HCFC and HFC degradation. Stable species are indicated by boxes; x = F or Cl.

to dominate as the loss process in the upper troposphere, while still being slow enough that transport to the stratosphere could be competitive. The potential for transport of chlorine into the stratosphere from CF₂ClC(O)OONO₂ and CFCl₂(O)OONO₂ is discussed later.

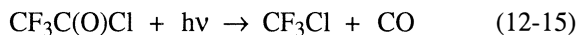
12.5.10 Carbonyl Halides

Carbonyl halides are produced in the stratosphere from degradation of all halocarbons, including CFCs. The photolysis of C(O)FCl and C(O)F₂ is slow in the lower stratosphere and significant amounts of these degradation products are present there, as shown from infrared spectroscopic observation from space (Zander *et al.*, 1992) and from the ground (Reisinger *et al.*, 1994). A fraction of these stratospheric carbonyls is transported back to the troposphere, where efficient physical removal takes place; when chlorine is removed from the stratosphere in this way, *e.g.*, as C(O)FCl or C(O)Cl₂, the ODP of the precursor halocarbons can be reduced because the assumption of complete Cl release in the stratosphere is not valid.

12.5.11 Acetyl Halides

The acetyl halides released in the stratosphere will behave similarly to the carbonyl halides, being removed mainly by photolysis. The available evidence suggests that the quantum yield for formation of fully halogen-

ated compounds, such as CF_3Cl , from photolysis of $\text{CF}_3\text{C(O)Cl}$,

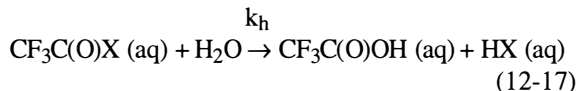
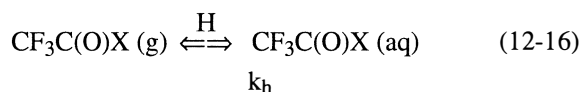


is sufficiently low (Meller *et al.*, 1993) that the ODP of the parent compounds will be increased by <0.01 .

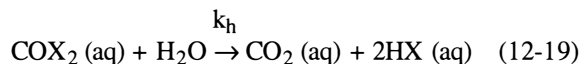
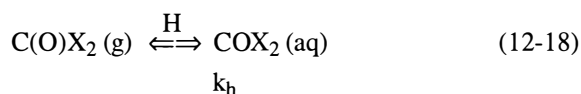
12.6 HETEROGENEOUS REMOVAL OF HALOGENATED CARBONYL COMPOUNDS

The carbonyl halides such as C(O)F_2 , HC(O)F , and C(O)FCl , and acetyl halides, especially $\text{CF}_3\text{C(O)Cl}$ and $\text{CF}_3\text{C(O)F}$, are soluble in water. In aqueous solution they undergo hydrolysis, forming halogenated carboxylic acids or hydrogen halides and carbon dioxide. They are therefore likely to be removed from the troposphere by heterogeneous processes such as rainout or uptake by cloud droplets or surface waters, possibly followed by hydrolysis (Wine and Chameides, 1990).

The rate of these removal processes is governed by the rate of mass transfer of material between the gas and the aqueous phase, the solubility in the liquid phase, which is defined by the Henry's Law constant, H , and the hydrolysis rate constant, k_h .



or



Both H and k_h are required to assess their fate. The Henry's Law constant controls aqueous phase uptake, and the hydrolysis constant the rate of aqueous phase destruction. For instance, if k_h is low, then efficient uptake into cloud droplets might not lead to destruction because most cloud droplets are transient and will evaporate on relatively short time scales, vaporizing unreacted absorbed carbonyl or haloacetyl halides back into the atmosphere.

The uptake coefficients, g , reflect a convolution of all processes at the interface that may influence the effective rate of mass transfer between gas and aqueous phases. If the uptake coefficient is greater than $\sim 10^{-3}$,

the tropospheric uptake rate will not be determined by the uptake coefficient, and removal time would be ~ 1 week. Values of less than $g = 5 \times 10^{-3}$ have been obtained for C(O)Cl_2 , C(O)F_2 , $\text{CCl}_3\text{C(O)Cl}$, $\text{CF}_3\text{C(O)F}$, and $\text{CF}_3\text{C(O)Cl}$ by Worsnop *et al.* (1989), De Bruyn *et al.* (1992a), Edney and Driscoll (1993), Ibusuki *et al.* (1992), and George *et al.* (1993), and hence the removal time of these compounds can be larger than 1 week. Estimated lifetime values are given in Table 12-2.

