POSSIBLE ATMOSPHERIC LIFETIMES AND CHEMICAL REACTION MECHANISMS FOR SELECTED HCFCs, HFCs, CH₂CCl₃, AND THEIR DEGRADATION PRODUCTS AGAINST DISSOLUTION AND/OR DEGRADATION IN SEAWATER AND CLOUDWATER

P.H. Wine and W.L. Chameides

Georgia Tech Research Institute and School of Geophysical Sciences
Georgia Institute of Technology
Atlanta, GA 30332
1. INTRODUCTION

For a wide variety of atmospheric species including CO₂, HNO₃, and SO₂, 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 CHCl₂CF₃ (HCFC-123), CCl₂FCH₃ (HCFC-141b), CClF₂CH₃ (HCFC-142b), CHClF₂ (HCFC-22), CHClF₂CF₃ (HCFC-124), CH₂FCF₃ (HFC-134a), CHF₂CH₃ (HFC-152a), CHF₂CF₃ (HFC-125), and CH₃CCI₃ 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, Φₒ, the steady state flux of a species from the atmosphere to the ocean (in molecules cm⁻² s⁻¹) is given by (Liss, 1983)

\[
Φₒ = \left[ \frac{1}{rₐ + rₕ/(HTNₐ 10^{-3})} \right] \left( \frac{Cₐ - [I]₀}{[I]₀/(HT)} \right)
\]

where \( rₐ \) and \( rₕ \) 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), \( R = 1.36 \times 10^{-22} \text{ atm cm}^3/\text{molecule/K} \) is the gas constant, \( T \) is temperature (assumed to be 285K), \( Nₐ \) is Avogadro’s number, \( Cₐ \) is the species’ concentration (in molecules cm⁻³) at the bottom of the atmospheric mixed layer, and \([I]₀\) 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 \( rₐ \) one would use a gas-phase diffusion coefficient of about 0.01 cm² s⁻¹, while for \( rₕ \) an aqueous-phase diffusion coefficient of about 10⁻⁵ cm² s⁻¹ would be used (Danckwerts, 1970). For conditions typical of the ocean, \( rₐ \) is about 1.25 s cm⁻¹, while \( rₕ \) is about 170 s cm⁻¹ (Liss, 1983). For the HCFCs and HFCs under consideration here, \( H < 0.2 \text{ M atm}^-¹ \) and thus

\[
rₕ/(HTNₐ 10^{-3}) \approx 7/H > 35 >> rₐ
\]

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

\[
Φₒ = \left[ \frac{HTNₐ 10^{-3}/rₕ}{[I]₀/(HT)} \right] Cₐ
\]
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

\[
[I] / t = - k[I] + \int_0^z (D [I] / z)
\]

(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 \( \phi_o \) (Johnson, 1981):

\[
\phi_o = (D k)^{1/2} [I]_o N_A 10^{-3}
\]

(5)

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

\[
[I]_o = (HRT) C_A / [1 + r_s (D k)^{1/2}]
\]

(6)

and substituting [6] into [5] yields a closed form for \( \phi_o \); i.e.,

\[
\phi_o = (D k)^{1/2} N_A 10^{-3} HRT C_A / [1 + r_s (D k)^{1/2}]
\]

(7)

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

\[
\phi_o = (H C_A / 0.04) [r_s + 1/(D k)^{1/2}]^{-1}
\]

(8)

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

<table>
<thead>
<tr>
<th>( H ) (M atm(^{-1}))</th>
<th>0.001</th>
<th>0.005</th>
<th>0.01</th>
<th>0.02</th>
<th>0.04</th>
<th>0.06</th>
<th>0.08</th>
<th>0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k ) (s(^{-1}))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 10^{-11} )</td>
<td>73,200</td>
<td>14,600</td>
<td>7,320</td>
<td>3,600</td>
<td>1,830</td>
<td>1,230</td>
<td>916</td>
<td>732</td>
</tr>
<tr>
<td>( 10^{-10} )</td>
<td>23,300</td>
<td>4,670</td>
<td>2,330</td>
<td>1,170</td>
<td>583</td>
<td>389</td>
<td>292</td>
<td>233</td>
</tr>
<tr>
<td>( 10^{-9} )</td>
<td>7,550</td>
<td>1,510</td>
<td>755</td>
<td>377</td>
<td>189</td>
<td>126</td>
<td>94</td>
<td>75</td>
</tr>
<tr>
<td>( 10^{-8} )</td>
<td>2,560</td>
<td>511</td>
<td>256</td>
<td>128</td>
<td>64</td>
<td>43</td>
<td>32</td>
<td>25</td>
</tr>
<tr>
<td>( 10^{-7} )</td>
<td>978</td>
<td>196</td>
<td>98</td>
<td>49</td>
<td>24.5</td>
<td>16</td>
<td>12</td>
<td>9.8</td>
</tr>
</tbody>
</table>
If the species is well-mixed in the atmosphere, it follows from [8] that $\tau_o$, the species’ atmospheric lifetime against dissolution in the ocean, is given by

$$\tau_o = (H_A \frac{0.04/f}{H}) \left[ r_s + \frac{1}{(Dk)^{1/2}} \right]$$  \hspace{1cm} (9)

where $H_A = 8 \text{ km}$ is the atmospheric scale height and $f = 0.7$ is the fraction of the earth’s surface covered by ocean. Values of $\tau_o$ 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 $\tau_o > 30$ - 60 days. Once the calculated $\tau_o$ 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 $\tau_o$ for the HFCs and HCFCs of interest in this work are listed in Table 2. For all species except CH$_3$CCI$_3$, 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$_3$CCI$_3$. The Henry’s law coefficients for CH$_3$CCI$_3$ 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...
AQUATIC MECHANISMS

