POSSIBLE ATMOSPHERIC LIFETIMES AND CHEMICAL REACTION MECHANISMS FOR SELECTED HCFCs, HFCs, CH₃CCl₃, AND THEIR DEGRADATION PRODUCTS AGAINST DISSOLUTION AND/OR DEGRADATION IN SEAWATER AND CLOUDWATER

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1. INTRODUCTION

For a wide variety of atmospheric species including CO_2, HNO_3, and SO_2, dissolution in seawater or cloudwater followed by hydrolysis or chemical reaction represents a primary pathway for removal from the atmosphere (Peters, 1983; Liss, 1983; Chameides and Davis, 1982). In order to determine if this mechanism can also remove significant amounts of atmospheric chlorofluorocarbons (HCFCs), fluorocarbons (HFCs), and their degradation products, an investigation was undertaken as part of the Alternative Fluorocarbons Environmental Acceptability Study (AFEAS). In this investigation, the rates at which $CHCl_2CF_3$ (HCFC-123), CCl_2FCH_3 (HCFC-141b), $CClF_2CH_3$ (HCFC-142b), $CHClF_2$ (HCFC-22), $CHClFCF_3$ (HCFC-124), CH_2FCF_3 (HFC-134a), CHF_2CH_3 (HFC-152a), CHF_2CF_3 (HFC-125), and CH_3CCl_3 can be dissolved in the oceans and in cloudwater were estimated from the species' thermodynamic and chemical properties using simple mathematical formulations to simulate the transfer of gases from the atmosphere to the ocean or cloudwater. The ability of cloudwater and rainwater to remove gas phase degradation products of these compounds was also considered as was the aqueous phase chemistry of the degradation products. The results of this investigation are described below.

2. OCEANIC REMOVAL OF HCFCs AND HFCs

The exchange of gases between the atmosphere and ocean is typically simulated with the "stagnant film" model (Danckwerts, 1970). In this model, transfer from the atmosphere to the ocean is assumed to be limited by the rate at which the gas can diffuse (via molecular diffusion) through a thin film of air residing directly above the ocean-atmosphere boundary and a thin film of seawater residing below the boundary. Under these conditions, ϕ_o, the steady state flux of a species from the atmosphere to the ocean (in molecules cm^{-2} s^{-1}) is given by (Liss, 1983)

$$\phi_o = \{C_A - [I]_o/(HRT)\} \left[\frac{1}{r_A + r_S/(HRT\ N_A\ 10^{-3})}\right] \qquad (1)$$

where r_A and r_S are the transfer resistances (in s cm^{-1}) of the atmospheric and oceanic film, respectively, H is the species Henry's or solubility constant (M atm^{-1}), $R = 1.36 \times 10^{-22}$ atm cm^3/molecule/K is the gas constant, T is temperature (assumed to be 285K), N_A is Avogadro's number, C_A is the species' concentration (in molecules cm^{-3}) at the bottom of the atmospheric mixed layer, and $[I]_o$ is the species concentration (in M or moles per liter) at the top of the oceanic mixed layer. It can be shown by solving the one-dimensional diffusion equation that the transfer resistances in Eqn. [1] are given by the thicknesses of the films divided by the molecular diffusion coefficient; in the case of r_A one would use a gas-phase diffusion coefficient of about 0.01 cm^2 s^{-1}, while for r_S an aqueous-phase diffusion coefficient of about 10^{-5} cm^2 s^{-1} would be used (Danckwerts, 1970). For conditions typical of the ocean, r_A is about 1.25 s cm^{-1}, while r_S is about 170 s cm^{-1} (Liss, 1983). For the HCFCs and HFCs under consideration here, $H \leq 0.2$ M atm^{-1} and thus

$$r_S/(HRT\ N_A\ 10^{-3}) \approx 7/H > 35 >> r_A \qquad (2)$$

It follows, therefore, that the oceanic resistance, r_S, dominates for these compounds and Eqn. [1] can be represented by

$$\phi_o = \{HRT\ N_A\ 10^{-3}/r_S\}\ \{C_A - [I]_o/(HRT)\} \qquad (3)$$

AQUATIC MECHANISMS

In order to evaluate Eqn. [3], the species' concentration, $[I]_o$, at the bottom of the oceanic stagnant layer must be defined. This can be accomplished by considering the downward transport of the species through the wave-mixed surface layer of the ocean, which typically extends from the surface (i.e., the bottom of the stagnant ocean film) to the beginning of the main thermocline at about 80 m depth. Following Johnson (1981), the one-dimensional form of the continuity equation for the species in this mixed layer is given by

$$\partial[I]/\partial t = -k[I] + \partial/\partial z (D \; \partial[I]/\partial z) \tag{4}$$

where [I] is the species' concentration in the layer, t is time, k is the species' pseudo first-order loss rate due to hydrolysis or chemical reaction, z is depth below the surface, and D is the eddy diffusion coefficient used to parameterize the effect of turbulence on vertical transport. The value of D assumed in our calculations is 40 cm^2 s^{-1} (Johnson, 1981).

Assuming that [I] tends to zero as z gets large, the steady state solution of [4] yields the following form for ϕ_o (Johnson, 1981):

$$\phi_o = (Dk)^{1/2} [I]_o \; N_A \; 10^{-3} \tag{5}$$

Equating [3] and [5], it follows that

$$[I]_o = (HRT) \; C_A/\{1 + r_S \; (Dk)^{1/2}\} \tag{6}$$

and substituting [6] into [5] yields a closed form for ϕ_o; i.e.,

$$\phi_o = (Dk)^{1/2} \; N_A \; 10^{-3} \; HRT \; C_A/\{1 + r_S \; (Dk)^{1/2}\} \tag{7}$$

Substituting for R, N_A, and T, Eqn [7] reduces to

$$\phi_o = (H \; C_A/0.04) \; \{r_S + 1/(Dk)^{1/2}\}^{-1} \tag{8}$$

Table 1. Atmospheric Lifetimes (in years) Against Oceanic Loss as a Function of Solubility (H) and First-Order Loss Coefficient in Ocean (k)

	H (M atm^{-1})							
	0.001	0.005	0.01	0.02	0.04	0.06	0.08	0.1
k(s^{-1})								
10^{-11}	73,200	14,600	7,320	3,600	1,830	1,230	916	732
10^{-10}	23,300	4,670	2,330	1,170	583	389	292	233
10^{-9}	7,550	1,510	755	377	189	126	94	75
10^{-8}	2,560	511	256	128	64	43	32	25
10^{-7}	978	196	98	49	24.5	16	12	9.8

If the species is well-mixed in the atmosphere, it follows from [8] that τ_0, the species' atmospheric life-time against dissolution in the ocean, is given by

$$\tau_0 = (H_A \ 0.04/f/H) \ \{r_S + 1/(Dk)^{1/2}\} \tag{9}$$

where $H_A = 8$ km is the atmospheric scale height and $f = 0.7$ is the fraction of the earth's surface co-vered by ocean. Values of τ_0 calculated from Eqn. [9] for H varying from 0.001 to 0.1 M atm^{-1} and k varying from 10^{-11} to 10^{-7} s^{-1} are listed in Table 1. It should be noted that Eqn. [9] is only valid for values of H and k such that $\tau_0 > 30$ - 60 days. Once the calculated ϕ_0 falls below this value, the assumption used in the above derivation that the species is well-mixed in the atmosphere is no longer valid. In this case, the actual atmospheric lifetime for removal in the oceans will be limited by the time required to transport the species to the marine boundary layer (i.e., about 30 to 60 days).

The values for H and k used to calculate τ_0 for the HFCs and HCFCs of interest in this work are listed in Table 2. For all species except CH_3CCl_3, values for H in seawater were assumed to be 80% of their pure water Henry's law coefficient at a temperature of 285K. Pure water values for H (see Figure 1) were taken from McLinden AFEAS, 1989 (this report) for all species considered except CH_3CCl_3. The Hen-ry's law coefficients for CH_3CCl_3 in pure water and seawater were obtained from the results of Gossett (1987). He found that $H = 5.8 \times 10^{-8}$ exp $(4130/T)$ M atm^{-1} in pure water and that addition of .75M
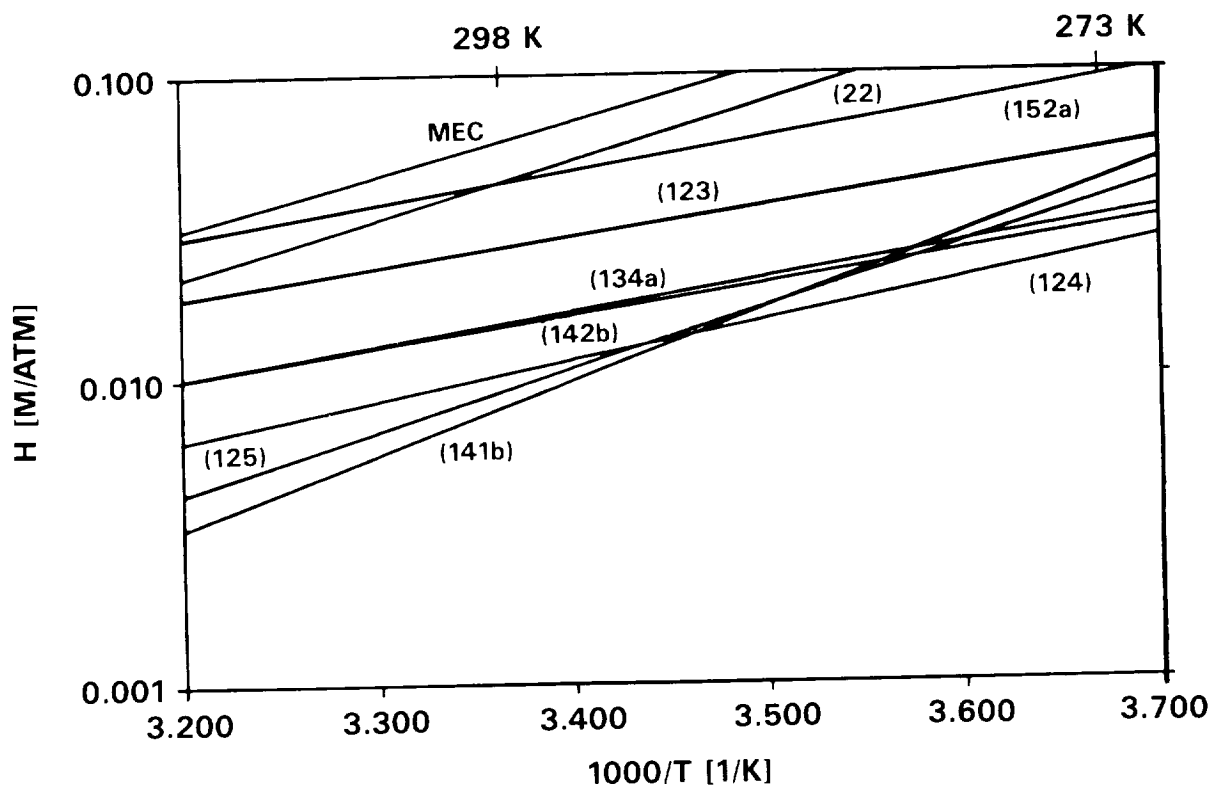

