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The Environmental Impact of CFC Replacements—HFCs and HCFCs

Recognition of the adverse impact of chlorofluorocarbons (CFCs) on stratospheric ozone has prompted an international effort to replace CFCs with environmentally acceptable alternatives (1–4) such as hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs). Examples include HFC-134a (CF_3CFH_2), a replacement for CFC-12 (CF_2Cl_2) in domestic refrigeration and automobile air conditioning units; HCFC-22 (CHF_2Cl), a replacement for CFC-12 in industrial refrigeration units; and HCFC-141b (CFCl_2CH_3), a replacement for CFC-11 in foam-blowing applications. Both HFCs and HCFCs are volatile and insoluble in water. Following release into the environment these compounds reside in the atmosphere where they are oxidized into a variety of degradation products.

The atmospheric chemistry of commercially important HFCs and HCFCs is well established. HFCs are “ozone friendly.” HCFCs have

small but nonnegligible ozone depletion potentials. The global warming potentials of HFCs and HCFCs are approximately an order of magnitude less than those of the CFCs they replace. At the concentrations expected from the atmospheric degradation of HFCs and HCFCs, none of the oxidation products can be considered to be noxious or toxic.

The choice of HFCs and HCFCs is motivated by a number of factors. In contrast to CFCs, HFCs and HCFCs contain one or more C–H bonds. Hence, HFCs and HCFCs are susceptible to attack by OH radicals in the lower atmosphere (troposphere). HFCs do not contain chlorine and so do not have the ozone depletion potential associated with the well-established chlorine catalytic cycles. Although HCFCs contain chlorine, the delivery of this chlorine to the stratosphere is relatively inefficient because of the scavenging of HCFCs by OH radicals in the troposphere. To define the environmental impact of HFCs and HCFCs, their ability to destroy stratospheric ozone, contribute to potential global warming, and produce noxious degradation products must be assessed. This assessment requires a detailed knowledge of the atmospheric chemistry of the halocarbons.

We present here an evaluation of the environmental impact of HFCs

and HCFCs in terms of their ozone depletion potentials, global warming potentials, and ability to form noxious degradation products. This evaluation is based on an overview of their atmospheric chemistry and the gas- and liquid-phase loss processes of their halocarbonyl decomposition products.

Conversion to carbonyl species

The gas-phase atmospheric chemistry of HFCs and HCFCs can be divided into two parts: reactions that convert the HFC/HCFC into halogenated carbonyl species, and reactions that remove these carbonyl compounds.

Reaction rates with OH radicals determine the atmospheric lifetimes of all HFCs and HCFCs. Lifetimes are 2–40 years (5, 6) and are listed in Table 1 along with those for CFC-11 and CFC-12 for comparison. A generic scheme for the atmospheric oxidation of a C_2 haloalkane is given in Figure 1. Reaction with OH radicals gives a haloalkyl radical, which reacts with O_2 to give the corresponding peroxy radical (RO_2). Peroxy radicals can react with three trace species in the atmosphere: NO, NO_2 , or HO_2 radicals. The importance of these reactions is dictated by the relative abundances and reaction rates of NO, NO_2 , and HO_2 radicals with RO_2 radicals. In the troposphere the concentrations of NO, NO_2 , and HO_2 are compara-