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

<table>
<thead>
<tr>
<th>Species</th>
<th>H(M/atm)</th>
<th>Pseudo First Order Loss Rates (s⁻¹)</th>
<th>Lifetimes (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>k_h</td>
<td>k_e</td>
</tr>
<tr>
<td>CH₃CCl₁</td>
<td>0.08</td>
<td>4 x 10⁻⁹</td>
<td>1.4 x 10⁻⁹</td>
</tr>
<tr>
<td>CF₂CHF₂(125)</td>
<td>&lt;0.015</td>
<td>&lt;10⁻¹⁰</td>
<td>&lt;10⁻¹¹</td>
</tr>
<tr>
<td>CF₂CHCl₂(134a)</td>
<td>0.02</td>
<td>&lt;10⁻¹⁰</td>
<td>&lt;10⁻¹¹</td>
</tr>
<tr>
<td>CH₃CHF₂(152a)</td>
<td>0.05</td>
<td>&lt;10⁻¹⁰</td>
<td>&lt;10⁻¹¹</td>
</tr>
<tr>
<td>CF₂CHClF₆(124)</td>
<td>0.015</td>
<td>10⁻⁹</td>
<td>10⁻⁹</td>
</tr>
<tr>
<td>CH₃CCIF₂(142b)</td>
<td>0.02</td>
<td>10⁻⁹</td>
<td>10⁻⁹</td>
</tr>
<tr>
<td>CF₂CHClCl(123)</td>
<td>0.03</td>
<td>10⁻⁹</td>
<td>10⁻⁹</td>
</tr>
<tr>
<td>CH₃CFCl(41b)</td>
<td>0.015 - 0.07</td>
<td>10⁻⁹</td>
<td>10⁻⁹</td>
</tr>
<tr>
<td>CHClF₂(22)</td>
<td>0.085</td>
<td>3 x 10⁻¹⁰</td>
<td>3 x 10⁻¹⁰</td>
</tr>
</tbody>
</table>

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 CF₃CHF₂ and CH₃CCl₃. To account for this possibility as well as other unknown systematic errors, we have adopted a range of H-values for CF₃CHF₂ and CH₃CCl₃. (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

\[ k = k_h + k_e + k_{OH} \]  

The hydrolysis rates in Table 2 for CHClF₂ and for CH₃CCl₃ were obtained from McLinden AFEAS, 1989 and Ellenrieder and Reinhard (1988), respectively. New unpublished results (Gerkens and Franklin, 1989) verify the CH₃CCl₃ hydrolysis rate in Table 2 and provide improved temperature dependence data.
AQUATIC MECHANISMS

The other hydrolysis rates were assumed to be intermediate between that of CH$_3$CCl$_3$ and CHCIF$_2$ 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 $k_\text{OH}$ 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$_3$CHClF, 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 $1 \times 10^{-19}$ 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 $5 \times 10^{-18}$ 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$_3$CCl$_3$ and CHCIF$_2$ with hydrated electrons were taken to be $1.4 \times 10^{-9}$ M$^{-1}$ s$^{-1}$ and $3 \times 10^{9}$ 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$_3$CCl$_3$ and CHCIF$_2$, 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 $10^{9}$ 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 $4 \times 10^{-19}$ M (Zepp et al., 1987b; Zafiriou and True, 1979). For CH$_3$CCl$_3$, a second-order aqueous-phase rate constant for the OH reaction of $4 \times 10^{7}$ 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$_3$CCl$_3$ 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$_3$CCl$_3$ and CH$_3$CFCI$_2$, 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 CH₃CCl₃ and CH₃CFCI₂, 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 CHClF₂ and CF₃CHCl₂. 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 CH₃CCI₃, probably the most readily removed of all the compounds considered here. As
discussed above, CH₃CCI₃ probably has a Henry’s law solubility in cloudwater (T ≥ 273K) of ≤ 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
10⁸ 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 CH₃CCI₃ in cloudwater of about 8 x 10⁻⁶ s⁻¹. Assuming an aver-
age 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 < 10⁵ 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

\[ RC = X \times (0.2 \text{ M atm}^{-1}) \times (10^{-4} \text{ L cm}^{-2}) \times N_A \times 8 \times 10^{-6} \text{ s}^{-1} \]  (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, \( \tau_c \), against removal by cloudwater of

\[ \tau_c = X \times (2.5 \times 10^{19} \text{ molec cm}^{-3}) \times H_A/RC \approx 5,000 \text{ years} \]  (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 C₂ halocarbons can proceed via either substitution or elimination mechanisms, while only
the substitution pathway is available for C₁ halocarbons. Primary halocarbons generally hydrolyze
predominantly by the substitution pathway, with elimination becoming more important for branched halocar-
bons (Roberts and Caserio, 1965). For CH₃CCl₃, hydrolysis is known to yield 70-80% CH₃C(O)OH (the
substitution product) and 20-30% H₂C = CC1₂ (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 in-
termediates such as α-haloalcohols and acid halides. Probable intermediate and end products are summa-
rized in Table 3. The expected stable products are: HC(O)OH from CHClF₂; CH₂C(O)OH from CH₃CFCI₂
and CH₃CF₂Cl; CF₃CHO from CF₃CHCl₂, CF₂CHF₂ and CF₃CHFCl; CF₂CH₂OH from CF₂CH₂F;
### Table 3. Probable Reaction Pathways for Hydrolysis of the Halocarbons of Interest via Substitution Mechanisms