Figure 1. Henry's Law solubilities in pure water for selected HFCs, HCFCs, and CH_3CCl_3 (MEC) as a function of temperature.

Table 2. Solubilities, Pseudo First-Order Loss Rates, and Lifetimes Against Oceanic Removal For Selected HFCs and HCFCs

Species	H(M/atm)	Pseudo First Order Loss Rates (s⁻¹)				Lifetime (years)	
		k_h	k_e	k_{OH}	k	b.e.	min
CH_3CCl_3	0.08	4×10^{-9}	1.4×10^{-9}	1.6×10^{-11}	5.4×10^{-9}	42	22
$CF_3CHF_2(125)$	<0.015	$<10^{-10}$	$<10^{-11}$	4×10^{-12}	$<10^{-10}$	>1500	>700
$CF_3CH_2F(134a)$	0.02	$<10^{-10}$	$<10^{-11}$	1.2×10^{-11}	$<10^{-10}$	>1100	>530
$CH_3CHF_2(152a)$	0.05	$<10^{-10}$	$<10^{-11}$	4×10^{-11}	$<10^{-10}$	>460	>210
$CF_3CHClF(124)$	0.015	10^{-9}	10^{-9}	1.6×10^{-11}	2×10^{-9}	360	170
$CH_3CClF_2(142b)$	0.02	10^{-9}	10^{-9}	4×10^{-12}	2×10^{-9}	270	130
$CF_3CHCl_2(123)$	0.03	10^{-9}	10^{-9}	4×10^{-11}	2×10^{-9}	180	85
$CH_3CFCl_2(141b)$	0.015 - 0.07	10^{-9}	10^{-9}	1×10^{-11}	2×10^{-9}	77-360	36
$CHClF_2(22)$	0.085	3×10^{-10}	3×10^{-10}	6×10^{-12}	6×10^{-10}	110	45

T is assumed to be 285K
b.e. = Lifetime calculated with H and k listed in Table
min = Lifetime calculated with maximum H value listed and k enhanced by a factor of 5

KCl resulted in a 40% decrease in H (the ionic strength of seawater is approximately 0.75M). Gossett's result in pure water at 298K is in excellent agreement with an estimate by Lyman (1985) which was based on solubility and vapor pressure data, but a factor of two larger than an earlier measurement reported by Dilling (1977). While the values for the Henry's law solubilities of most of the species were judged to be known to within about 15%, McLinden AFEAS 1989 has noted the possibility of a significant error in the Henry's Law solubilities cited for CF_3CHF_2 and CH_3CFCl_2. To account for this possibility as well as other unknown systematic errors, we have adopted a range of H-values for CF_3CHF_2 and CH_3CFCl_2. (See Table 2).

Three processes were considered to determine the pseudo first-order loss rate, k, for the compounds of interest. These were hydrolysis, indicated by k_h in Table 2, reaction with hydrated electrons, indicated by k_e in Table 2, and reaction with OH, indicated by k_{OH} in Table 2. The total loss rate is thus given by

$$k = k_h + k_e + k_{OH} \tag{10}$$

The hydrolysis rates in Table 2 for $CHClF_2$ and for CH_3CCl_3 were obtained from McLinden AFEAS, 1989 and Ellenrieder and Reinhard (1988), respectively. New unpublished results (Gerkens and Franklin, 1989) verify the CH_3CCl_3 hydrolysis rate in Table 2 and provide improved temperature dependence data.

The other hydrolysis rates were assumed to be intermediate between that of CH_3CCl_3 and $CHClF_2$ for those species which contain at least one Cl atom (i.e., 10^{-9} s^{-1}) and less than 10^{-10} s^{-1} for those species which do not contain any Cl. It should be noted that the k_h values listed in Table 2 are based on data obtained from fresh water and that the actual hydrolysis rates in seawater may be significantly different. For instance, ionic strength effects have the potential to increase or decrease the hydrolysis rates by as much as 50% (Neely, 1985). In the case of the fluorinated compounds, hydrolysis can be enhanced by perhaps an order of magnitude or more because the large levels of Cl^- ions in seawater can catalyze hydrolysis of fluorocarbons via nucleophilic substitution of Cl for F followed by hydrolysis of the chlorocarbon (Zafiriou, 1975). In order to indicate the possible impact of these effects on our results, sensitivity calculations will be presented in which our estimated values for k are arbitrarily increased by a factor of 5. It should be noted, however, that it does not appear possible for Cl^- catalysis to cause any of the HFCs to have an "effective" hydrolysis rate faster than that of CF_3CHClF, because nucleophilic substitution of OH for Cl is expected to be considerably faster than nucleophilic substitution of Cl for F.

The values for k_e in Table 2 were obtained by assuming an average hydrated electron level in the mixed layer of the ocean of 1 x 10^{-19} M. This estimate for the concentration of hydrated electrons in the oceans is based on: 1. the observations of Zepp et al. (1987a) which implied a diurnally averaged abundance of free electrons at the surface of fresh water lakes and rivers of about 5 x 10^{-18} M from the irradiation of dissolved organic matter; 2. the fact that dissolved organic matter is about 10 times less abundant in the ocean than in fresh water (Stumm and Morgan, 1970); and 3. the assumption that free electrons will decrease with increasing depth with a scale depth of 15m due to the attenuation of sunlight in the ocean. (Note that the upper limit for e^- in seawater of 10^{-15} M reported by Swallow (1969) seems much too high based on current information). Second-order rate constants for the reaction of CH_3CCl_3 and $CHClF_2$ with hydrated electrons were taken to be 1.4 x 10^{10} M^{-1} s^{-1} and 3 x 10^9 M^{-1} s^{-1}, respectively, based on the observations of Lal et al. (1988) and Salih et al. (1976). Rate constants for the other HFCs and HCFCs which contain Cl atoms were assumed to be intermediate between that of CH_3CCl_3 and $CHClF_2$, i.e. 10^{10} M^{-1} s^{-1} for species containing Cl atoms (cf., Balkas et al., 1971; Anbar and Hart, 1965; Balkas, 1972; Afanassiev et al., 1979; Salih, et al., 1976; Hart et al., 1964; Bullock and Cooper, 1970), and less than 10^8 M^{-1} s-1 for those species which contain no Cl atoms.

The values of k_{OH} listed in Table 2 were estimated assuming a seawater OH concentration of 4 x 10^{-19} M (Zepp et al., 1987b; Zafiriou and True, 1979). For CH_3CCl_3, a second-order aqueous-phase rate constant for the OH reaction of 4 x 10^7 M^{-1} s^{-1} (Lal et al., 1988) was adopted. The second-order rate constants for the other HFCs and HCFCs were assigned values based on their gas phase rate constants relative to the gas phase OH + CH_3CCl_3 rate constant. Comparison of the aqueous phase rate constants reported by Lal, et al. (1988) with known gas phase rate constants for the same reactions seems to justify this procedure.

The resulting lifetimes obtained from Eqn [9] for each of the HFCs and HCFCs considered here are listed in Table 2. Note that two sets of lifetimes are listed in the Table: the 'best estimate' for the values of H and k obtained in the manner described above, and a minimum lifetime obtained from the maximum value estimated for H and a k enhanced by a factor of 5 over the value listed in the Table. With the exception of CH_3CCl_3 and CH_3CFCl_2, it appears likely that the lifetimes for HFCs and HCFCs against removal by dissolution in the oceans are of the order of 100 years or more indicating that this process is unlikely

to be of significance. In the case of CH_3CCl_3 and CH_3CFCl_2, however, oceanic removal could be non-negligible depending on the exact Henry's law solubilities and loss rates of these species in seawater. There is also a possibility that the same may be true of $CHClF_2$ and CF_3CHCl_2. Further research to better define the Henry's Law coefficients and loss rates for these species in seawater might prove to be a useful endeavor.