Trifluoroacetic acid (TFA), $\text{CF}_3\text{C(O)OH}$, is the hydrolysis product of both $\text{CF}_3\text{C(O)F}$ and $\text{CF}_3\text{C(O)Cl}$. Currently it is believed that $\text{CF}_3\text{C(O)OH}$, like other organic acids, is removed from the atmosphere primarily by rainout (Ball and Wallington, 1993; Rodriguez *et al.*, 1993). Other processes, such as gas phase reactions with OH (Carr *et al.*, 1994) or surface photolysis (Meller *et al.*, 1993), are unlikely to lead to significant reduction in the amount of $\text{CF}_3\text{C(O)OH}$ rained out. Although the environmental fate of TFA cannot be defined yet (Edney *et al.*, 1992; Franklin, 1993), there are indications that many natural organisms are capable of degrading it (Visscher *et al.*, 1994).

The physical removal of carbonyl compounds in the troposphere is the key requirement for the eventual removal of the degradation products from the atmosphere. A comparison of the tropospheric lifetimes of halogenated carbonyl compounds with respect to loss by OH radicals, photolysis, and/or physical removal processes is shown in Table 12-2.

The data in Table 12-2 indicate that the carbonyl compounds C(O)F_2 , C(O)FCl , HC(O)F , $\text{CF}_3\text{C(O)F}$, and $\text{CF}_3\text{C(O)OH}$ have long tropospheric lifetimes with respect to photolysis or OH reaction. Consequently, physical removal will be the most likely loss process that competes with transport into the stratosphere, where the compounds are slowly photolyzed. The other chlorinated and brominated compounds will primarily undergo photolysis in the troposphere. Depending on the location, photolysis of $\text{CF}_3\text{C(O)Cl}$ will compete with wet deposition.

12.7 RELEASE OF FLUORINE ATOMS IN THE STRATOSPHERE

The atmospheric degradation of HFCs, HCFCs, and PFCs can lead to the release of F atoms. For example, the reaction of CF_3O and FC(O)O with NO leads to FNO, which because of its strong absorption in the 290-340 nm region (Johnston and Bertin, 1959) will rapidly photolyze to F atoms. In fact most CFCs also yield F

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Table 12-2. Tropospheric lifetimes of halogenated carbonyl compounds.

	Photolysis (a)	OH (b)	Heterogeneous (c)
Carbonyl halides			
C(O)Cl ₂	16 years	> 30 years	< a few weeks
C(O)F ₂	> 1 × 10 ⁸ years	—	< a few weeks
C(O)FCl	> 1 × 10 ⁷ years	—	no data
Formyl halides			
HC(O)F	> 1 × 10 ⁸ years	> 8 years	~ 1 month
HC(O)Cl	3 years	> 36 days	no data
HC(O)Br	4 days	no data	no data
Acetyl halides			
CF ₃ C(O)F	1700 years	—	< a few weeks
CF ₃ C(O)Cl	85 days	—	< a few weeks
CH ₃ C(O)F	24 years	—	no data
CH ₃ C(O)Cl	23 days	3 years	no data
CCl ₃ C(O)Cl	6 days	—	no data
CClH ₂ C(O)Cl	30 days	—	no data
CCl ₂ HC(O)Cl	9 days	—	no data
Organic acids			
CF ₃ C(O)OH	> 7 × 10 ⁵ years	4 months	< a few weeks