<table>
<thead>
<tr>
<th>Reaction Pathway</th>
<th>Net Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O} \quad -\text{HCl} \quad \text{H}_2\text{O}$</td>
<td>$\text{CH}_3\text{CCI}_3 \rightarrow \text{CH}_3\text{CCl}_2\text{OH} \rightarrow \text{CH}_3\text{CClO} \rightarrow \text{CH}_3\text{C(O)OH}$</td>
</tr>
<tr>
<td></td>
<td>$\text{NET: CH}_3\text{CCI}_3 + 2\text{H}_2\text{O} \rightarrow \text{CH}_3\text{C(O)OH} + 3\text{H}^+ + 3\text{Cl}^-$</td>
</tr>
<tr>
<td>$\text{H}_2\text{O} \quad -\text{HF} \quad \text{H}_2\text{O}$</td>
<td>$\text{CH}_2\text{CF}_2 \rightarrow \text{CHF}_2\text{OH} \rightarrow \text{HCFO} \rightarrow \text{HC(O)OH}$</td>
</tr>
<tr>
<td></td>
<td>$\text{NET: CHClF}_2 + 2\text{H}_2\text{O} \rightarrow \text{HC(O)OH} + 3\text{H}^+ + 2\text{F}^- + \text{Cl}^-$</td>
</tr>
<tr>
<td>$\text{H}_2\text{O} \quad -\text{HCl}$</td>
<td>$\text{CF}_3\text{CHCl}_2 \rightarrow \text{CF}_3\text{CHClO} \rightarrow \text{CF}_3\text{CHO}$</td>
</tr>
<tr>
<td></td>
<td>$\text{NET: CF}_3\text{CHCl}_2 + \text{H}_2\text{O} \rightarrow \text{CF}_3\text{CHO} + 2\text{H}^+ + 2\text{Cl}^-$</td>
</tr>
<tr>
<td>$\text{H}_2\text{O} \quad -\text{HF}$</td>
<td>$\text{CH}_3\text{CFCl}_2 \rightarrow \text{CH}_3\text{CFClO} \rightarrow \text{CH}_3\text{CFHO} \rightarrow \text{CH}_3\text{C(O)OH}$</td>
</tr>
<tr>
<td></td>
<td>$\text{NET: CH}_3\text{CFCl}_2 + 2\text{H}_2\text{O} \rightarrow \text{CH}_3\text{C(O)OH} + 3\text{H}^+ + 3\text{H}^+ + 2\text{Cl}^- + \text{F}^-$</td>
</tr>
<tr>
<td>$\text{H}_2\text{O} \quad -\text{HF}$</td>
<td>$\text{CH}_3\text{CF}_2\text{Cl} \rightarrow \text{CH}_3\text{CF}_2\text{OH} \rightarrow \text{CH}_3\text{CFO} \rightarrow \text{CH}_3\text{C(O)OH}$</td>
</tr>
<tr>
<td></td>
<td>$\text{NET: CH}_3\text{CF}_2\text{Cl} + 2\text{H}_2\text{O} \rightarrow \text{CH}_3\text{C(O)OH} + 3\text{H}^+ + 2\text{F}^- + \text{Cl}^-$</td>
</tr>
<tr>
<td>$\text{H}_2\text{O} \quad -\text{HF}$</td>
<td>$\text{CF}_3\text{CHFCl} \rightarrow \text{CF}_3\text{CHFCO} \rightarrow \text{CF}_3\text{CHO}$</td>
</tr>
<tr>
<td></td>
<td>$\text{NET: CF}_3\text{CHFCl} + \text{H}_2\text{O} \rightarrow \text{CF}_3\text{CHO} + 2\text{H}^+ + \text{Cl}^- + \text{F}^-$</td>
</tr>
<tr>
<td>$\text{Cl}^- \quad \text{H}_2\text{O}$</td>
<td>$\text{CF}_3\text{CH}_2\text{F} \rightarrow \text{CF}_3\text{CH}_2\text{Cl} \rightarrow \text{CF}_3\text{CH}_2\text{OH}$</td>
</tr>
<tr>
<td></td>
<td>$\text{NET: CF}_3\text{CH}_2\text{F} + \text{H}_2\text{O} \rightarrow \text{CF}_3\text{CH}_2\text{OH} + \text{H}^+ + \text{F}^-$</td>
</tr>
<tr>
<td>$\text{Cl}^- \quad \text{H}_2\text{O}$</td>
<td>$\text{CH}_3\text{CHF}_2 \rightarrow \text{CH}_3\text{CHFCl} \rightarrow \text{CH}_3\text{CHFCO} \rightarrow \text{CH}_3\text{CHO}$</td>
</tr>
<tr>
<td></td>
<td>$\text{NET: CH}_3\text{CHF}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CHO} + 2\text{H}^+ + 2\text{F}^-$</td>
</tr>
<tr>
<td>$\text{Cl}^- \quad \text{H}_2\text{O}$</td>
<td>$\text{CF}_3\text{CHF}_2 \rightarrow \text{CF}_3\text{CHFCI} \rightarrow \text{CF}_3\text{CHFOH} \rightarrow \text{CF}_3\text{CHO}$</td>
</tr>
<tr>
<td></td>
<td>$\text{NET: CF}_3\text{CHF}_2 + \text{H}_2\text{O} \rightarrow \text{CF}_3\text{CHO} + 2\text{H}^+ + 2\text{F}^-$</td>
</tr>
</tbody>
</table>
AQUATIC MECHANISMS