3. REMOVAL OF HCFCs AND HFCs IN CLOUDWATER

The removal of HCFCs and HFCs by dissolution and chemical degradation in cloudwater appears to be much smaller than the rate of removal in the oceans. To illustrate this fact, consider the removal by cloudwater of CH_3CCl_3, probably the most readily removed of all the compounds considered here. As discussed above, CH_3CCl_3 probably has a Henry's law solubility in cloudwater (T $\geq$ 273K) of $\leq$ 0.2 M atm^{-1}. Its pseudo first-order rate of removal in cloudwater is probably controlled by reaction with aqueous-phase OH radicals; given a second-order, aqueous-phase rate constant against reaction with OH of 4 x 10^7 M^{-1} s^{-1} (Lal et al., 1988) and a cloudwater OH concentration of about 2 x 10^{-13} M (Chameides, 1984; Jacob, 1986), we estimate a k-value for CH_3CCl_3 in cloudwater of about 8 x 10^{-6} s^{-1}. Assuming an average column content of liquid water in the atmosphere of about 10^{-4} L cm^{-2} (Junge, 1963) and assuming gas-aqueous-phase equilibration, (appropriate for H $\leq$ 10^3 M atm^{-1}, cf., Xing and Chameides, 1989) it follows that RC, the rate of loss of the species in cloudwater (in molecules cm^{-2} s^{-1}), is given by

$$RC = X\ (0.2\ M\ atm^{-1})\ (10^{-4}\ L\ cm^{-2})\ N_A\ 8\ x\ 10^{-6}\ s^{-1} \tag{11}$$

where X is the species volume mixing ratio. If we further assume that the species is well-mixed in the atmosphere, Eqn. [11] implies an atmospheric lifetime, τ_c, against removal by cloudwater of

$$\tau_c = X\ (2.5\ x\ 10^{19}\ molec\ cm^{-3})\ H_A/RC \approx 5,000\ years \tag{12}$$

Even longer lifetimes are obtained as H and k are decreased for the other HFCs and HCFCs.

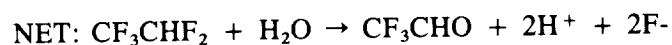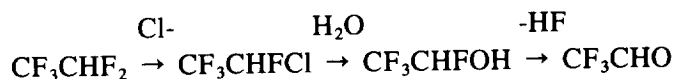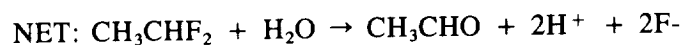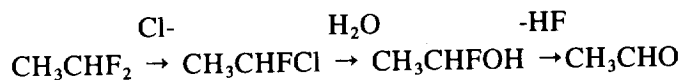## 4. DEGRADATION PRODUCTS OF HYDROLYSIS AND HYDRATED ELECTRON REACTIONS

Hydrolysis of C_2 halocarbons can proceed via either substitution or elimination mechanisms, while only the substitution pathway is available for C_1 halocarbons. Primary halocarbons generally hydrolyze predominantly by the substitution pathway, with elimination becoming more important for branched halocarbons (Roberts and Caserio, 1965). For CH_3CCl_3, hydrolysis is known to yield 70-80% $CH_3C(O)OH$ (the substitution product) and 20-30% $H_2C=CCl_2$ (the elimination product) (Ellenrieder and Reinhard, 1988; Gerkens and Franklin, 1989). Product information is not available for the other halocarbons of interest in this assessment.

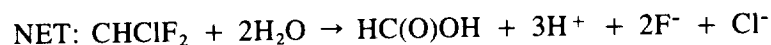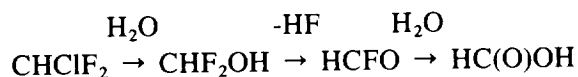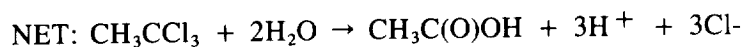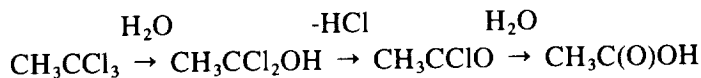The haloethylenes formed via elimination are resistant to hydrolysis and relatively insoluble in water (see, for example, Gossett, 1987). Degradation of these compounds is expected to occur rapidly in the gas phase following volatilization from the aqueous phase.

Hydrolysis via the substitution pathway is a multistep process which involves formation of unstable intermediates such as α-haloalcohols and acid halides. Probable intermediate and end products are summarized in Table 3. The expected stable products are: $HC(O)OH$ from $CHClF_2$; $CH_3C(O)OH$ from CH_3CFCl_2 and CH_3CF_2Cl; CF_3CHO from CF_3CHCl_2, CF_3CHF_2 and CF_3CHFCl; CF_3CH_2OH from CF_3CH_2F;

Table 3. Probable Reaction Pathways for Hydrolysis of the Halocarbons of Interest via Substitution Mechanisms

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$$CH_3CCl_3 \xrightarrow{H_2O} CH_3CCl_2OH \xrightarrow{-HCl} CH_3CClO \xrightarrow{H_2O} CH_3C(O)OH$$

NET: $CH_3CCl_3 + 2H_2O \rightarrow CH_3C(O)OH + 3H^+ + 3Cl-$

$$CHClF_2 \xrightarrow{H_2O} CHF_2OH \xrightarrow{-HF} HCFO \xrightarrow{H_2O} HC(O)OH$$

NET: $CHClF_2 + 2H_2O \rightarrow HC(O)OH + 3H^+ + 2F^- + Cl^-$

$$CF_3CHCl_2 \xrightarrow{H_2O} CF_3CHClOH \xrightarrow{-HCl} CF_3CHO$$

NET: $CF_3CHCl_2 + H_2O \rightarrow CF_3CHO + 2H^+ + 2Cl-$

$$CH_3CFCl_2 \xrightarrow{H_2O} CH_3CFClOH \xrightarrow{-HCl} CH_3CFHO \xrightarrow{H_2O} CH_3C(O)OH$$

NET: $CH_3CFCl_2 + 2H_2O \rightarrow CH_3C(O)OH + 3H^+ + 3H^+ + 2Cl- + F-$

$$CH_3CF_2Cl \xrightarrow{H_2O} CH_3CF_2OH \xrightarrow{-HF} CH_3CFO \xrightarrow{H_2O} CH_3C(O)OH$$

NET: $CH_3CF_2Cl + 2H_2O \rightarrow CH_3C(O)OH + 3H^+ + 2F- + Cl-$

$$CF_3CHFCl \xrightarrow{H_2O} CF_3CHFOH \xrightarrow{-HF} CF_3CHO$$

NET: $CF_3CHFCl + H_2O \rightarrow CF_3CHO + 2H^+ + Cl- + F-$

$$CF_3CH2F \xrightarrow{Cl-} CF_3CH_2Cl \xrightarrow{H_2O} CF_3CH_2OH$$

NET: $CF_3CH_2F + H_2O \rightarrow CF_3CH_2OH + H^+ + F-$

$$CH_3CHF_2 \xrightarrow{Cl-} CH_3CHFCl \xrightarrow{H_2O} CH_3CHFOH \xrightarrow{-HF} CH_3CHO$$

NET: $CH_3CHF_2 + H_2O \rightarrow CH_3CHO + 2H^+ + 2F-$

$$CF_3CHF_2 \xrightarrow{Cl-} CF_3CHFCl \xrightarrow{H_2O} CF_3CHFOH \xrightarrow{-HF} CF_3CHO$$

NET: $CF_3CHF_2 + H_2O \rightarrow CF_3CHO + 2H^+ + 2F-$

CH_3CHO from CH_3CHF_2. The fluorine containing end product CF_3CH_2OH is expected to be volatilized from the ocean to the gas phase where it would be oxidized by OH radicals. The recent work of Betterton and Hoffmann (1988) suggests that the other fluorine containing end product, CF_3CHO, will have a large effective Henry's law solubility (10^5 - 10^6 M atm^{-1}) due to efficient hydration,

$$CF_3CHO + H_2O \rightarrow CF_3CH(OH)_2 \tag{R1}$$
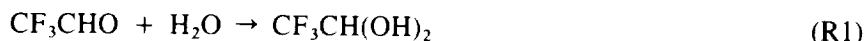
The gem-diol species $CF_3CH(OH)_2$ is expected to be relatively stable in seawater. The lifetime of $CF_3CHO \rightleftarrows CF_3CH(OH)_2$ in seawater may be limited by oxidation of the small equilibrium concentration of $CF_3CHO(g)$ via reaction with OH radicals.

The reactions of hydrated electrons with halocarbons result in the formation of halo-substituted peroxy radicals.

$$RX + e^- \rightarrow R + X^- \tag{R2}$$

$$R + O_2 \rightarrow RO_2 \tag{R3}$$

As mentioned in an earlier section, (R2) proceeds at a diffusion controlled rate for most chlorocarbons, but is considerably slower for fluorocarbons. Attack of chlorofluorocarbons by e$^-$ will always result in removal of a chlorine atom. Haloperoxy radicals are strong oxidizing agents which, in seawater, are expected to undergo electron transfer reactions with resultant production of halohydroperoxides. The aqueous phase chemistries of haloperoxy radicals and halohydroperoxides are considered in some detail in later sections of this report.

5. ALTERNATIVE DEGRADATION PATHWAYS

In addition to hydrolysis and reaction with hydrated electrons, a number of other halocarbon degradation pathways are operative in selected environments such as anoxic contaminant groundwaters, surface waters with high concentrations of metal ion reductants, and regions of high biological activity. These pathways are discussed in a recent review by Vogel, et al. (1987). They include metal catalyzed hydrogenolysis and dihalo-elimination, nucleophilic substitution of SH$^-$ for X$^-$, and enzyme catalyzed hydrolysis and halogenation reactions. It seems unlikely that the above processes will make significant contributions to the global removal rate of HCFCs, HFCs, and CH_3CCl_3 from the atmosphere, although research aimed at quantifying their contribution would be worthwhile.