TIMOTHY J. WALLINGTON
WILLIAM F. SCHNEIDER

Ford Motor Company
Dearborn, MI 48121-2053

DOUGLAS R. WORSNOP

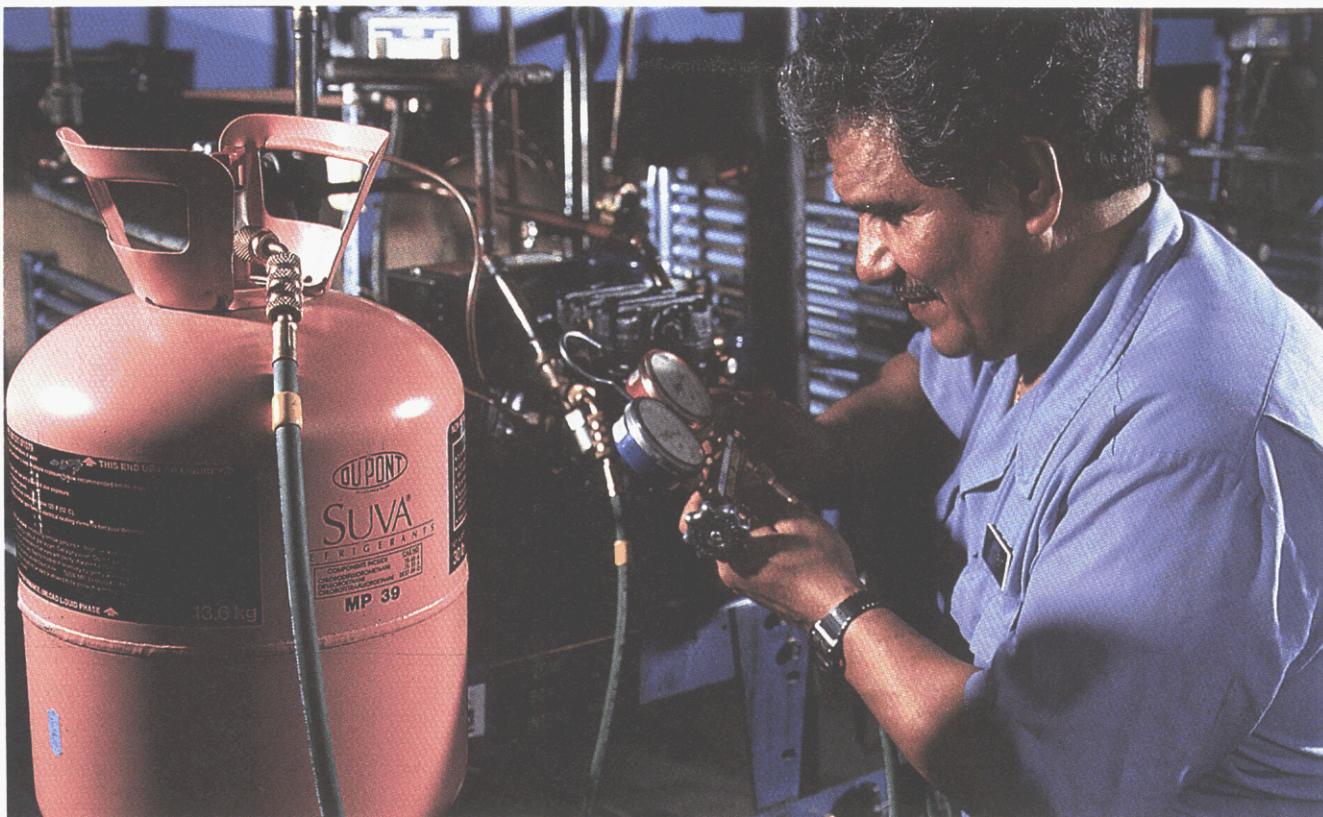
Aerodyne Research, Inc.
Billerica, MA 01821-3976

OLE J. NIELSEN
JENS SEHESTED

Risø National Laboratory
DK-4000 Roskilde, Denmark

WARREN J. DEBRUYN
JEFFREY A. SHORTER

Boston College
Chestnut Hill, MA 02167



ble ($2.5\text{--}10 \times 10^8 \text{ cm}^{-3}$) (4).

The reactions of peroxy radicals with NO and NO_2 have been studied extensively (6–10). The peroxy radicals derived from the HFCs and HCFCs considered in this article all react rapidly with NO to give NO_2 and an alkoxy radical RO (9, 10). The atmospheric lifetime of RO_2 radicals with respect to reaction with NO is 3–7 min (9, 10). Peroxy radicals react rapidly with NO_2 to give alkyl peroxy nitrates (RO_2NO_2). By analogy to the measured rate of reaction of CF_2ClO_2 and $\text{CF}_3\text{CH}_2\text{O}_2$ radicals with NO_2 (10, 11), the lifetime of RO_2 radicals with respect to reaction with NO_2 will be approximately 10 min. Alkyl peroxy nitrates are thermally unstable and decompose rapidly to regenerate RO_2 radicals and NO_2 (12, 13).