- (a) Absorption cross sections have been measured by Libuda *et al.*, (1991); Meller *et al.* (1991, 1993); Nölle *et al.* (1992, 1993); Rattigan *et al.*, (1993). Photolysis processes become important in the lower troposphere at wavelengths beyond 295 nm. Unit quantum yields for the dissociation of the molecules have been assumed for the calculation of the approximate tropospheric photolytic lifetimes near the boundary layer (2 km).
- (b) An average OH concentration of 1×10^6 molecules cm⁻³ was used for the calculation of the tropospheric lifetimes with respect to OH loss. Rate constant data are for 298 K, since temperature dependencies are not available. The rate coefficients for the OH reactions are from Wallington and Hurley (1993), Nelson *et al.* (1990), and Libuda *et al.* (1990). For compounds with no H atom, it can be assumed that OH loss is negligible.
- (c) There are considerable discrepancies in the values of the uptake rate coefficients measured in different laboratories. Therefore, conservative upper limits for the heterogeneous removal rates are quoted. (Behnke *et al.*, 1992; DeBruyn *et al.*, 1992; Exner *et al.*, 1992; Rodriguez *et al.*, 1992; Ugi and Beck, 1961.)

atoms upon degradation in the stratosphere. Hence, the possibility of the involvement of fluorine in catalytic destruction of O₃ needs to be addressed.

The reaction of F atoms with O₃ is much more rapid than the corresponding reaction of Cl atoms (DeMore *et al.*, 1992; Atkinson *et al.*, 1992). Further, the reaction of FO with O is also rapid, so that the catalytic cycle:



can occur rapidly. Other catalytic cycles involving F atoms are also possible. However, the reactions of F atoms with CH₄ and H₂O to form HF are also very fast and can compete with the reaction between F and O₃ (DeMore *et al.*, 1992; Atkinson *et al.*, 1992). Therefore, any catalytic cycle involving F atoms that destroys ozone cannot have a large chain length, because F atoms are efficiently removed to form HF.

Unlike the case of HCl, HBr, and HI, which can react with various gas phase free radicals to regenerate the corresponding halogen atoms, HF is inert to attack by stratospheric free radicals, except for very reactive, and hence very low abundance, species such as O(¹D) atoms. Further, HF does not absorb at wavelengths longer than 165 nm and, consequently, is not photolyzed efficiently in the stratosphere (Safary *et al.*, 1951; Nee *et al.*, 1985). Lastly, HF cannot be converted to an active F-containing species via heterogeneous reactions on ice (Hanson and Ravishankara, 1992) and it is expected to be very insoluble in sulfuric acid and unable to take part in heterogeneous reactions. Therefore, release of fluorine into the stratosphere from either CFCs or their substitutes leads to the formation of stable HF and does not lead to catalytic ozone destruction.

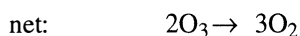
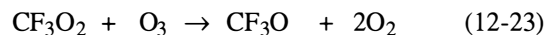
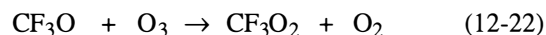
12.8 CF₃O_x AND FC(O)O_x RADICAL CHEMISTRY IN THE STRATOSPHERE – DO THESE RADICALS DESTROY OZONE?

12.8.1 CF₃O_x Radical Chemistry

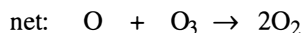
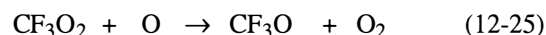
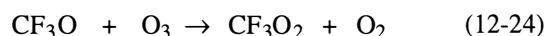
As shown in Figures 12-2 and 12-3 and discussed above, the trifluoromethyl radical is a major intermediate in the atmospheric degradation of HCFCs, HFCs, and halons that contain the CF₃ group. As discussed

previously for other haloalkyl radicals, it is expected that the CF₃ radical will be quantitatively converted to CF₃O, by addition to O₂ followed by reaction with NO. Halomethoxy radicals containing hydrogen, bromine, or chlorine atoms are removed under atmospheric conditions either by halogen atom elimination or by H atom abstraction with molecular oxygen to give the corresponding carbonyl or formyl species. In contrast, CF₃O does not undergo unimolecular elimination of a fluorine atom because it is too endothermic, and reaction of CF₃O with O₂ is too slow to be important (Batt and Walsh, 1982, 1983; Schneider and Wallington, 1994; Turnipseed *et al.*, 1994). Hence, further degradation of CF₃O radicals must occur by reaction with atmospheric trace gas species.