6. AQUEOUS PHASE REMOVAL OF GAS PHASE DEGRADATION PRODUCTS

Several assessments of potential gas phase degradation products have been prepared as part of the Alternative Fluorocarbons Environmental Acceptability Study. The degradation products include a large variety of halo-substituted carbonyls, acids, peroxyacids, hydroperoxides, alcohols, nitrates, peroxynitrates, and peroxyacetylnitrates. Our attempt to assess the lifetimes of the above compounds toward aqueous phase removal is somewhat hampered by the total absence of Henry's law solubilities for any of the compounds of interest. An Appendix is attached to this report which contains tables of Henry's law solubilities for non-halo-substituted analogs, vapor pressure data, acid-base equilibria, and one-electron redox potentials. These data were used extensively in our evaluation. Possible aqueous phase removal rates and degradation mechanisms for each class of gas phase products are considered below.

Acid Halides

Acid halides are known to hydrolyze rapidly. For Cl_2CO, F_2CO, and $ClFCO$, substitution of OH for X (X = Cl, F) produces a halohydroxycarbonyl which rapidly eliminates HX to yield the end product CO_2. Hydrolysis of the other acid halides of interest, (i.e., HCXO, CH_3CXO, CX_3CXO) proceeds by a single step substitution route to give the corresponding carboxylic acid.

Kinetic data for acid halide hydrolysis in water solvent are rather sparse. Bunton and Fendler (1966) studied the kinetics of CH_3CFO hydrolysis in water as a function of temperature and pH. They obtained the result k_h = 2.9 x 10^7 exp (-6290/T) s^{-1} independent of pH over the range 2.8-6.8, i.e. k_h = 0.0051 s^{-1} at 280K and 0.023 s^{-1} at 300K. Hudson and Moss (1962) used stop-flow techniques to investigate the kinetics of CH_3CClO hydrolysis at 300K in 75.6% H_2O - 24.4% dioxan; they measured k_h = 292 s^{-1}, a rate which is expected to be even faster in pure H_2O solvent. Swain and Scott (1953) measured the relative rates of hydrolysis of CH_3CClO and CH_3CFO in 75% acetone - 25% water at 298K and found that CH_3CClO was 7700 times more reactive, in agreement with the reactivity trend suggested by the above-mentioned absolute rate measurements. Ugi and Beck (1961) studied the hydrolysis kinetics of a series of acid chlorides in 10.9 vol % H_2O + 89.1 vol % acetone at 298K and obtained the following rate constants in units of s^{-1}: CH_3CClO, 0.0011; $ClCH_2CClO$, 0.020; $Cl_2CHCClO$, 3.1; Cl_3CClO, >10; Cl_2CO, 1.02. Substitution of Cl for H on the alkyl carbon dramatically increases the rate of hydrolysis, presumably because the electron withdrawing power of Cl results in stabilization of the transition state for water attack on the carbonyl carbon. Substitution of F for H on the alkyl carbon should increase the hydrolysis rate even more dramatically. Based on the above information it seems clear that, with the possible exception of HFCO, all acid halides of interest will hydrolyze more rapidly than CH_3CFO. Hence, the kinetic data of Bunton and Fendler (1966) for CH_3CFO hydrolysis provide a useful lower limit rate coefficient for assessing the maximum lifetime of acid halides toward uptake and hydrolysis in the ocean and in cloudwater.

For temperatures typical of cloudwater and surface seawater, it seems safe to assume that k_h will be greater than 10^{-3} s^{-1} for all acid halides of interest. Using the 285K effective Henry's law solubility for acetaldehyde of 45 M atm^{-1} (Snider and Dawson, 1985; Betterton and Hoffmann, 1988) as a guide, it also seems safe to assume that H > 10 M atm^{-1} for all acid halides of interest, particularly since electron withdrawing substituents such as Cl and F are known to increase the solubility of carbonyls (Betterton and Hoffmann, 1988). On the basis of the formulations described above, these lower limit values for k_h and H imply upper limit lifetimes for the acid halides against removal in the ocean and removal in cloudwater of the order of a month and 2 years, respectively. It should be noted that the maximum lifetime for removal of acid halides by hydrolysis in the ocean is transport limited, and would be only one or two months even if the above lower limits for k_h and H were reduced by a factor of ten each. Hence, there seems to be very little chance that (apparently) important gas phase degradation products such as ClFCO and CF_3CClO (R.A. Cox, AFEAS, 1989 (this report)) will survive in the atmosphere long enough to represent significant sources of stratospheric chlorine.

CF_3OH

In the condensed phase, CF_3OH is known to be unstable toward elimination of HF (Seppelt, 1977),

$$CF_3OH \rightarrow CF_2O + HF \qquad (R4)$$
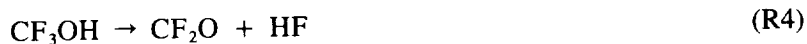
(R4) probably also occurs in the gas phase. If not, it will occur very rapidly upon uptake of CF_3OH into

cloudwater or seawater. Henry's law solubilities for aliphatic alcohols are typically an order of magnitude larger than those of the corresponding aldehydes (Snider and Dawson, 1985). Hence, conversion of CF_3OH to CO_2 + 3HF via HF elimination and subsequent hydrolysis of CF_2O will be as fast as CF_2O hydrolysis if HF elimination occurs in the gas phase and faster if HF elimination occurs in the aqueous phase.

Peroxyacetylnitrates
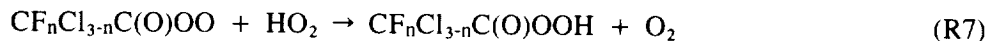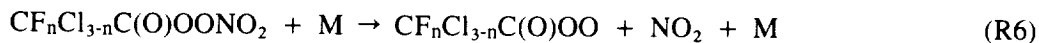
Both hydrolysis and Henry's law data are available for PAN. At 285K, $H \approx 7$ M atm^{-1} and $k_h \approx 1$ x 10^{-4} s^{-1} (Lee, 1984; Holdren, et al., 1984). Based on our earlier discussions, these values suggest a lifetime of about 10 years for PAN removal by cloudwater and of the order of a month for removal in the ocean. Holdren, et al. (1984) have shown that the PAN hydrolysis rate is independent of pH over the range 4.0 - 5.6, and that nitrate is produced as a product. Hence, the hydrolysis reaction is probably

$$CH_3C(O)OONO_2 + H_2O \rightarrow CH_3C(O)OOH + NO_3^- + H^+. \tag{R5}$$
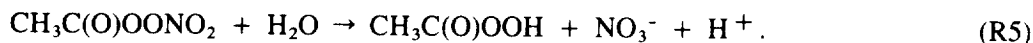
In the absence of experimental data, it seems reasonable to assume that removal of $CF_nCl_{3-n}C(O)OONO_2$ by hydrolysis in seawater and cloudwater will proceed at a rate somewhat faster than that for PAN due to stabilization of the transition state for water attack on the carbonyl carbon by the electron withdrawing nature of Cl and F. The hydrolysis products are expected to be halo-substituted peroxy acids and nitrate. Lifetimes toward hydrolysis in seawater and cloudwater on the order of a few weeks and few years, respectively seem likely.

Despite the rapid removal rate estimated above, ocean hydrolysis may not be an important atmospheric removal mechanism for the halogenated peroxyacetylnitrates. The marine boundary layer is typified by relatively warm temperatures, low NO_x levels, and high HO_x levels. Under such conditions, conversion of peroxyacetylnitrates to peroxyacetic acids should occur in the gas phase, i.e.

$$CF_nCl_{3-n}C(O)OONO_2 + M \rightarrow CF_nCl_{3-n}C(O)OO + NO_2 + M \tag{R6}$$

$$CF_nCl_{3-n}C(O)OO + HO_2 \rightarrow CF_nCl_{3-n}C(O)OOH + O_2 \tag{R7}$$

The stoichiometry of PAN hydrolysis in alkaline solution is (Nicksic, et al., 1967; Stephens, 1967)

$$CH_3C(O)OONO_2 + 2OH^- \rightarrow CH_3C(O)O^- + NO_2^- + O_2 + H_2O \tag{R8}$$
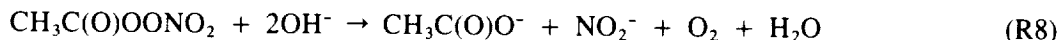
At a typical seawater pH of 8.1 it is not clear what the relative contributions of (R5) and (R8) to PAN hydrolysis will be. However, since peroxyacetic acid is known to hydrolyze rapidly to acetic acid and H_2O_2 (Lind and Kok, 1986), acetate is produced in either case. Similarly, the long-lived halogen-containing products of $CF_nCl_{3-n}C(O)OONO_2$ hydrolysis are expected to be halo-substituted acetates, although halo-substituted peroxyacetates may be produced as intermediates with lifetimes of hours to days. The chemistry of peroxyacetates is discussed in more detail in a later section.

CF₃ONO₂

It has been suggested in the literature (Hohorst and DesMarteau, 1974) that CF_3ONO_2 is thermally unstable in condensed phases.
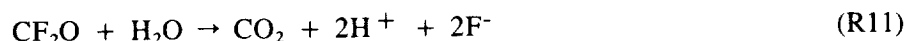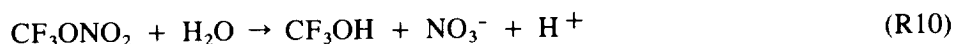
$$CF_3ONO_2 \rightarrow CF_2O + FNO_2 \tag{R9}$$

(R9) may also occur in the gas phase.