CH$_3$CHO from CH$_3$CHF$_2$. The fluorine containing end product CF$_3$CH$_2$OH 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$_3$CHO, will have a large effective Henry’s law solubility ($10^5 - 10^6$ M atm$^{-1}$) due to efficient hydration,

$$\text{CF}_3\text{CHO} + \text{H}_2\text{O} \rightarrow \text{CF}_3\text{CH(OH)}_2$$

(R1)

The gem-diol species CF$_3$CH(OH)$_2$ is expected to be relatively stable in seawater. The lifetime of CF$_3$CHO + CF$_3$CH(OH)$_2$ in seawater may be limited by oxidation of the small equilibrium concentration of CF$_3$CHO(g) via reaction with OH radicals.

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

$$\text{RX} + \text{e}^- \rightarrow \text{R} + \text{X}^-$$  \hspace{1cm} (R2)

$$\text{R} + \text{O}_2 \rightarrow \text{RO}_2$$  \hspace{1cm} (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$_3$CCl$_3$ 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 Cl₂CO, F₂CO, and ClFCO, substitution of OH for X (X = Cl, F) produces a halohyroxycarbonyl which rapidly eliminates HX to yield the end product CO₂. Hydrolysis of the other acid halides of interest, (i.e., HCXO, CH₃CXO, CX₃CXO) 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 CH₃CFO hydrolysis in water as a function of temperature and pH. They obtained the result $k_h = 2.9 \times 10^7 \exp(-6290/T)$ 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 CH₃CCIO hydrolysis at 300K in 75.6% H₂O - 24.4% dioxan; they measured $k_h = 292$ s⁻¹, a rate which is expected to be even faster in pure H₂O solvent. Swain and Scott (1953) measured the relative rates of hydrolysis of CH₃CCIO and CH₃CFO in 75% acetone - 25% water at 298K and found that CH₃CCIO 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 % H₂O + 89.1 vol % acetone at 298K and obtained the following rate constants in units of s⁻¹: CH₃CCIO, 0.0011; ClCH₂CCIO, 0.020; Cl₂CHCCIO, 3.1; Cl₃CCIO, > 10; Cl₂CO, 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 CH₃CFO. Hence, the kinetic data of Bunton and Fendler (1966) for CH₃CFO 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 cloud-water 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 CIFCO and CF₃CCIO (R.A. Cox, AFEAS, 1989 (this report)) will survive in the atmosphere long enough to represent significant sources of stratospheric chlorine.

CF₃OH

In the condensed phase, CF₃OH is known to be unstable toward elimination of HF (Seppelt, 1977).

$$\text{CF}_3\text{OH} \rightarrow \text{CF}_3\text{O} + \text{HF}$$  \hspace{1cm} (R4)

(R4) probably also occurs in the gas phase. If not, it will occur very rapidly upon uptake of CF₃OH into
AQUATIC MECHANISMS

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$_3$OH to CO$_2$ + 3HF via HF elimination and subsequent hydrolysis of CF$_2$O will be as fast as CF$_2$O 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 = 7 M atm$^{-1}$ and $k_h$ = 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

$$\text{CH}_3\text{C(O)OOONO}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{C(O)OOH} + \text{NO}_3^- + \text{H}^+.$$  \hspace{1cm} (R5)

In the absence of experimental data, it seems reasonable to assume that removal of CF$_n$Cl$_{3-n}$C(O)OOONO$_2$ 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.

$$\text{CF}_n\text{Cl}_{3-n}\text{C(O)OOONO}_2 + \text{M} \rightarrow \text{CF}_n\text{Cl}_{3-n}\text{C(O)OO} + \text{NO}_2 + \text{M}$$  \hspace{1cm} (R6)

$$\text{CF}_n\text{Cl}_{3-n}\text{C(O)OO} + \text{HO}_2 \rightarrow \text{CF}_n\text{Cl}_{3-n}\text{C(O)OOH} + \text{O}_2$$  \hspace{1cm} (R7)

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

$$\text{CH}_3\text{C(O)OOONO}_2 + 2\text{OH}^- \rightarrow \text{CH}_3\text{C(O)O}^- + \text{NO}_2^- + \text{O}_2 + \text{H}_2\text{O}$$  \hspace{1cm} (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$_2$O$_2$ (Lind and Kok, 1986), acetate is produced in either case. Similarly, the long-lived halogen-containing products of CF$_n$Cl$_{3-n}$C(O)OOONO$_2$ 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.
It has been suggested in the literature (Hohorst and DesMarteau, 1974) that CF$_3$ONO$_2$ is thermally unstable in condensed phases.

\[ \text{CF}_3\text{ONO}_2 \rightarrow \text{CF}_3\text{O} + \text{FNO}_2 \]  

(R9) may also occur in the gas phase.

If CF$_3$ONO$_2$ turns out to be thermally stable, then in the absence of Henry's law solubility data and hydrolysis data, we assume that CF$_3$ONO$_2$ will behave similarly to CH$_3$ONO$_2$ (methyl nitrate). The Henry's law solubility of CH$_3$ONO$_2$ is nearly identical to that of PAN (Lee, et al., 1983). Robertson, et al. (1982) studied the hydrolysis kinetics of isopropynitrate 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 isopropynitrate was 340-369K. Extrapolation of Robertson, et al.'s results to lower temperatures suggests \( k_h \sim 2 \times 10^{-7} \text{ s}^{-1} \) at 300K and \( 5 \times 10^{-9} \text{ s}^{-1} \) at 280K. Baker and Easty (1952), have studied the kinetics of neutral hydrolysis (H$_2$O nucleophile) of methyl-, ethyl-, and isopropynitrinate in 60% ethanol/40% water at 60.2°C; they obtain the relative activities 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 \( 4 \times 10^{-9} \text{ s}^{-1} \).