There has been speculation that CF₃O_x (CF₃O and CF₃O₂) radicals could participate in catalytic ozone destruction cycles in the stratosphere (Francisco *et al.*, 1987; Biggs *et al.*, 1993). As discussed recently by Ko *et al.* (1994), there are a number of potential catalytic ozone destruction cycles involving CF₃O_x radicals that are analogous to the corresponding HO_x cycles. In the lower stratosphere the cycle:



could be important, whereas in the mid-stratosphere the reaction sequence:



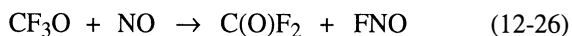
may also lead to ozone depletion. The reactions of CF₃O and CF₃O₂ radicals with ozone are chain-propagating steps in the cycles, and the efficiencies of the chain processes depend on the rate of these reactions relative to those for the sink reactions of CF₃O_x radicals.

The kinetics of the reaction of CF₃O radicals with ozone have recently been investigated using a number of different techniques (Biggs *et al.*, 1993; Nielsen and Sehested, 1993; Wallington *et al.*, 1993b; Maricq and Szenté, 1993; Fockenberg *et al.*, 1994; Ravishankara *et al.*, 1994; Meller and Moortgat, 1994; O'Reilly *et al.*, 1994; Turnipseed *et al.*, 1994). With the exception of the

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data of Biggs *et al.* (1993), the data indicate that $k(\text{CF}_3\text{O} + \text{O}_3) < 5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. For the reaction of CF_3O_2 with O_3 , only upper limits for the rate constant have been estimated (Nielsen and Sehested, 1993; Maricq and Szente, 1993; Fockenberg *et al.*, 1994; Ravishankara *et al.*, 1994; Meller and Moortgat, 1994; O'Reilly *et al.*, 1994) and these studies suggest $k(\text{CF}_3\text{O}_2 + \text{O}_3) < 1 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. The upper limits to the rate constants determined for the reactions of CF_3O and CF_3O_2 with O_3 at 298 K are similar to the measured rate coefficients for the analogous reactions of OH and HO_2 radicals with O_3 (Atkinson *et al.*, 1992; DeMore *et al.*, 1992).

In the stratosphere the main chain terminating processes will be the reactions of CF_3O with NO and CH_4 . The reaction of CF_3O radicals with NO over the pressure range 1-760 Torr and at 298 K leads to stoichiometric formation of $\text{C}(\text{O})\text{F}_2$ and FNO (Chen *et al.*, 1992a, 1993; Bevilacqua *et al.*, 1993; Sehested and Nielsen, 1993):



The rate constant for this reaction has been shown to be independent of both pressure and temperature (Fockenberg *et al.*, 1993; Turnipseed *et al.*, 1994). These results suggest that the reaction of CF_3O with NO provides a permanent sink for CF_3O . In contrast, the sink mechanisms for ClO_x and HO_x generate only temporary reservoirs for these O_3 -depleting species. The reaction of CF_3O with CH_4 appears to involve a direct hydrogen abstraction process with an activation energy of approximately 3 kcal mol^{-1} (Bednarek *et al.*, 1994; Barone *et al.*, 1994):



CF_3OH will be a temporary reservoir for CF_3O only if subsequent reactions in the stratosphere lead to regeneration of CF_3 or CF_3O . The available evidence indicates that photolysis or reaction with OH will be negligible under stratospheric conditions (Wallington and Schneider, 1994) and that circulation back into the troposphere with loss by precipitation is the likely sink for CF_3OH (Ko *et al.*, 1994). From the kinetic parameters and the stratospheric concentrations of trace gas species, the chain length of the catalytic cycles for O_3 loss by reaction with CF_3O_x are estimated to be less than unity. This value, compared with a chain length of

around 1000-10,000 for the ClO_x ozone loss cycle, suggests that catalytic cycles involving CF_3O_x will be of negligible importance. The permanency of the sink mechanism further reduces its effectiveness.

In the troposphere the major fate of CF_3O radicals will be by reaction with hydrocarbons (Chen *et al.*, 1992b; Saathoff and Zellner, 1993; Kelly *et al.*, 1993; Sehested and Wallington, 1993; Bevilacqua *et al.*, 1993; Ravishankara *et al.*, 1994; Bednarek *et al.*, 1994; Barone *et al.*, 1994), H_2O (Wallington *et al.*, 1993a), CO (Saathoff and Zellner, 1992; Ravishankara, private communication, 1994), and NO (Chen *et al.*, 1992a; Saathoff and Zellner, 1992; Fockenberg *et al.*, 1993; Sehested and Nielsen, 1993; Ravishankara *et al.*, 1994). As was the case in the stratosphere, the ultimate fate of CF_3O in the troposphere is the formation of either CF_3OH or CF_2O . Under tropospheric conditions, the most probable fate of both CF_3OH and CF_2O is uptake by cloud, rain, or ocean water to yield CO_2 and HF (Franklin, 1993).