If CF_3ONO_2 turns out to be thermally stable, then in the absence of Henry's law solubility data and hydrolysis data, we assume that CF_3ONO_2 will behave similarly to CH_3ONO_2 (methyl nitrate). The Henry's law solubility of CH_3ONO_2 is nearly identical to that of PAN (Lee, et al., 1983). Robertson, et al. (1982) studied the hydrolysis kinetics of isopropylnitrate and three other secondary nitrates in water. Because the observed rates were very slow at room temperature, Robertson, et al.'s experiments were carried out at elevated temperature; the temperature range covered for isopropylnitrate was 340-369K. Extrapolation of Robertson, et al.'s results to lower temperatures suggests $k_h \sim 2 \times 10^{-7}$ s^{-1} at 300K and 5×10^{-9} s^{-1} at 280K. Baker and Easty (1952), have studied the kinetics of neutral hydrolysis (H_2O nucleophile) of methyl-, ethyl-, and isopropylnitrate in 60% ethanol/40% water at 60.2ºC; they obtain the relative reactivities methyl:ethyl:isopropyl = 2.0:1.1:4.8. Alkaline hydrolysis (OH⁻ nucleophile) was found to be about 100 times faster than neutral hydrolysis, but the neutral reaction is expected to dominate under atmospheric conditions. The above results suggest that at 285K, a typical seawater temperature, k_h for methylnitrate is about 4×10^{-9} s^{-1}.

Clearly, removal of CF_3ONO_2 by hydrolysis in cloudwater will be of no importance as an atmospheric loss process. For H = 1 - 10 M atm^{-1} and k_h = (1 - 10) $\times 10^{-9}$ s^{-1}, the lifetime of CF_3ONO_2 toward hydrolysis in seawater will be in the range 0.1 - 10 years. Measurements of H and k_h for CF_3ONO_2 in seawater would clearly be worthwhile.

It is well established that neutral hydrolysis of simple primary and secondary alkyl nitrates proceeds via an S_N2 mechanism to yield the corresponding alcohol (Baker and Easty, 1952; Robertson, et al., 1982). Hence, while the CF_3ONO_2 hydrolysis rate is highly uncertain and could be quite long, the degradation mechanism can be predicted with a reasonable degree of certainty:

$$CF_3ONO_2 + H_2O \rightarrow CF_3OH + NO_3^- + H^+ \tag{R10}$$

$$CF_3OH \rightarrow CF_2O + H^+ + F^- \tag{R4}$$

$$CF_2O + H_2O \rightarrow CO_2 + 2H^+ + 2F^- \tag{R11}$$

Peroxynitrates

No quantitative solubility or hydrolysis rate data is available for alkylperoxynitrates (which are thermally unstable) or the halo-substituted species. The synthesis and characterization of CF_3OONO_2 is reported in the literature (Hohorst and DesMarteau, 1974). Thermal decomposition of CF_3OONO_2 is found to be rather slow in the liquid phase, but hydrolysis to $CF_3OOH + NO_3^-$ is rapid. The Henry's law solubilities of the halo-substituted peroxynitrates are probably similar to those of the peroxyacetylnitrates and the alkylnitrates, i.e. 1 - 10 M atm^{-1}.
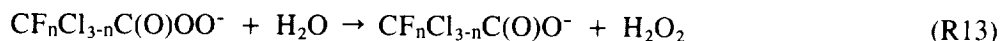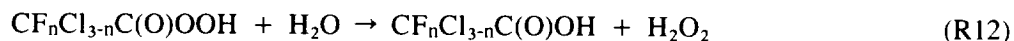
AQUATIC MECHANISMS

The above information suggests that the lifetime of halo-substituted peroxynitrates in the atmosphere will be short. In the marine boundary layer, gas phase conversion to halo-substituted alkylhydroperoxides via a mechanism analogous to (R6) and (R7) will occur if the lifetime toward unimolecular decomposition is of the order of 10^6s or less. Otherwise, removal will be dominated by dissolution and hydrolysis in seawater.

Peroxyacids

Lind and Kok (1986) have determined the Henry's law solubility of peracetic acid to be $\exp(6171/T - 14.55)$M atm^{-1} (i.e. 1790 M atm^{-1} at 280K). These authors have also observed that peracetic acid hydrolyzes to acetic acid and hydrogen peroxide, with the hydrolysis reaction going to completion in a day or two, (i.e. $k_h \sim 10^{-5}$ s^{-1} at 298K). The negative log of the acid dissociation constant (pKa) for peracetic acid is 8.2 (Koubek, et al., 1963). The halogenated peracetic acids will be more acidic than peracetic acid itself. We estimate that the pKa for trichloroperacetic acid will be in the range 6-7, while the pKa for trifluoroperacetic acid will be in the range 5-6. Hence, the halogenated peroxyacids will be partially dissociated in cloudwater, and almost completely dissociated in seawater. For reasons discussed above in conjunction with acid halide and peroxyacetylnitrate hydrolysis, halogenated peroxyacids are expected to hydrolyze considerably more rapidly than alkylperoxyacids.

Based on the above information, we estimate that under cloudwater conditions, pH $\sim$ 5 and T $\sim$ 280K, reasonable values for H and k_h for the halogenated peroxyacetic acids are (1-5) x 10^3 M atm^{-1} and (1-100) x 10^{-5} s^{-1}, respectively, with the fluorinated species expected to be the most reactive. Under seawater conditions, pH $\sim$ 8.1 and T $\sim$ 285K, the effective Henry's law solubilities of the halogenated peroxyacetic acids are expected to be quite large. Reasonable estimates for $CCl_3C(O)OOH$ and $CF_3C(O)OOH$ are 3 x 10^4 M atm^{-1} and 3 x 10^5 M atm^{-1}, respectively. Assuming that the unprotonated acid hydrolyzes about as efficiently as the protonated acid, we estimate that $k_h \sim$ (2-200) x 10^{-5} s^{-1} with $CF_3C(O)OO^-$ expected to be the most reactive species. The above parameters suggest that the lifetimes of the halogenated peroxyacids toward hydrolysis in cloudwater and the ocean are quite short; probably of the order of a week to a month and limited by the rate of transport to cloudy regions and/or the marine boundary layer.

The products of peroxyacid hydrolysis are expected to be the corresponding acids (Lind and Kok, 1986), i.e.,

$$CF_nCl_{3-n}C(O)OOH + H_2O \rightarrow CF_nCl_{3-n}C(O)OH + H_2O_2 \tag{R12}$$

$$CF_nCl_{3-n}C(O)OO^- + H_2O \rightarrow CF_nCl_{3-n}C(O)O^- + H_2O_2 \tag{R13}$$

Acids

The halo-substituted acetic acids are very acidic species. The pKa's for $CF_3C(O)OH$ and $CCl_3C(O)OH$ are 0.25 and 0.64, respectively (Lange, 1979). Hence, these species are almost totally deprotonated in environmental aqueous phase systems. Taking 10^3 M atm^{-1} as a reasonable lower limit Henry's law solubility for $CF_nCl_{3-n}C(O)OH$ at 280 - 285K, effective Henry's law solubilities are $> 10^7$ M atm^{-1} in cloudwater, $> 10^9$ M atm^{-1} in freshwater lakes and rivers, and $> 10^{10}$ M atm^{-1} in seawater.

As discussed in detail below, we expect the halo-acids to be resistant to chemical degradation. The combination of low reactivity and high solubility suggests that the principal fate of atmospheric halo-acids

will be rainout. Rainout of highly soluble species has been modelled in some detail by Giorgi and Chameides (1985), who showed that the rainout rate depends not only on the average rainfall, but also on the period of the storm cycle. The difference between rainout rates calculated for continuous light rainfall versus a short period of heavy rain followed by a long dry period is about an order of magnitude with continuous light rainfall resulting in more rapid rainout. A typical rainout rate for $CF_nCl_{3-n}C(O)OH$ is estimated to be 10^{-6} s^{-1}, or about 12 days.

Once the halo-acids are deposited into freshwater or seawater, they may undergo a number of reactions. These include reaction with hydrated electrons, oxidation-decarboxylation, thermal decarboxylation, hydrolysis, and microbial degradation. Probable rates and mechanisms for these reactions are discussed below.

The rate coefficient for the reaction

$$e^- + CCl_3C(O)O^- \rightarrow CCl_2C(O)O^- + Cl^- \tag{R14}$$
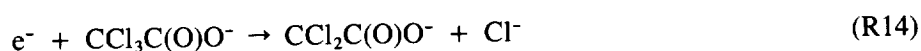
is known to be 8.5×10^9 M^{-1} s^{-1} (Anbar and Hart, 1965). As discussed previously in this report, estimated hydrated electron concentrations in freshwater and seawater are 10^{-18} M and 10^{-19} M, respectively. Hence, the lifetime of $CCl_3C(O)O^-$ toward removal via (R14) is estimated to be 3.7 years in freshwater and 37 years in seawater. $CF_3C(O)O^-$ is expected to be at least 100 times less reactive with e^- than is $CCl_3C(O)O^-$, while $CF_2ClC(O)O^-$ and $CFCl_2C(O)O^-$ will react at intermediate rates. The radical products of (R14) and its analogs will rapidly add O_2 to form peroxy radicals,

$$CX_2C(O)O^- + O_2 \rightarrow OOCX_2C(O)O^- \tag{R15}$$
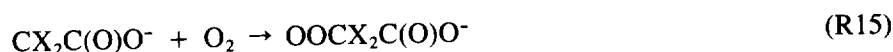
Halo-substituted peroxy radicals are known to be strong oxidizing agents (Packer, et al., 1980; Monig, et al., 1983; Alfassi, et al., 1987; Huie, et al., 1987; Lal et al., 1988). For example, Huie and Neta (private communication) have found that the reactions

$$CX_3OO + I^- \rightarrow CX_3OO^- + I \tag{R16}$$

proceed rapidly with $k \sim 10^8$ M^{-1} s^{-1} for $X = Cl$ and F. Kinetics studies of CCl_3OO, $OOCCl_2(O)O^-$, and $OOCF_2C(O)O^-$ reactions with a number of antioxidants have shown that $OOCCl_2(O)O^-$ and $OOCF_2C(O)O^-$ are about equally reactive, but both are 3 - 10 times less reactive than CCl_3OO (Packer, et al., 1980). A typical iodide concentration in seawater is 10^{-7} M, suggesting that the lifetime of $OOCX_2C(O)O^-$ toward reduction by I^- is about one second. Analogous reactions are also expected to proceed rapidly in freshwater due to the availability of good reducing agents such as, for example, NO_2^-. The probable chemistry of $^-OOCX_2C(O)O^-$ and their protonated species $HOOCX_2C(O)O^-$ is discussed in the next section.