Clearly, removal of CF$_3$ONO$_2$ by hydrolysis in cloudwater will be of no importance as an atmospheric loss process. For \( H = 1 - 10 \text{ M atm}^{-1} \) and \( k_h = (1 - 10) \times 10^{-9} \text{ s}^{-1} \), the lifetime of CF$_3$ONO$_2$ toward hydrolysis in seawater will be in the range 0.1 - 10 years. Measurements of \( H \) and \( k_h \) for CF$_3$ONO$_2$ in seawater would clearly be worthwhile.

It is well established that neutral hydrolysis of simple primary and secondary alkyl nitrates proceeds via an SN$_2$ mechanism to yield the corresponding alcohol (Baker and Easty, 1952; Robertson, et al., 1982). Hence, while the CF$_3$ONO$_2$ hydrolysis rate is highly uncertain and could be quite long, the degradation mechanism can be predicted with a reasonable degree of certainty:

\[ \text{CF}_3\text{ONO}_2 + \text{H}_2\text{O} \rightarrow \text{CF}_3\text{OH} + \text{NO}_3^- + \text{H}^+ \]  

(R10)

\[ \text{CF}_3\text{OH} \rightarrow \text{CF}_3\text{O} + \text{H}^+ + \text{F}^- \]  

(R4)

\[ \text{CF}_3\text{O} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{F}^- \]  

(R11)

**Peroxyxinitrates**

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$_3$OONO$_2$ is reported in the literature (Hohorst and DesMarteau, 1974). Thermal decomposition of CF$_3$OONO$_2$ is found to be rather slow in the liquid phase, but hydrolysis to CF$_3$OOH + NO$_3^-$ is rapid. The Henry's law solubilities of the halo-substituted peroxyxinitrates are probably similar to those of the peroxyacetylinitrates and the alkylxinitrates, i.e. 1 - 10 M atm$^{-1}$. 283
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 10^6 s 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 $\exp(6171/T - 14.55) \text{M atm}^{-1}$ (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. $k_h \sim 10^{-5} \text{s}^{-1}$ 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 peroxyacetinyltrinitrate 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$_3$C(O)OOH and CF$_3$C(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 $k_h \sim (2-200) \times 10^{-5} \text{s}^{-1}$ with CF$_3$C(O)OOH 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.,

$$\text{CF}_n\text{Cl}_{3-n}\text{C(O)OOH} + \text{H}_2\text{O} \rightarrow \text{CF}_n\text{Cl}_{3-n}\text{C(O)OH} + \text{H}_2\text{O}_2 \quad (R12)$$

$$\text{CF}_n\text{Cl}_{3-n}\text{C(O)OO}^- + \text{H}_2\text{O} \rightarrow \text{CF}_n\text{Cl}_{3-n}\text{C(O)O}^- + \text{H}_2\text{O}_2 \quad (R13)$$

Acids

The halo-substituted acetic acids are very acidic species. The pKa's for CF$_2$C(O)OH and CCl$_3$C(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$_2$Cl$_3$-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 CF₃Cl₃-nC(O)OH is estimated to be $10^{-6} \text{ s}^{-1}$, 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
\[ \text{e}^- + \text{CCl}_3\text{C(O)O}^- \rightarrow \text{CCl}_2\text{C(O)O}^- + \text{Cl}^- \] (R14)
is known to be $8.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Anbar and Hart, 1965). As discussed previously in this report, estimated hydrated electron concentrations in freshwater and seawater are $10^{-18} \text{ M}$ and $10^{-19} \text{ M}$, respectively. Hence, the lifetime of $\text{CCl}_3\text{C(O)O}^-$ toward removal via (R14) is estimated to be 3.7 years in freshwater and 37 years in seawater. CF₃C(O)O⁻ is expected to be at least 100 times less reactive with $\text{e}^-$ than is $\text{CCl}_3\text{C(O)O}^-$, while CF₂ClC(O)O⁻ and CFCl₂C(O)O⁻ will react at intermediate rates. The radical products of (R14) and its analogs will rapidly add O₂ to form peroxy radicals,

\[ \text{CX}_2\text{C(O)O}^- + \text{O}_2 \rightarrow \text{OOCX}_2\text{C(O)O}^- \] (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

\[ \text{CX}_3\text{OO}^- + \text{I}^- \rightarrow \text{CX}_2\text{OO}^- + \text{I} \] (R16)

proceed rapidly with $k \sim 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for $X = \text{Cl}$ and F. Kinetics studies of $\text{CCl}_3\text{OO}$, $\text{OOCCl}_2\text{O}^-$, and $\text{OOCF}_2\text{C(O)O}^-$ reactions with a number of antioxidants have shown that $\text{OOCCl}_2\text{O}^-$ and $\text{OOCF}_2\text{C(O)O}^-$ are about equally reactive, but both are 3 - 10 times less reactive than $\text{CCl}_3\text{OO}$ (Packer, et al., 1980). A typical iodide concentration in seawater is $10^{-7} \text{ M}$, suggesting that the lifetime of $\text{OOCX}_2\text{C(O)O}^-$ 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, NO₂⁻. The probable chemistry of $\text{OOCX}_2\text{C(O)O}^-$ and their protonated species $\text{HOOCX}_2\text{C(O)O}^-$ is discussed in the next section.