Peroxy radicals react with HO_2 radicals (7, 8) to give hydroperoxides and possibly, in the case of RO₂ radicals containing an α-H atom (e.g., CF_3CFHO_2), carbonyl products [e.g., $\text{CF}_3\text{C(O)F}$]. The relative importance of the hydroperoxide and aldehyde forming channels is uncertain (14). It seems reasonable to suppose that the peroxy radicals formed from HFCs and HCFCs react with rates similar to those measured for CF_3CFHO_2 , $\text{CF}_2\text{ClCH}_2\text{O}_2$, and $\text{CF}_3\text{CCl}_2\text{O}_2$ (i.e., in the range $2\text{--}7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) (15, 16; Maricq, M. M.; Szentze, J. J., personal communication, 1993). Using

an HO_2 concentration of $10^9 \text{ molecule cm}^{-3}$ gives a lifetime of 2–8 min for CX_3CXYO_2 radicals with respect to reaction with HO_2 . The hydroperoxide CX_3CXYOOH is returned to the CX_3CXYO_X radical pool via reaction with OH or photolysis (4). The fate of the carbonyl product $\text{CX}_3\text{C(O)X}$ is discussed later.

The atmospheric fate of the alkoxy radical, CX_3CXYO , is either decomposition or reaction with O_2 (10, 17–27). Decomposition can occur either by C–C bond fission or Cl atom elimination. Reaction with O_2 is possible only when an α-H atom is available. In the case of the alkoxy radicals derived from HFC-32 (28), HFC-125 ($\text{CF}_3\text{CF}_2\text{H}$) (19, 21, 22), and HCFC-22 (29, 30), only one reaction pathway is available. The alkoxy radicals derived from HFC-143a, HCFC-123 ($\text{CF}_3\text{CCl}_2\text{H}$), HCFC-124, HCFC-141b and HCFC-142b all have two or more possible fates. For HCFCs 123 and 124 the dominant loss process is elimination of a Cl atom to give $\text{CF}_3\text{C(O)Cl}$ (17, 21, 25) and $\text{CF}_3\text{C(O)F}$ (19, 21), respectively. For HFC-143a, HCFC-141b, and HCFC-142b, reaction with O_2 dominates, giving CF_3CHO (10), CFCl_2CHO (26, 31), and CF_2ClCHO (26, 31), respectively. The case of HFC-134a is the most complex. Under atmospheric conditions, the alkoxy radical derived from HFC-134a, CF_3CFHO , decomposes and

reacts with O_2 at comparable rates (18, 20).

The usual modes of alkoxy radical loss are not possible for CF_3O . The fate of CF_3O radicals is reaction with NO (32–35; Zellner, R., personal communication, 1993), hydrocarbons (36–43), and possibly water vapor (44). Reaction of CF_3O radicals with NO gives C(O)F_2 . Reaction of CF_3O radicals with hydrocarbons and water produces CF_3OH . CF_3OH decomposes heterogeneously and possibly homogeneously (44–46) to give C(O)F_2 and HF. CF_3OH is also expected to be incorporated into water droplets (47). The principle gas-phase atmospheric degradation products of a series of important HFCs and HCFCs are given in Table 2.

Reactions of carbonyl intermediates

The sequence of gas-phase reactions that follow from the initial attack of OH radicals on the parent halocarbon are sufficiently rapid that heterogeneous and aqueous processes play no role. In contrast, the lifetimes of the carbonyl products [e.g., HC(O)F , C(O)F_2 , $\text{CF}_3\text{C(O)F}$] are relatively long (weeks). Incorporation into water droplets followed by hydrolysis plays an important role in the removal of halogenated carbonyl compounds (48). In the cases of HC(O)F , C(O)F_2 , C(O)FCl , and

TABLE 1
Atmospheric lifetimes, ozone depletion,
and global warming potentials

Compound	Lifetime ^a years	Ozone depletion potential ^b	Halocarbon global warming potential ^c
HFC-32 (CH_2F_2)	6.7	0	0.094 ^d
HFC-125 ($\text{CF}_3\text{CF}_2\text{H}$)	26	0	0.58
HFC-134a (CF_3CFH_2)	14	0	0.27
HFC-143a (CF_3CH_3)	40	0	0.74
HCFC-22 (CHF_2Cl)	14	0.047	0.36
HCFC-123 ($\text{CF}_3\text{CCl}_2\text{H}$)	1.5	0.016	0.019
HCFC-124 ($\text{CF}_3\text{CFCI}\text{H}$)	6.0	0.018	0.096
HCFC-141b (CFCl_2CH_3)	7.1	0.085	0.092
HCFC-142b (CF_2ClCH_3)	17.8	0.053	0.36
CFC-11 (CFCI_3)	60	1.0 ^e	1.0 ^e
CFC-12 (CF_2Cl_2)	105	0.95	3.1
CO_2			0.00076 ^f

^a Average of values given by Derwent et al. (4), p. 124.