It is known that strong oxidizing agents can undergo the following reaction with acetate:

$$X + CH_3C(O)O^- \rightarrow X^- + CH_3C(O)O \rightarrow CH_3 + CO_2 \tag{R17}$$
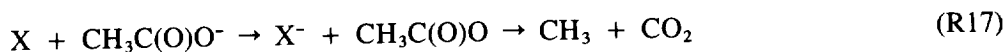
The sulfate radical, for example, is known to react with acetate at a moderate rate ($k = 3.7 \times 10^6$ M^{-1} s^{-1} in the zero ionic strength limit) (Wine, et al., 1989) to produce CO_2 (Madhavan, et al., 1978). The

one electron redox potential (E^0) is 2.41 volts (versus the normal hydrogen electrode) for the $CH_3C(O)O/CH_3C(O)O^-$ couple and 2.52 volts for the SO_4^-/SO_4^{2-} couple (Eberson, 1982). Substitution of electron withdrawing substituents such as Cl and F on the alkyl carbon are expected to significantly increase E^0. Hence, it appears that SO_4^-, one of the strongest oxidizing agents found in environmental aqueous systems, is not capable of oxidizing $CF_nCl_{3-n}C(O)O^-$. Another possibility worth considering is oxidation of the halo-acetates by valence band holes in colloidal metal oxide particles which can be generated photolytically in surface natural waters. For example, the bandgaps of TiO_2 and ZnO are 3.0 volts (Morrison, 1980) and 3.4 volts (Bahnemann, et al., 1987), respectively. Because the electron donor (i.e. $CF_nCl_{3-n}C(O)O^-$) must interact with the hole within nanoseconds after the hole is created in order to compete with rapid electron-hole recombination (Rothenberger, et al., 1985), the oxidation process can only occur for donors which are adsorbed to the particle surface. Kormann, et al. (1989), using relatively high concentrations of donor and metal oxide, have found that chloroacetates can be degraded with quantum yields in the range of 3% for TiO_2 and 0.1% for ZnO at pH = 5. Improved knowledge of particle size distributions and concentration profiles in natural waters, rates of adsorption and desorption of the haloacetates to particle surfaces, and degradation quantum yields as a function of wavelength are needed before the potential importance of haloacetate oxidation by valence band holes in semiconductor particles can be assessed with any degree of confidence.

Thermal decarboxylation of halo-substituted acetic acids at elevated temperatures are a well-known set of organic reactions, which are discussed in most undergraduate organic chemistry textbooks (see, for example, Roberts and Caserio, 1965). Verhoek (1934) studied the kinetics of CCl_3COO^- thermal decarboxylation in aqueous solution over the temperature range 50 - 90°C; measured rate coefficients varied from 6.2×10^{-7} s^{-1} at 50°C to 3.1×10^{-4} s^{-1} at 90°C. Extrapolation of Verhoek's results to 285K, a typical surface seawater temperature, suggests that k $\sim$ 3.7×10^{-9} s^{-1} (lifetime $\sim$86 years). At 300K, however, the lifetime of $CCl_3C(O)O^-$ toward thermal decarboxylation appears to be only about 2 years. Clearly, thermal decarboxylation in the tropical oceans could be an important removal process for $CCl_3C(O)O^-$. The thermal decarboxylation kinetics of $CF_3C(O)O^-$ (Auerbach, et al., 1950), $CCl_2FC(O)O^-$ (Hine and Duffey, 1959a) and $CF_2ClC(O)O^-$ (Hine and Duffey, 1959b) have also been studied in aqueous solution. Extrapolation of available data suggests that at T $\le$ 300K all three reactions have rate coefficients of less than 10^{-10} s^{-1}. The more fluorine atoms on the alkyl carbon, the slower the reaction proceeds. For $CCl_3C(O)O^-$, $CCl_2FC(O)O^-$, and $CF_3C(O)O^-$, the mechanism of the thermal decarboxylation reaction is

$$CX_3C(O)O^- \rightarrow CO_2 + CX_3^- \rightarrow CHX_3 \qquad (R18)$$

For $CClF_2C(O)O^-$, Hine and Duffey (1959b) have shown that the detailed mechanism is somewhat different

$$CClF_2C(O)O^- \rightarrow CO_2 + Cl^- + CF_2 \qquad (R19$$
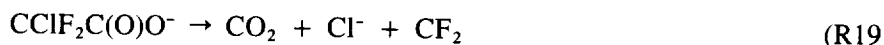
In seawater the CF_2 radical should react with chloride, then protonate to form $CHClF_2$:

$$CF_2 + Cl^- \rightarrow CF_2Cl^- \rightarrow CHF_2Cl \qquad (R20)$$
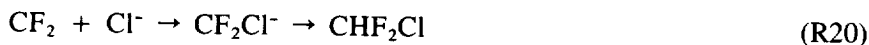
Very little information is available concerning hydrolysis of trihaloacetic acids. It appears that S_N2 attack by H_2O does not compete with thermal decarboxylation, at least over the temperature regime where the overall reaction rate is convenient for experimental determination. Hine and Duffey (1959b) did ob-

serve oxalic acid as a minor product of $CF_2ClC(O)O^-$ degradation in aqueous solution and attributed its production to a hydrolysis reaction:

$$CClF_2C(O)O^- + H_2O \rightarrow HOCF_2COO^- + H^+ + Cl^- \tag{R21}$$

$$HOCF_2C(O)O^- \rightarrow OFCC(O)O^- + H^+ + F^- \tag{R22}$$

$$OFCC(O)O^- + H_2O \rightarrow HO(O)CC(O)O^- + H^+ + F^- \tag{R23}$$
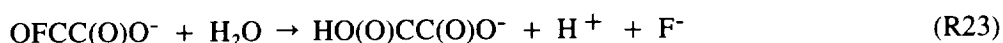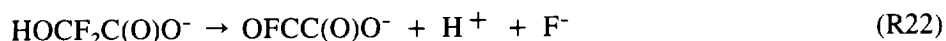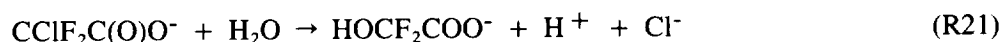
In seawater oxalic acid exists primarily in the singly protonated form with a smaller but significant concentration of the fully protonated acid.

It is known that enzymes found in soil microorganisms and higher plants can cleave the C-X bonds in a number of haloacetates, including $CH_2FC(O)O^-$, $CH_2ClC(O)O^-$ and $CHCl_2C(O)O^-$, by catalyzing hydrolysis (Goldman, 1969). It seems reasonable to expect that plant and/or microbial enzymes can remove fluorine atoms from $CF_nCl_{3-n}C(O)O^-$ as well. Further research is needed to establish the rates of $CF_nCl_{3-n}C(O)O^-$ degradation via biological processes in natural environments such as soils, vegetation, fresh water, and seawater.

In summary, it appears that $CCl_3C(O)O^-$ can react at appreciable rates in natural waters with hydrated electrons and by thermal decarboxylation; the lifetime of $CCl_3C(O)O^-$ toward removal by these processes is probably a few years. The other chlorofluoroacetates are more stable toward chemical removal. The most stable species, $CF_3C(O)O^-$, could have a lifetime in natural waters as long as several hundred years. Processes which could possibly degrade $CF_nCl_{3-n}C(O)O^-$ on shorter time scales than those suggested above, but whose rates cannot be estimated with any degree of confidence at this time, include oxidation by photochemically generated valence band holes in semiconductor particles and hydrolysis catalyzed by enzymes in microorganisms and plants; further research aimed at characterizing these processes is needed.
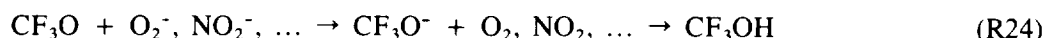
Hydroperoxides

Lind and Kok (1986) have determined the Henry's law solubility of CH_3OOH to be $\exp(5607/T - 13.41)$ M atm^{-1} (i.e. 746 M atm^{-1} at 280K). These authors have also observed that CH_3OOH hydrolyzes to methanol and hydrogen peroxide; the lifetime of CH_3OOH toward hydrolysis appeared to be a month or two at 298K. The pKa for CH_3OOH is 11.5 (Lange, 1979). However, the halogenated hydroperoxides are expected to be considerably more acidic. Bernstein, et al.,(1971) report a pKa of 6.4 for CF_3OOH, suggesting that this species is > 90% protonated in cloudwater but > 90% unprotonated in seawater. Although no Henry's law data is available for the halogenated hydroperoxides, the vapor pressure of CF_3OOH is known to be about 2 atmospheres at 298K (Bernstein, et al., 1971) whereas the vapor pressure of CH_3OOH is only 54.2 Torr at 298K (G.L. Vaghjiani, private communication). Hence, it seems likely that the Henry's law solubility of CF_3OOH is smaller than that of CH_3OOH.