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

\[ X + \text{CH}_3\text{C(O)O}^- \rightarrow X^- + \text{CH}_3\text{C(O)O} \rightarrow \text{CH}_3 + \text{CO}_2 \] (R17)

The sulfate radical, for example, is known to react with acetate at a moderate rate ($k = 3.7 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ in the zero ionic strength limit) (Wine, et al., 1989) to produce CO₂ (Madhavan, et al., 1978). The
AQUATIC MECHANISMS

one electron redox potential \( E^0 \) is 2.41 volts (versus the normal hydrogen electrode) for the \( \text{CH}_3\text{C(O)O}/\text{CH}_3\text{C(O)O}^- \) couple and 2.52 volts for the \( \text{SO}_4^-/\text{SO}_4^{2-} \) 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 \( \text{SO}_4^- \), one of the strongest oxidizing agents found in environmental aqueous systems, is not capable of oxidizing \( \text{CF}_3\text{Cl}_{3-n}\text{C(O)O}^- \). 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. \( \text{CF}_3\text{Cl}_{3-n}\text{C(O)O}^- \)) 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 \( \text{CCl}_3\text{COO}^- \) thermal decarboxylation in aqueous solution over the temperature range 50 - 90°C; measured rate coefficients varied from \( 6.2 \times 10^{-7} \text{ s}^{-1} \) at 50°C to \( 3.1 \times 10^{-4} \text{ s}^{-1} \) at 90°C. Extrapolation of Verhoek’s results to 285K, a typical surface seawater temperature, suggests that \( k \sim 3.7 \times 10^{-9} \text{ s}^{-1} \) (lifetime \( \sim 86 \text{ years} \)). At 300K, however, the lifetime of \( \text{CCl}_3\text{C(O)O}^- \) toward thermal decarboxylation appears to be only about 2 years. Clearly, thermal decarboxylation in the tropical oceans could be an important removal process for \( \text{CCl}_3\text{C(O)O}^- \). The thermal decarboxylation kinetics of \( \text{CF}_3\text{C(O)O}^- \) (Auerbach, et al., 1950), \( \text{CCl}_2\text{FC(O)O}^- \) (Hine and Duffey, 1959a) and \( \text{CF}_2\text{ClC(O)O}^- \) (Hine and Duffey, 1959b) have also been studied in aqueous solution. Extrapolation of available data suggests that at \( T < 300 \text{K} \) all three reactions have rate coefficients of less than \( 10^{-10} \text{ s}^{-1} \). The more fluorine atoms on the alkyl carbon, the slower the reaction proceeds. For \( \text{CCl}_3\text{C(O)O}^- \), \( \text{CCl}_2\text{FC(O)O}^- \), and \( \text{CF}_3\text{C(O)O}^- \), the mechanism of the thermal decarboxylation reaction is

\[
\text{C}_x\text{C(O)O}^- \rightarrow \text{CO}_2 + \text{CX}_3^- \rightarrow \text{CHX}_3
\]  

(R18)

For \( \text{CCIF}_2\text{C(O)O}^- \), Hine and Duffey (1959b) have shown that the detailed mechanism is somewhat different

\[
\text{CCIF}_2\text{C(O)O}^- \rightarrow \text{CO}_2 + \text{Cl}^- + \text{CF}_2
\]  

(R19)

In seawater the \( \text{CF}_2 \) radical should react with chloride, then protonate to form \( \text{CHClF}_2 \):

\[
\text{CF}_2 + \text{Cl}^- \rightarrow \text{CF}_2\text{Cl}^- \rightarrow \text{CHF}_2\text{Cl}
\]  

(R20)

Very little information is available concerning hydrolysis of trihaloacetic acids. It appears that \( \text{SO}_4^- \) attack by \( \text{H}_2\text{O} \) 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 CF₂CIC(O)O⁻ degradation in aqueous solution and attributed its production to a hydrolysis reaction:

\[
\text{CCl}_2\text{F}_2\text{C}(-\text{O})\text{O}^- + \text{H}_2\text{O} \rightarrow \text{HOCl}_2\text{F}_2\text{COO}^- + \text{H}^+ + \text{Cl}^- \quad \text{(R21)}
\]

\[
\text{HOCl}_2\text{F}_2\text{C}(-\text{O})\text{O}^- \rightarrow \text{OFFCC}(-\text{O})\text{O}^- + \text{H}^+ + \text{F}^- \quad \text{(R22)}
\]

\[
\text{OFFCC}(-\text{O})\text{O}^- + \text{H}_2\text{O} \rightarrow \text{HO(O)CC}(-\text{O})\text{O}^- + \text{H}^+ + \text{F}^- \quad \text{(R23)}
\]

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 CH₂FC(O)O⁻, CH₂CIC(O)O⁻ and CHCl₂C(O)O⁻, by catalyzing hydrolysis (Goldman, 1969). It seems reasonable to expect that plant and/or microbial enzymes can remove fluorine atoms from CFₙCl₃₋ₙC(O)O⁻ as well. Further research is needed to establish the rates of CFₙCl₃₋ₙC(O)O⁻ degradation via biological processes in natural environments such as soils, vegetation, fresh water, and seawater.