12.8.2 FC(O) O_x Radical Chemistry

Atmospheric degradation of HCFCs and HFCs gives rise to formation of $\text{HC}(\text{O})\text{FCOFCI}$ and $\text{C}(\text{O})\text{F}_2$. In the stratosphere, photolysis of $\text{HC}(\text{O})\text{F}$ and $\text{C}(\text{O})\text{F}_2$ may be a minor source of $\text{FC}(\text{O})$ radicals. Reaction of $\text{FC}(\text{O})$ with O_2 is rapid and leads to formation of $\text{FC}(\text{O})\text{O}_2$ (Maricq *et al.*, 1993; Wallington *et al.*, 1994b). It has been suggested that $\text{FC}(\text{O})\text{O}_x$ radicals could participate in a catalytic ozone destruction cycle (Francisco *et al.*, 1990) similar to that described for CF_3O_x ,



Wallington *et al.* (1994b) have recently shown that $\text{FC}(\text{O})\text{O}_2$ and $\text{FC}(\text{O})\text{O}$ both react rapidly with NO, whereas the rate constant for reaction of $\text{FC}(\text{O})\text{O}$ with O_3 has an upper limit of $6 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Reaction of $\text{FC}(\text{O})\text{O}$ with NO gives FNO and CO_2 and is hence a permanent sink for $\text{FC}(\text{O})\text{O}$. Use of these rate parameters, together with the concentrations of NO and O_3 in the stratosphere, shows that the contribution to ozone destruction for cycles involving $\text{FC}(\text{O})\text{O}_x$ radicals can have no significance.

12.9 MODEL CALCULATIONS OF THE ATMOSPHERIC BEHAVIOR OF HCFCs AND HFCs

The aim of this section is to review the state of knowledge of the atmospheric behavior of the CFC substitutes as determined by calculations using 2- and 3-dimensional numerical models, which are formulated on the basis of knowledge of atmospheric motions and solar radiation, and on laboratory data related to atmospheric chemistry. These models have been formulated using global transport, validated against atmospheric observations of chemically inert tracers such as CFCs, ^{85}Kr , etc. Chemical schemes have been incorporated to provide time-dependent fields of oxidizing species such as OH, which allow the atmospheric loss by photochemical oxidation of reactive substitutes and their oxidation products to be calculated. This allows the evolving distribution and concentration levels of a particular substitute molecule and its degradation products to be calculated for a given emission scenario. Physical removal in the precipitation and at the Earth's surface has been incorporated in a parameterized way so that rainout and hydrolysis of degradation products can be assessed, and the distribution and fate of the degradation products determined.

Some models include transport to and from the stratosphere and allow a detailed treatment of stratospheric loss of these substitutes. This allows a treatment of the delivery of halogen to the stratosphere, either directly by the halocarbon itself or by its degradation products. This information has relevance for assessment of the ODP of the substitutes, but the evaluation of these comparative indices is dealt with in a later chapter in this assessment. It is unlikely that observations of the C_2 carbonyls, peroxy nitrates, or acids expected as degradation products of HCFCs and HFCs will help validation of the models, since the abundance of these molecules in the troposphere will be extremely small; even with the future anticipated buildup in the emission rates of the substitutes, the abundance of these molecules will be too small to detect with foreseeable technology. Analysis of the model results allows determination of the atmospheric lifetime of the various chemical species; assessment of atmospheric lifetimes is dealt with in Chapter 13. In this chapter the principal focus is the behavior of the degradation products.