If photolysis, rates for halogenated hydroperoxides in the gas phase are similar to those of H_2O_2 and CH_3OOH, then gas phase photolysis will be the dominant atmospheric sink for these species ($\tau \approx$ 1-2 weeks). However, it is possible that the UV spectra of halogenated hydroperoxides are blue-shifted from the spectra of H_2O_2 and CH_3OOH, in which case gas phase photolysis could be very slow and aqueous phase removal could become important.
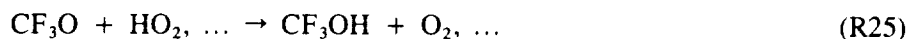
The halogenated hydroperoxides' lifetimes against dissolution in cloudwater and photolysis or reaction with OH radicals is likely to be slow. For a Henry's law solubility of 300 M atm^{-1}, a relatively fast photolysis rate in cloudwater of 2 x 10^{-6} s^{-1}, and a rate constant for reaction with aqueous-phase OH of 1 x 10^7 M^{-1} s^{-1}, we estimate a cloudwater removal lifetime using equations [11] and [12] of the order of years.

With regard to photolysis it is interesting to note that hydroperoxides photolyze via rupture of the O-O bond to give an alkoxy radical and an OH radical. In solution, chlorinated alkoxy radicals are thermally unstable and would be expected to rapidly eliminate a Cl atom to form an acid halide which, as discussed above, would rapidly hydrolyze. Totally fluorinated alkoxy radicals such as CF_3O should react rapidly either by electron transfer, i.e.

$$CF_3O + O_2^-, NO_2^-, \ldots \rightarrow CF_3O^- + O_2, NO_2, \ldots \rightarrow CF_3OH \qquad (R24)$$

or by hydrogen abstraction, i.e.

$$CF_3O + HO_2, \ldots \rightarrow CF_3OH + O_2, \ldots \qquad (R25)$$

As discussed above, CF_3OH rapidly eliminates HF to produce CF_2O, which rapidly hydrolyzes to CO_2 + HF. On the other hand, in the case of OH attack on the hydroperoxides, we expect that the products will undergo rapid reactions in solution regenerating hydroperoxide (see above).

In seawater, reactions of the type

$$X^- + ROOH \rightarrow X + RO + OH^- \qquad (R26)$$

can compete with photodissociation as a removal mechanism for hydroperoxides. The species X can be halide ions or transition metal ions. It is worth noting that the reactions where X = I$^-$ and Fe^{2+} are used for quantitative analysis of peroxides (Siggia and Hanna, 1979). While quantitative kinetic data for X$^-$ + ROOH reactions seem to be available only for hydrogen peroxide (i.e. R = H), it is worth noting that all hydroperoxides are known to react rapidly with iodide (Siggia and Hanna, 1979). Parameters relevant to the assessment of the importance of reactions of I$^-$, Br$^-$, Cl$^-$, Cu(I), and Fe(II) with H_2O_2 as peroxide destruction mechanisms in seawater are given in Table 4. It should be noted that complexation with OH$^-$ and Cl$^-$ leads to complicated speciation patterns for the transition metal ions. The dominant reacting Cu(I) and Fe(II) species are not the bare metal ions, but CuCl$_2^-$ and Fe(OH)$^+$ (Moffett and Zika, 1987a). The results presented in Table 4 suggest that reaction with Fe(II) is the dominant sink for H_2O_2 in seawater, since photolysis in surface water and hydrolysis are expected to proceed at rates on the order of 10^{-7} s^{-1} each.

To estimate the lifetime of halogenated hydroperoxides toward chemical or photochemical removal in seawater, we assume that they undergo reactions with X$^-$, hydrolysis, and photolysis at rates similar to those observed for H_2O_2, i.e. k $\approx$ 10^{-4} s^{-1}. The Henry's law solubilities for the halogenated hydroperoxides under seawater conditions (T $\sim$ 285K, $\mu \sim$ 0.75 M) are estimated to lie in the range 50 - 500 M atm^{-1}. For the above range of values for k and H, it is likely that hydroperoxide removal in seawater will be of the order of 1 month and be limited by transport to the marine boundary layer. Reduction of k by a factor of 100 would have no effect on the (transport limited) lifetime.

Table 4. Sinks for H_2O_2 in Seawater via the Reaction $X^- + H_2O_2 \rightarrow X + OH + OH^-$

	$k(M^{-1} s^{-1})^{(a)}$	$[X](M)$	$k(s^{-1})$	References
I^-	0.26	1×10^{-7}	2.6×10^{-8}	1
Br^-	4.4×10^{-6}	8×10^{-4}	3.5×10^{-9}	2
Cl^-	$1.7 \times 10^{-8(b)}$	0.54	9.2×10^{-9}	2
$Cu(I)^{(c)}$	70	1×10^{-10}	7.0×10^{-9}	3,4
$Fe(II)^{(d)}$	3×10^4	5×10^{-9}	1.5×10^{-4}	5,6

(a) $T = 285K$
(b) highly uncertain
(c) the reactive species in seawater is thought to be $CuCl_2^-$
(d) the reactive species in seawater is thought to be $Fe(OH)^+$

1. Liebhafsky and Mohammed, 1933
2. Mohammed and Liebhafsky, 1934
3. Moffett and Zika, 1987a
4. Moffett and Zika, 1987b
5. Hong and Kester, 1986
6. Landing and Westerlund, 1988

X^- + ROOH reactions and photolysis lead to the production of haloalkoxy radicals which decay via mechanisms discussed above in conjunction with the cloud chemistry of hydroperoxides. Hydrolysis is expected to produce haloalcohols; these compounds rapidly eliminate HX to form acid halides which, in turn, rapidly hydrolyze via mechanisms discussed earlier.

As discussed in an earlier section, reactions of the hydrated electron with haloacetic acids results in the production of acid hydroperoxides, i.e. $HOOCF_nCl_{2-n}C(O)O^-$. These species are expected to be degraded via mechanisms completely analogous to those described above for haloalkyl hydroperoxides. The end products are expected to be oxalic acid (HOOCCOOH), HF, and HCl.

7. SUMMARY

The rates at which eight potential alternative HCFCs and HFCs and methyl chloroform (CH_3CCl_3) can be removed from the atmosphere by dissolution and reaction in the oceans and in cloudwater have been estimated from the species' thermodynamic and chemical properties using simple mathematical formulations to simulate the transfer of gases from the atmosphere to the aqueous phase. The HCFCs and HFCs considered are $CHCl_2CF_3$ (HCFC-123), $CFCl_2CH_3$ (HCFC-141b), CF_2ClCH_3 (HCFC-142b), CHF_2Cl (HCFC-22), $CHFClCF_3$ (HCFC-124), CH_2FCF_3 (HFC-134a), CHF_2CH_3 (HFC-152a), and CHF_2CF_3 (HFC-125).

Cloudwater is found to be of no importance as an atmospheric sink for any of the above compounds. Best-estimate lifetimes for all eight HCFCs and HFCs toward removal in the oceans are greater than 77 years, with only HCFC-22, HCFC-123, and HCFC-141b having lifetimes shorter than 200 years. The most reactive of the nine species, considered toward removal in the oceans is methyl chloroform, with a best-estimate lifetime of 42 years and a minimum reasonable lifetime of 22 years. Important removal mechanisms for methyl chloroform, HCFC-22, HCFC-123, and HCFC-141b in seawater are hydrolysis and reaction with hydrated electrons. Improved hydrolysis kinetics data and Henry's law solubility data for methyl chloroform, HCFC-22, HCFC-123, and HCFC-141b would help to reduce the uncertainties in the aqueous phase removal rates of these species as would improved estimates of the hydrated electron concentration in seawater.

Gas phase degradation products of the eight HCFCs and HFCs include a large variety of halo-substituted carbonyls, acids, peroxyacids, hydroperoxides, alcohols, nitrates, peroxynitrates, and peroxyacetylnitrates.

Although handicapped by the total absence of Henry's law solubility data for any of the compounds of interest and the limited availability of relevant kinetic data, an assessment of the rates and mechanisms of aqueous phase removal of the gas phase degradation products has been carried out.

The species X_2CO, $HXCO$, CH_3CXO, CF_3OH, CX_3OONO_2, and $ROOH$ (X = F or Cl, R = halo-substituted methyl or acetyl) are all expected to be removed from the atmosphere on time scales limited by transport to cloudy regions or the marine boundary layer (i.e. about 1 month); aqueous phase reactions of these species result in the formation of chloride, fluoride, and carbon dioxide, as well as formic, acetic, and oxalic acids. The species CX_3CXO, CX_3CX_2OOH, $CX_3CX_2OONO_2$, $CX_3C(O)OONO_2$, and $CX_3C(O)OOH$ are also expected to be removed from the atmosphere rapidly, and their aqueous phase reactions result in the formation of halo-substituted acetates, $CX_3C(O)O^-$.

The species $CX_3C(O)OH$ are very acidic and, as a result, are highly soluble in cloudwater. These acids are expected to be rapidly removed from the atmosphere by rainout. However, the aqueous phase species $CX_3C(O)O^-$ are expected to be resistant to chemical degradation. Trichloroacetate can thermally decompose on a time scale of 2-10 years to yield carbon dioxide and chloroform. In fresh water, the reaction of $CCl_3C(O)O^-$ with the hydrated electron is also expected to occur on a time scale of a few years. The species $CFCl_2C(O)O^-$, $CF_2ClC(O)O^-$, and $CF_3C(O)O^-$ may have very long aqueous phase lifetimes. The longest lived species, $CF_3C(O)O^-$, could have a lifetime in natural waters as long as several hundred years. Processes which could possibly degrade $CF_nCl_{3-n}C(O)O^-$ on shorter time scales than suggested above, but whose rates cannot be estimated with any degree of confidence at this time, include oxidation by photochemically generated valence band holes in semiconductor particles and hydrolysis catalyzed by enzymes in microorganisms and plants; further research aimed at characterizing these processes is needed.