In summary, it appears that CCl₃C(O)O⁻ can react at appreciable rates in natural waters with hydrated electrons and by thermal decarboxylation; the lifetime of CCl₃C(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, CF₃C(O)O⁻, could have a lifetime in natural waters as long as several hundred years. Processes which could possibly degrade CFₙCl₃₋ₙC(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 CH₃OOH to be \( \exp(5607/T - 13.41) \) M atm⁻¹ (i.e. 746 M atm⁻¹ at 280K). These authors have also observed that CH₃OOH hydrolyzes to methanol and hydrogen peroxide; the lifetime of CH₃OOH toward hydrolysis appeared to be a month or two at 298K. The pKa for CH₃OOH 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 CF₃OOH, 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 CF₃OOH is known to be about 2 atmospheres at 298K (Bernstein, et al., 1971) whereas the vapor pressure of CH₃OOH is only 54.2 Torr at 298K (G.L. Vaghjiani, private communication). Hence, it seems likely that the Henry’s law solubility of CF₃OOH is smaller than that of CH₃OOH.

If photolysis, rates for halogenated hydroperoxides in the gas phase are similar to those of H₂O₂ and CH₃OOH, 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 H₂O₂ and CH₃OOH, in which case gas phase photolysis could be very slow and aqueous phase removal could become important.
AQUATIC MECHANISMS

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 \(2 \times 10^{-6} \text{s}^{-1}\), and a rate constant for reaction with aqueous-phase OH of \(1 \times 10^7 \text{M}^{-1} \text{s}^{-1}\), 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 CF₃O should react rapidly either by electron transfer, i.e.

\[
\text{CF}_3\text{O} + \text{O}_2^- , \text{NO}_2^- , \ldots \rightarrow \text{CF}_3\text{O}^- + \text{O}_2 , \text{NO}_2 , \ldots \rightarrow \text{CF}_3\text{OH}
\]  

(R24)

or by hydrogen abstraction, i.e.

\[
\text{CF}_3\text{O} + \text{HO}_2 , \ldots \rightarrow \text{CF}_3\text{OH} + \text{O}_2 , \ldots
\]  

(R25)

As discussed above, CF₃OH rapidly eliminates HF to produce CF₃O, which rapidly hydrolyzes to CO₂ + 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

\[
X^- + \text{ROOH} \rightarrow X + \text{RO} + \text{OH}^-
\]  

(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 \(X = \text{I}^-\) and Fe²⁺ are used for quantitative analysis of peroxides (Siggia and Hanna, 1979). While quantitative kinetic data for \(X^- + \text{ROOH}\) reactions seem to be available only for hydrogen peroxide (i.e. \(R = \text{H}\)), 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 \(\text{I}^-, \text{Br}^-, \text{Cl}^-, \text{Cu}(I), \text{and Fe}(II)\) with \(\text{H}_2\text{O}_2\) 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 CuCl²⁻ and Fe(OH)⁺ (Moffett and Zika, 1987a). The results presented in Table 4 suggest that reaction with Fe(II) is the dominant sink for \(\text{H}_2\text{O}_2\) in seawater, since photolysis in surface water and hydrolysis are expected to proceed at rates on the order of \(10^{-7} \text{s}^{-1}\) 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 \(\text{H}_2\text{O}_2\), i.e. \(k \approx 10^{-4} \text{s}^{-1}\). The Henry's law solubilities for the halogenated hydroperoxides under seawater conditions (\(T \sim 285K, \mu \sim 0.75 \text{M}\)) 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$_2$O$_2$ in Seawater via the Reaction X$^-$ + H$_2$O$_2$ → X + OH + OH$^-$

<table>
<thead>
<tr>
<th></th>
<th>k(M$^{-1}$ s$^{-1}$)(a)</th>
<th><a href="M">X</a></th>
<th>k(s$^{-1}$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>I$^-$</td>
<td>0.26</td>
<td>1 x 10$^{-7}$</td>
<td>2.6 x 10$^{-8}$</td>
<td>1</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>4.4 x 10$^{-6}$</td>
<td>8 x 10$^{-4}$</td>
<td>3.5 x 10$^{-9}$</td>
<td>2</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>1.7 x 10$^{-8}$(b)</td>
<td>0.54</td>
<td>9.2 x 10$^{-9}$</td>
<td>2</td>
</tr>
<tr>
<td>Cu(I)(c)</td>
<td>70</td>
<td>1 x 10$^{-10}$</td>
<td>7.0 x 10$^{-9}$</td>
<td>3, 4</td>
</tr>
<tr>
<td>Fe(II)(d)</td>
<td>3 x 10$^4$</td>
<td>5 x 10$^{-9}$</td>
<td>1.5 x 10$^{-4}$</td>
<td>5, 6</td>
</tr>
</tbody>
</table>

(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

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$_n$Cl$_{12-n}$C(O)O$. These species are expected to be degraded via mechanisms completely analogous to those described above for haloalkyl hydroperoxides. The end products are expected to be oxalic acid (HOOC$\text{COOH}$), HF, and HCl.

7. SUMMARY

The rates at which eight potential alternative HCFCs and HFCs and methyl chloroform (CH$_3$CCl$_3$) 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$_2$CF$_3$ (HCFC-123), CFCl$_2$CH$_3$ (HCFC-141b), CF$_2$CICH$_3$ (HCFC-142b), CHF$_2$Cl (HCFC-22), CHFCICF$_3$ (HCFC-124), CH$_2$FCF$_3$ (HFC-134a), CH$_2$CH$_3$ (HFC-152a), and CHF$_2$CF$_3$ (HFC-125).
AQUATIC MECHANISMS

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, peroxycarboxylic acids, peroxides, alcohols, nitrates, peroxynitrates, and peroxyacetyl nitrate.