^b Average of values given in Table 4 of Fisher et al. (65).

^c Average of values given in Table 5 of Fisher et al. (77).

^d Estimated from lifetime to be midway between HCFCs 124 and 141b.

^e By definition.

^f The global warming potential of CFC-11 is approximately 1300 times greater than that of CO_2 (80).

As shown in Figure 2, photolysis of $\text{CF}_3\text{C}(\text{O})\text{Cl}$ gives CF_3 , CO , and Cl (27). In addition, trace amounts (<1% yield) of CF_3Cl have been reported (27). CF_3Cl is a long-lived compound that efficiently transports chlorine to the stratosphere. However, the low yield of CF_3Cl from $\text{CF}_3\text{C}(\text{O})\text{Cl}$ photolysis renders this pathway environmentally insignificant. The photolysis of $\text{CF}_3\text{C}(\text{O})\text{H}$ in air may produce CF_3H (preliminary data suggest a 56% yield) (53). $\text{CF}_2\text{ClC}(\text{O})\text{H}$ and $\text{CFCl}_2\text{C}(\text{O})\text{H}$ may also be photolyzed to give significant yields of CF_2ClH and CFCl_2H , respectively. Because these species have shorter atmospheric lifetimes than their parent HCFCs (141b and 142b) (4), the potential formation of CF_2ClH and CFCl_2H is of little environmental consequence. In contrast, CF_3H is approximately an order of magnitude more persistent than HFC-143a. CF_3H is a potent greenhouse gas, and its formation may increase the global warming potential of HFC-143a.

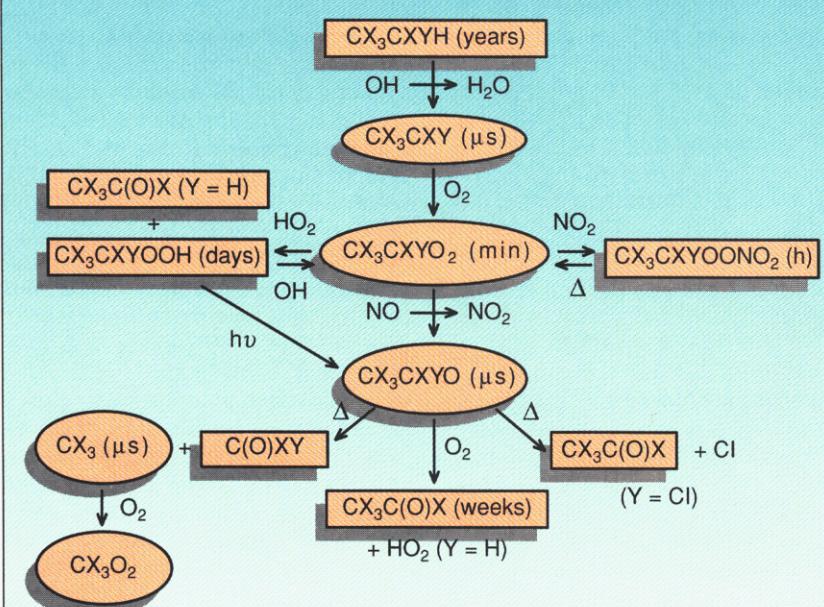
Following reaction of the parent aldehyde with OH radicals, $\text{CF}_3\text{C}(\text{O})$, $\text{CF}_2\text{ClC}(\text{O})$, and $\text{CFCl}_2\text{C}(\text{O})$ radicals can either react with O_2 or decompose to give CO and a halogenated methyl radical. Recent work has shown that reaction with O_2 is the fate of $\text{CF}_3\text{C}(\text{O})$ radicals (54, 55) and possibly $\text{CF}_2\text{ClC}(\text{O})$ and $\text{CFCl}_2\text{C}(\text{O})$ radicals. The resulting $\text{CX}_3\text{C}(\text{O})\text{O}_2$ radical can react with NO or NO_2 , ultimately yielding CX_3 radicals and CO_2 (54–56).