One possible gas phase degradation product about which very little is known is CF_3ONO_2. This compound has never been observed, and may be thermally unstable. If CF_3ONO_2 is thermally stable, then it may have a long lifetime toward aqueous phase removal. Henry's law solubility data and hydrolysis kinetics data for CF_3ONO_2 are needed before its aqueous phase removal rate can be assessed with any degree of confidence.

8. ACKNOWLEDGMENTS

APPENDIX
(R.H. WINE AND W.L. CHAMEIDES)

Tables of Relevant Physical Constants

AI   Henry's law solubilities

AII   Vapor Pressures

AIII   Acid-base equilibrium constants

AIV   One-electron redox potentials

Table AI. Henry's Law Solubilities

Species	$(M\ atm^{-1})$		
	5°C	**25°C**	**Reference**
HOOH	360000	74000	1
CH_3OOH	850	220	1
$CH_3C(O)OOH$	2100	470	1
HCOOH	1500	3700	2
CH_3COOH	41000	8700	3
CH_3CHO	49	13	4
CH_3OH	720	220	4
CH_3ONO_2		3(22°C)	5
$CH_3C(O)OONO_2$	12	2.9	6
CH_2CCl_2	0.096	0.039	7

1. Lind and Kok, 1986
2. Latimer, 1952
3. Jacob and Wofsy, 1988
4. Snider and Dawson, 1985
5. Lee, et al., 1983
6. Lee, 1984
7. Gossett, 1987

Table AII. Vapor Pressure of Selected Compounds

Species	Vapor Pressure (Torr)		Reference
	0°C	30°C	
HFCO	1590	2420	1
Cl_2CO	563	1670	1
CH_3CClO	90.4	353	1
CCl_3CClO	4.72	27.0	1
CH_3OOH	10.9	70	2
CF_3OOH	444	1670	3
CF_3COOH	2.90	14.3	1
CCl_3COOH	0.0043	0.130	1
CH_3OH	29.1	162	1
CH_2CH_2OH	12.2	79.2	1
CF_3CH_2OH	13.7	93.5	1

1. Lange, 1979
2. G.L. Vaghjiani, private communication
3. Bernstein, et al., 1971

Table AIII. Acid-Base Equilibrium Constants

Equilibrated Species	pKa	Reference
$CO_2 \cdot H_2O/HCO_3^-$	6.35	1
HCO_3^-/CO_3^{2-}	10.33	1
HCl/Cl^-	-6.1	1
HF/F^-	3.18	1
$HC(O)OH/HC(O)O^-$	3.75	1
$CH_3C(O)OH/CH_3C(O)O^-$	4.76	1
$CCl_3C(O)OH/CCl_3C(O))^-$	0.64	1
$CF_3C(O)OH/CF_3C(O)O^-$	0.25	1
$CH_3C(O)OOH/CH_3C(O)OO^-$	8.20	1
$ClCH_2C(O)OOH/ClCH_2C(O)OO^-$	7.2	2
CH_3OOH/CH_3OO^-	11.5	2
CF_3OOH/CF_3OO^-	6.4	3
$CH_3CH_2OH/CH_3CH_2O^-$	15	4
$CF_3CH_2OH/CF_3CH_2O^-$	12.37	4
HO_2/O_2^-	4.69	5

1. Lange, 1979
2. Richardson, 1983
3. Bernstein, et al., 1971
4. Ballinger and Long, 1960
5. Bielski, 1978

Table AIV. One-Electron Redox Potentials

Couple	E^0(volts)*	Reference
F/F⁻	3.6	1
Cl/Cl⁻	2.41	2
Br/Br⁻	1.93	2
I/I⁻	1.33	3
NO_2/NO_2^-	1.03	4
NO_3/NO_3^-	2.3	1
OH/OH⁻	1.89	2
SO_4^-/SO_4^{2-}	2.52	5
SO_3^-/SO_3^{2-}	0.63	6
$CH_3C(O)O/CH_3C(O)O^-$	2.41	7
HO_2/HO_2^-	0.8	1
O_2/O_2^-	⁻0.2	1
CO_3^-/CO_3^{2-}	1.59	8
Fe^{3+}/Fe^{2+}	0.771	9
$Fe(OH)^{2+}/Fe(OH)^+$	0.304	9
Cu^{2+}/Cu^+	0.153	9
$CuCl_2/CuCl_2^-$	0.567	9

*in water, versus the normal hydrogen electrode

1. Berdnikov and Bazhin, 1970
2. Schwarz and Dodson, 1984
3. Stanbury, et al., 1980
4. Wilmarth, et al., 1983
5. Eberson, 1982
6. Huie and Neta, 1984
7. Eberson, 1963
8. R.E. Huie, private communication
9. Moffett and Zika, 1987a

VIII.   OZONE DEPLETION POTENTIALS

Relative Effects on Stratospheric Ozone of Halogenated Methanes and Ethanes of Social and Industrial Interest

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EXECUTIVE SUMMARY

Ozone Depletion Potentials (ODPs) have been defined and calculated in order to allow estimates of the relative effects of halocarbons on stratospheric ozone. Models using representations of homogeneous atmospherics chemical processes have estimated relative effects on global ozone. These estimates indicate that the ODPs of the hydrohalocarbons are generally one-tenth or less those of the CFC-11 and -12. The reduction in ODP that might be expected due to replacement of uses of a CFC by a hydrohalocarbon can be estimated by taking the ratio of the ODP of the hydrohalocarbon to the ODP of the CFC it might replace. For example, the reduction in ODP in replacing uses of CFC-12 by HCFC-22 is $(0.049 \pm .015)/(.93)$ $= .053 \pm .015$. Of course, the relative quantities of the compound required in the use application must also be taken into account.

Although the values of ODPs reported here agree reasonably well among models, uncertainties in the values still exist due to the uncertainties in modeled chemistry and dynamics. Since reaction with OH dominates the chemistry of the HCFCs, uncertainties in the model calculated OH values remain a major source of uncertainty for both lifetimes and ODPs of these compounds. Uncertainties for some compounds may be reduced with new laboratory data on the ultraviolet absorption properties and the rate constants with hydroxyl for the HCFCs and HFCs.

Sensitivity analyses reveal that the global ODP values are affected to only a minor degree by the levels of N_2O, CH_4, CO_2, CO, and Brx used in model calculations. Latitudinal relative effects on ozone depletion depend on the species - species with high altitude sinks show more latitudinal dependency than CFC-11. Those species destroyed in the lower stratosphere have latitudinal effects equivalent to CFC-11. Seasonal variation of relative ozone depletions are second order.

Another major uncertainty centers on the potential effects of heterogeneous chemistry in the lower stratosphere, particularly near the poles in winter-time. While these effects are believed to cause the Antarctic spring-time ozone decreases, they are not included in any of the model calculations of ODPs. Due to the cold stratospheric temperatures, polar stratospheric clouds become activation sites for chlorine compounds (by-products from the decomposition of the chlorocarbons) resulting in increased chlorine catalytic loss for ozone. Since ODP is defined relative to CFC-11, the effect of including heterogeneous chemistry will have little effect on the local ODP value compared to values determined assuming only homogeneous chemistry. However, polar contribution to global ozone loss would be greater such that global ODP values would be more heavily weighted by the polar values. Thus, species with large, positive latitudinal gradients in ODP would have global ODPs that are fractionally increased. On the other hand, inclusion of stronger polar dynamics would affect both the transport and the distribution of chlorine species and would directly impact both the local and global ODP values.

Upper bounds are placed on the local effects by a chlorine loading potential, i.e. the relative amount of chlorine added to the stratosphere by a given gas. A less conservative estimate derived from the relative values of Cly in the lower polar stratosphere in spring indicates that the potential effect can be substantially less than the Chlorine Loading Potential but would be above the homogeneous chemisty ODP value. The geographic extent of the heterogeneous effect on global ODP outside of the polar vortex is impossible to estimate at the present time.

Time-dependent Relative Ozone Depletions and Relative Chlorine Loading for HCFCs have values above the ODP and CLP values derived from steady-state calculations. For longer lived CFCs, the time-dependent values are always less than the ODP and CLP values.

Range of Ozone Depletion Potentials (ODP) determined by one-dimensional and two-dimensional models, assuming scaling for HCFC ODPs by CH_3CCl_3 observed lifetime (6.3 years).

Species	1-D Models*	2-D Models**
CFC-11	1.0	1.0
CFC-12	0.9-1.0	0.9
CFC-113	0.8-0.9	0.8-0.9
CFC-114	0.6-0.8	0.6-0.8
CFC-115	0.4-0.5	0.3-0.4
HCFC-22	0.4-0.05	0.04-0.06
HCFC-123	0.013-0.016	0.013-0.022
HCFC-124	0.016-0.018	0.017-0.024
HFC-125	0	0
HFC-134a	0	0
HCFC-141b	0.07-0.08	0.09-0.11
HCFC-142b	0.05-0.06	0.05-0.06
HFC-134a	0	0
HFC-152a	0	0
CCl_4	1.0-1.2	1.0-1.2
CH_3CCl_3	0.10-0.12	0.13-0.16

* 1-D models from AER, LLNL and DuPont.
** 2-D models from AER, LLNL, University of Oslo, and DuPont.