12.9.1 The Models

Three 2-dimensional models—from Harwell (Hayman and Johnson, 1992), AER (Rodriguez *et al.*, 1993, 1994) and Cambridge (Rattigan *et al.*, 1992)—and the Max-Planck-Institute 3-D MOGUNTIA model (Kanakidou *et al.*, 1993) have been employed for the assessment of the atmospheric behavior of the degradation products of HCFCs and HFCs. There are some differences in model domain; for example, only the AER and Cambridge models provide full treatment of the stratosphere. All models have detailed schemes for tropospheric chemistry and degradation schemes for a range of substitutes are included in all models except for the AER model, which is restricted to HFC-134a, and HCFC-123, and -124. The models all use different emission scenarios, and so calculated concentration fields cannot be compared directly. However, the conclusions drawn from analysis of model output can be compared.

Model calculations of the degradation of the proposed CFC substitutes have been carried out using the mechanisms and photochemical kinetic data described in the previous sections. The main questions addressed by the modeling studies of the degradation of the proposed CFC substitute molecules are:

- To what extent do any long-lived degradation products of the substitutes transport chlorine and bromine to the stratosphere, thereby enhancing ozone depletion?
- To what extent can the reactions of CF_3O_x radicals lead to ozone destruction in the stratosphere?
- To what extent does the atmospheric degradation of the substitutes lead to products that have other environmental concerns, *e.g.*, toxicity, enhanced GWPs?

12.9.2 Transport of Chlorine and Bromine from the Troposphere to the Stratosphere

The classes of degradation product that could potentially carry Cl and Br to the stratosphere are the formyl, carbonyl, and acetyl halides; the fully halogenated peroxy nitrates, especially the acylperoxy nitrates, formed in the degradation of compounds of general formula CH_3CX_3 ; and halocarbons formed by photochemical decomposition of carbonyl compounds, *e.g.*, CX_3Y from $\text{CX}_3\text{C(O)Y}$.

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The effectiveness of the formyl, carbonyl, and acetyl halides as chlorine and/or bromine carriers is reduced essentially to zero by their removal through hydrolysis and removal in precipitation. The model calculations of Rodriguez *et al.* (1993), Kanakidou *et al.* (1993), and Rattigan *et al.* (1992) show that the lifetimes of these molecules is of the order of a few days, resulting from removal at the surface, rainout, and loss in clouds.

In the upper troposphere the halogenated peroxyacetylnitrates $CX_3C(O)O_2NO_2$ are relatively unreactive. The oxidation of HCFC-141b and 142b in the troposphere produces the aldehydes CCl_2FCHO and $CClF_2CHO$, which, following OH attack (in competition with the photolysis of the aldehydes), may sometimes form $CCl_2FC(O)O_2NO_2$ and $CClF_2C(O)O_2NO_2$. Rodriguez *et al.* (1994) and Kanakidou *et al.* (1993) have modeled the degradation of HCFC-141b (and 142b) using a variety of assumptions regarding the rate parameters for the relevant photochemical reactions. Even when the assumptions maximized the formation of peroxyacetylnitrates, the calculated tropospheric concentrations of $CFC1_2C(O)O_2NO_2$ and $CClF_2C(O)O_2NO_2$ were well below the 1×10^{-12} (pptv) level and comprised only a small fraction (~1-2%) of the corresponding concentrations of HFC-141b and 142b at the steady state. Thus it can be concluded that transfer of Cl to the stratosphere in these product molecules is insignificant.

The only other long-lived product containing chlorine is the halocarbon CF_3Cl , possibly formed by photolysis of $CF_3C(O)Cl$. Model studies of this process in the atmosphere have not been performed, but the very low quantum yields of CF_3Cl observed in laboratory studies imply that it is of negligible importance in conveying Cl to the stratosphere.

12.9.3 Transfer of Cl to the Stratosphere by HCFC Molecules

Although the HCFCs are removed predominantly in the troposphere, there is some degradation and release of Cl in the stratosphere by reaction with OH and by photolysis. For example, Kanakidou *et al.* (1993) find that stratospheric loss accounts for 7% for HCFC-22 and 10% for HCFC-141b. Except for CF_2HCl (F22), these are the most important potential chlorine carriers; the other HCFCs are a factor of 3-10 less effective in terms of the fraction of their chlorine delivered to the strato-

sphere. These factors are taken into account in the ODP calculations discussed further in Chapter 13.