Removal of oxidized species

The final step in the removal of any species from the atmosphere involves heterogeneous deposition to the Earth's surface. Removal processes include wet deposition via rainout (following uptake into tropospheric clouds) and dry deposition to the Earth's surface, principally to the oceans. The rates of these processes are largely determined by the species' chemistry in aqueous solution. For the viability of CFC replacements, the question is whether the rate of removal of any degradation product is slow compared to the OH reaction limited lifetime of the parent compounds listed in Table 1. Heterogeneous lifetimes of the parent compounds themselves are on the order of hundreds of years because of their low aqueous solubility and reactivity.

The degradation products listed in Table 2 have gas-phase removal rates (via reaction or photolysis)

FIGURE 1
Generalized scheme for the atmospheric oxidation of a halogenated organic compound, CX_3CXYH (X, Y = H, Cl, or F)^a



^a Transient radical intermediates are enclosed in ellipses, products with less transitory existence are given in the boxes. Order-of-magnitude lifetime estimates are indicated parenthetically.

$\text{CF}_3\text{C}(\text{O})\text{F}$ reaction with OH radicals (49) and photolysis (50) are too slow to be of any significance. These compounds are removed essentially entirely into water droplets.

The gas-phase oxidation mechanisms for $\text{CX}_3\text{C}(\text{O})\text{H}$ and $\text{CF}_3\text{C}(\text{O})\text{Cl}$ are shown in Figure 2. For $\text{CX}_3\text{C}(\text{O})\text{H}$ species, reaction with OH radicals is important (51). The lifetimes of $\text{CF}_3\text{C}(\text{O})\text{H}$, $\text{CF}_2\text{ClC}(\text{O})\text{H}$,

and $\text{CFCl}_2\text{C}(\text{O})\text{H}$ with respect to OH attack have been estimated to be 24, 19, and 11 days, respectively (51). Photolysis and scavenging by water probably both play a role in the atmospheric fate of these halogenated aldehydes. $\text{CF}_3\text{C}(\text{O})\text{Cl}$ does not react with OH, but undergoes photolysis (27, 52), which competes with incorporation of $\text{CF}_3\text{C}(\text{O})\text{Cl}$ into water droplets.

FIGURE 2
Generalized scheme for the gas-phase atmospheric chemistry of $\text{CX}_3\text{C(O)H}$ and $\text{CF}_3\text{C(O)Cl}$

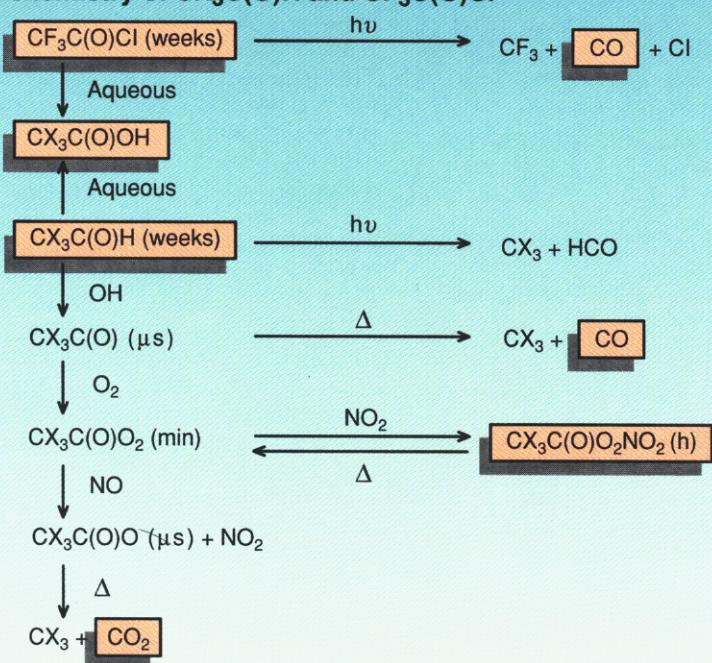


TABLE 2
Gas-phase atmospheric degradation products

Compound	Carbon-containing degradation products ^a
HFC-32 (CH_2F_2)	C(O)F_2
HFC-125 ($\text{CF}_3\text{CF}_2\text{H}$)	C(O)F_2 , CF_3OH
HFC-134a (CF_3CFH_2)	HC(O)F , CF_3OH , C(O)F_2 , $\text{CF}_3\text{C(O)F}$
HFC-143a (CF_3CH_3)	$\text{CF}_3\text{CO(H)}$, CF_3OH , C(O)F_2 , CO_2
HCFC-22 (CHF_2Cl)	C(O)F_2
HCFC-123 ($\text{CF}_3\text{CCl}_2\text{H}$)	$\text{CF}_3\text{C(O)Cl}$, CF_3OH , C(O)F_2 , CO
HCFC-124 (CF_3CFClH)	$\text{CF}_3\text{C(O)F}$
HCFC-141b (CFCl_2CH_3)	CFCl_2CHO , C(O)FCl , CO , CO_2
HCFC-142b (CF_2CICH_3)	CF_2CICHO , C(O)F_2 , CO , CO_2

^a Hydroperoxides (ROOH) and alkylperoxy nitrates (RO_2NO_2) products will also be formed but are expected to be converted back into peroxy radicals (RO_2^{\cdot}) and thence into the products listed above.

that are slow enough (days or longer) that heterogeneous processing might be significant. They are thought to undergo aqueous interactions sufficiently rapidly for efficient wet and dry deposition (57). For example, although the acid halides are relatively insoluble in water, they hydrolyze to produce the acids HX and $\text{CX}_3\text{C(O)OH}$ (see Table 3). Because the acids are very water soluble, hydrolysis removes the halides from the gas phase irreversibly.

It is difficult to measure the relevant aqueous kinetics of such species. Atmospheric removal rates depend on both solubility (expressed in terms of the Henry's law constant, H , M atm^{-1}) and hydrolysis rate (k_{hyd} , s^{-1}). Because these spe-

cies do not form stable aqueous solutions, neither parameter is simply measurable in bulk solution. As a result, laboratory determinations involve heterogeneous processes that typically measure combinations of H and k_{hyd} . Estimation of atmospheric lifetimes requires deconvolution of these parameters.

The relevant aqueous-phase kinetics of the halocarbonyls, $[\text{C(O)F}_2]$, $\text{CF}_3\text{C(O)F}$, and $\text{CF}_3\text{C(O)Cl}$, in particular have been studied by a number of experimental techniques utilizing droplets (48, 58), bubbles (DeBruyn, W. et al., unpublished results, 1994), wetted wall reactors, and aerosol chambers (59). The results of these experiments are summarized in Table 3 in terms of the product $H^*k_{\text{hyd}}^{1/2}$, which is the pa-

rameter typically measured in gas-liquid mass transfer experiments. For the two related chlorinated species, C(O)Cl_2 (DeBruyn, W. et al., unpublished results, 1994; 63, 64) and $\text{CCl}_3\text{C(O)Cl}$ (58; above-cited unpublished results; 61), a combination of studies has determined $k_{\text{hyd}} \approx 100-150 \text{ s}^{-1}$. The H^*k_{hyd} values for C(O)Cl_2 and $\text{CCl}_3\text{C(O)Cl}$, 0.2 and $9 \text{ M atm}^{-1} \text{ s}^{-1}$ (above-cited unpublished results), respectively, span the range of the fluorine-containing species listed in Table 3.

Assuming $k_{\text{hyd}} \approx 100 \text{ s}^{-1}$ is representative of all the halocarbonyl species, one obtains $H \approx 0.1-0.6 \text{ M atm}^{-1}$. With H and k_{hyd} values, tropospheric lifetimes for heterogeneous uptake into clouds and into the ocean can be estimated, as listed in Table 3 (57, 62, 63). For tropospheric cloud processing, the lower limit of 5 days represents transport limitations, that is, the time taken for transport of the materials into the clouds.