12.9.4 Modeling of Ozone Loss Due to CF_3O Chemistry

The influence of additional O_3 loss mechanisms involving the CF_3O reactions on the Ozone Depletion Potentials of HCFCs and HFCs has been investigated in model calculations (Ko *et al.*, 1994; Ravishankara *et al.*, 1994).

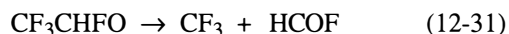
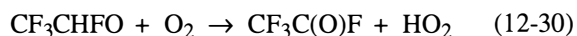
In both studies the efficiency of CF_3O_x as a catalyst for ozone depletion was calculated relative to the efficiency of chlorine release from CFCs. Ravishankara *et al.* (1994) showed that the new kinetics measurements for the key reactions of CF_3O lead to negligibly small ODPs. For example, the best estimate of the ODP for the key substitute HFC-134a is only $(1-2) \times 10^{-5}$. The results of Ko *et al.* (1994), which were based on estimates for the relevant kinetic parameters, are consistent with this conclusion.

12.9.5 Degradation Products That Have Other Potential Environmental Impacts

Trifluoroacetic acid, formyl, and fluoride formed from the degradation of HCFCs and HFCs have been identified as a potential environmental concern because of their toxicity.

Trifluoroacetic acid (TFA) is produced by hydrolysis of $CF_3C(O)F$ formed in the degradation of HFC-134a and HCFC-124 and hydrolysis of $CF_3C(O)Cl$ from degradation of HCFC-123. The yield of $CF_3C(O)F$ from HCFC-124 is almost 100%, but the competitive pathway forming $HC(O)F$ reduces the yield from HFC-134a. Tropospheric photolysis of $CF_3C(O)Cl$ competes with hydrolysis and consequently reduces the yield of TFA from HFC-123.

Most interest has focused on the production of TFA from HFC-134a (Rodriguez *et al.*, 1993; Rattigan *et al.*, 1994; Kanakidou *et al.*, 1993; Ball and Wallington, 1993). Using the most recent laboratory data, cloud hydrolysis of atmospheric $CF_3C(O)F$ is sufficiently rapid so that TFA production is equal to the rate of $CF_3C(O)F$ production, and is therefore controlled by the local rate of HFC-134a reaction with OH and by the branching ratio for the competing reactions of CF_3CHFO :



Because of the temperature, total pressure, and O₂ partial pressure dependence of this branching ratio, there is significant latitude and altitude dependence in the fraction of HFC-134a producing CF₃C(O)F. For average atmospheric conditions, about 40% of HFC-134a is degraded to TFA.

Rodriguez *et al.* (1993) have calculated the zonally averaged concentrations of TFA in rainwater, making various assumptions regarding the extent to which the gaseous acid is dry deposited at the surface after evaporation from clouds. The results show considerable latitudinal and seasonal variation in rainfall TFA, the pattern depending on the assumptions made. The key results of this study are:

- Predicted global average concentrations of TFA in rain are of the order of 1 mg/l for a 1 Tg year⁻¹ source of HFC-134a in the Northern Hemisphere. These concentrations are relatively insensitive to the parameters adopted for uptake of CF₃C(O)F in cloud droplets.
- The concentrations of TFA in rain are primarily determined by the source strength of HFC-134a, the relative yields of CF₃C(O)F from the CF₃CHFO radical, and the loss processes for gas phase TFA.
- Calculated local concentrations of TFA in rain could be very sensitive to other loss processes of CF₃C(O)F, as well as to rainfall patterns.

Calculations in the same study indicate a 50-100% yield of TFA in rain from degradation of HCFC-124 and HCFC-123. The smaller values for HCFC-123 reflect the removal of CF₃C(O)Cl by photolysis in the troposphere. The results from the other model studies of HFC-134a oxidation are in broad agreement with these conclusions concerning the formation of TFA. There are differences in quantitative detail that may be a result of different model formulation as well as uncertainties in the input data.

No laboratory data are available for the uptake and hydrolysis rates of HC(O)F in aqueous solution. Its gas phase loss processes are extremely slow in the troposphere and, if the hydrolysis and uptake rates are also low, this molecule could build up in the troposphere and be transported to the stratosphere (Kanakidou *et al.*, 1993). Stratospheric photolysis leads to FC(O)O_x but, as discussed above, this will not lead to ozone depletion.

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