Two conclusions can be drawn from Table 3. First, and most importantly, despite the considerable uncertainty in the laboratory kinetic results, heterogeneous removal of halocarbonyl species is fast enough to have no effect on the overall halogen lifetime compared to the lifetime of the parent halocarbon. Second, tropospheric cloud rainout will predominate over deposition to the ocean. This conclusion, based on the most recent laboratory results, reverses earlier predictions of ocean-dominated deposition that assumed $H > 10 \text{ M atm}^{-1}$ (57).

Ozone depletion potentials

In discussions of the effects of halocarbons on stratospheric ozone the concept of "ozone depletion potential" (ODP) is useful (64). Ozone depletion potential is defined as the ratio of the calculated ozone column change per mass of a given compound released to the column change for the same mass of CFC-11. Halocarbon ODPS have been calculated by a number of atmospheric modeling groups. Selected results from Fisher et al. (65) are given in Table 1.

HFCs do not contain any chlorine and so have no ozone depletion potential associated with the well-established chlorine-based catalytic ozone destruction cycles. Recently, there has been speculation regarding the possibility of an impact of HFCs on stratospheric ozone by virtue of their degradation into CF_3O_x , FCO_x , and FO_x radicals that could

TABLE 3
Aqueous-phase atmospheric degradation products

Compound	$H^*k_{hyd}^{1/2}$ (M atm ⁻¹ s ^{-1/2})	Lifetime			Degradation products
		Clouds (days)	Ocean (years)		
C(O)F ₂	6 ^a	≈5–10	0.3–2.0	HF, CO ₂	
C(O)ClF	≈2 ^b	≈5–20	0.5–5.0	HF, HCl, CO ₂	
CF ₃ C(O)F	4 ^a	≈5–15	0.3–3.0	CF ₃ C(O)OH, HF	
CF ₃ C(O)Cl	1 ^a	≈5–30	1.0–10.0	CF ₃ C(O)OH, HCl	
HC(O)F		150–1500 ^c	80 ^c	HF, HCOOH	

^a Values measured by DeBruyn et al., personal communication, 1994. George et al. (58, 61) have reported higher values; quoted lifetimes should be considered as upper limits.
^b Interpolation of data for C(O)Cl₂ and C(O)F₂.
^c Conservative estimate based on $k_{hyd} = 0.01$ s⁻¹ (63).

participate in catalytic ozone destruction cycles (66–68). However, experimental studies have shown that no such cycles are viable (35, 69–75). The ODPs of HFCs are essentially zero (<10⁻³) (73).

In ODP calculations it is assumed that attack by OH radicals removes HCFCs and that no long-lived products are formed that could transport chlorine to the stratosphere. Uncertainty regarding the potential importance of halogenated peroxy acetyl nitrates [CX₃C(O)O₂NO₂] as carriers of chlorine to the stratosphere has been resolved (54). In the lower troposphere thermal decomposition is rapid. At 282 K [1 km in U.S. Standard Atmosphere (76)] the lifetimes of CF₂ClC(O)O₂NO₂ and CFCl₂C(O)O₂NO₂ are 43 and 33 h, respectively (54). Circulation of air through the lower troposphere acts as an efficient removal mechanism of CX₃C(O)O₂NO₂ species. There are no known HCFC oxidation products that transport significant amounts of chlorine to the stratosphere.

HCFCs are considerably less harmful toward stratospheric ozone than CFCs. However, HCFCs do transport chlorine into the stratosphere. Recognition of this fact led to the development of a schedule of production caps and application bans culminating in a complete ban on the manufacture and importation of HCFCs in the United States by the year 2030.

Halocarbon global warming potentials

In discussions of the potential impact of HFCs and HCFCs on global warming the concept of halocarbon global warming potential is useful (77). Halocarbon global warming potential (HGWP) is defined as the ratio of the calculated warming at

steady state for a fixed mass release of gas relative to that calculated for the release of the same mass of CFC-11. HGWPs reported by Fisher et al. (77) are listed in Table 1.

In HGWP calculations it is assumed that the oxidation products are short-lived in comparison with the parent halocarbon, so that once a halocarbon molecule has reacted with OH there is no further contribution to radiative forcing. As discussed above, with the possible exception of HFC-143a, this is a valid assumption. The atmospheric degradation of HFC-143a may yield a significant amount of CF₃H, which has a lifetime that is approximately 10 times that of HFC-143a (4). Further work is needed to quantify the yield of CF₃H from oxidation of HFC-143a. The HGWP for HFC-143a listed in Table 1 should be regarded as a lower limit.

As seen in Table 1, the HGWPs scale approximately linearly with atmospheric lifetime. This is not surprising as CFCs, HFCs, and HCFCs all have similar molecular structures and chemical bonds. Hence, the strengths and positions of their infrared absorptions are similar. The impact of these species is then largely determined by their atmospheric concentration and hence lifetime.

The global warming potentials of HFCs and HCFCs are less than those of CFCs but substantially greater than CO₂. For example, the HGWP of CFC-12 is 4100 times greater than for CO₂, whereas the HGWP of HFC-134a is only 350 times greater than for CO₂.

Formation of toxic/noxious degradation products

The atmospheric degradation of HFCs and HCFCs gives rise to a wide variety of products (Tables 2

and 3). The atmospheric concentration of these products will be extremely small (<< ppb). There are no known adverse environmental impacts associated with these compounds at such low concentrations. The ultimate removal mechanism for all products is incorporation into rain-sea-cloud water where hydrolysis will take place. With the exception of CF₃C(O)OH, the hydrolysis products are ubiquitous, naturally occurring species that have no adverse environmental impact.

There is no known sink for CF₃C(O)OH. From the available toxicological data concerning CF₃C(O)OH (see discussion by Kaminsky, 4), it has been concluded that the formation of this compound from the atmospheric degradation of HFC-134a is of no concern with respect to human health (78). High concentrations of CF₃C(O)OH ($\geq 5 \times 10^{-4}$ mol) have been reported to adversely impact wheat and tomato seedlings (79). The concentration of CF₃C(O)OH in rainwater expected from the atmospheric degradation of HFCs and HCFCs is $< 10^{-7}$ mol (78). Research is needed to establish the fate of CF₃C(O)OH and the environmental impact of low CF₃C(O)OH concentrations.

Acknowledgments

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Timothy J. Wallington is a senior research scientist in the Chemistry Department of the Scientific Research Laboratories of Ford Motor Company, working to establish the environmental impact of vehicle and manufacturing emissions. He received a Ph.D. in physical chemistry from Oxford University, U.K., and has been working in the field of atmospheric chemistry for the past 12 years.



William F. Schneider (l) is a senior research scientist in the Atmospheric Modeling group at the Scientific Research Laboratories of Ford Motor Company. He received a B.S. degree from the University of Michigan-Dearborn in 1986 and a Ph.D. in chemistry from the Ohio State University in 1991, after which he joined Ford. His current work includes application of ab initio electronic structure calculations to fundamental reactions of atmospheric import.

Douglas R. Worsnop (r) is a principal research scientist at Aerodyne Research, Inc., and an adjunct professor in the Department of Chemistry at Boston College. His research interests include laboratory studies of homogeneous and heterogeneous kinetics underlying chemical processes throughout the atmosphere.



Ole John Nielsen (l) is head of the Chemical Reactivity Section at the Environmental Science & Technology Department, Risø National Laboratory, Denmark. He received his Ph.D. in environmental chemistry from the University of Copenhagen and did his postdoctoral work at Risø National Laboratory. He has done atmospheric chemistry research for 16 years with focus on laboratory investigations on reactions of relevance in atmospheric chemistry. He manages research on atmospheric chemistry.

Jens Sehested (r) is finishing his Ph.D. work at the Chemical Reactivity Section at the Environmental Science & Technology Department, Risø National Laboratory. He received his M.S. degree from the University of Copenhagen. His research projects have been concentrated around atmospheric degradation of HFCs and the fate of CF_3O radicals in the atmosphere.



Warren J. DeBruyn (l) is a doctoral candidate in the Department of Chemistry at Boston College. He holds B.S. and M.S. degrees from the University of Natal, South Africa. His doctoral research has focused on the development of experimental techniques for investigating heterogeneous kinetics of gases with low solubility in aqueous solution.

Jeffrey A. Shorter (r) is a senior scientist at Mission Research, Inc. (Nashua, NH 03062). He received his Ph.D. in physical chemistry from MIT and held a postdoctoral fellowship jointly at Boston College and Aerodyne Research, Inc. His current research interests include chemical modeling of the atmosphere with emphasis on NLTE environments and heterogeneous chemistry.

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