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 X₂CO, HXCO, CH₃CXO, CF₃OH, CX₃OONO₂, 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 CX₂CXO, CX₂CX₂OOH, CX₂CX₃OONO₂, CX₃C(O)OONO₂, and CX₃C(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, CX₃C(O)O⁻.

The species CX₃C(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 CX₃C(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 CCl₃C(O)O⁻ with the hydrated electron is also expected to occur on a time scale of a few years. The species CFCl₂C(O)O⁻, CF₂ClC(O)O⁻, and CF₂C(O)O⁻ may have very long aqueous phase lifetimes. The longest lived species, CF₂C(O)O⁻, could have a lifetime in natural waters as long as several hundred years. Processes which could possibly degrade CF₃Cl₃C(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 CF₃ONO₂. This compound has never been observed, and may be thermally unstable. If CF₃ONO₂ is thermally stable, then it may have a long lifetime toward aqueous phase removal. Henry’s law solubility data and hydrolysis kinetics data for CF₃ONO₂ are needed before its aqueous phase removal rate can be assessed with any degree of confidence.
8. ACKNOWLEDGMENTS

The authors would like to thank the reviewers, M.R. Hoffmann and D.D. DesMarteau, for a number of constructive comments which greatly improved the quality of this assessment. They would also like to acknowledge L. Clever, D. Creed, R.E. Huie, E.M. Perdue, A.R. Ravishankara, E.S. Saltzman, G.J. Vaghjiani, O.C. Zafiriou, and R.G. Zepp for helpful discussions concerning various aspects of this work, and R.P. Thorn for assistance with the literature search.

In preparing this assessment the authors made use of information from a number of other AFEAS reports. Authors of these reports were R. Atkinson, R.A. Cox, R.F. Hampson, M.J. Kurylo, R. Lesclaux, D.C. McCune, M.O. McLinden, H. Niki, S.P. Sander, L.H. Weinstein, and R. Zellner.

---

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 Al. Henry's Law Solubilities

<table>
<thead>
<tr>
<th>Species</th>
<th>5°C</th>
<th>25°C</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOOH</td>
<td>360000</td>
<td>74000</td>
<td>1</td>
</tr>
<tr>
<td>CH₃OOH</td>
<td>850</td>
<td>220</td>
<td>1</td>
</tr>
<tr>
<td>CH₃C(O)OOH</td>
<td>2100</td>
<td>470</td>
<td>1</td>
</tr>
<tr>
<td>HCOOH</td>
<td>1500</td>
<td>3700</td>
<td>2</td>
</tr>
<tr>
<td>CH₃COOH</td>
<td>41000</td>
<td>8700</td>
<td>3</td>
</tr>
<tr>
<td>CH₃CHO</td>
<td>49</td>
<td>13</td>
<td>4</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>720</td>
<td>220</td>
<td>4</td>
</tr>
<tr>
<td>CH₃ONO₂</td>
<td></td>
<td>3(22°C)</td>
<td>5</td>
</tr>
<tr>
<td>CH₃C(O)OONO₂</td>
<td>12</td>
<td>2.9</td>
<td>6</td>
</tr>
<tr>
<td>CH₂CCL₂</td>
<td>0.096</td>
<td>0.039</td>
<td>7</td>
</tr>
</tbody>
</table>

1. Lind and Kok, 1986
2. Latimer, 1952
3. Jacob and Wofsy, 1988
4. Snider and Dawson, 1985
5. Lee, et al., 1983
7. Gossett, 1987
## Table AII. Vapor Pressure of Selected Compounds

<table>
<thead>
<tr>
<th>Species</th>
<th>0°C</th>
<th>30°C</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFCO</td>
<td>1590</td>
<td>2420</td>
<td>1</td>
</tr>
<tr>
<td>Cl₂CO</td>
<td>563</td>
<td>1670</td>
<td>1</td>
</tr>
<tr>
<td>CH₃CClO</td>
<td>90.4</td>
<td>353</td>
<td>1</td>
</tr>
<tr>
<td>CCl₃CClO</td>
<td>4.72</td>
<td>27.0</td>
<td>1</td>
</tr>
<tr>
<td>CH₃OOH</td>
<td>10.9</td>
<td>70</td>
<td>2</td>
</tr>
<tr>
<td>CF₃OOH</td>
<td>444</td>
<td>1670</td>
<td>3</td>
</tr>
<tr>
<td>CF₃COOH</td>
<td>2.90</td>
<td>14.3</td>
<td>1</td>
</tr>
<tr>
<td>CCl₃COOH</td>
<td>0.0043</td>
<td>0.130</td>
<td>1</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>29.1</td>
<td>162</td>
<td>1</td>
</tr>
<tr>
<td>CH₂CH₂OH</td>
<td>12.2</td>
<td>79.2</td>
<td>1</td>
</tr>
<tr>
<td>CF₃CH₂OH</td>
<td>13.7</td>
<td>93.5</td>
<td>1</td>
</tr>
</tbody>
</table>

1. Lange, 1979
2. G.L. Vaghjiani, private communication
Table AIII. Acid-Base Equilibrium Constants

<table>
<thead>
<tr>
<th>Equilibrated Species</th>
<th>pKa</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$H$_2$O/HCO$_3^-$</td>
<td>6.35</td>
<td>1</td>
</tr>
<tr>
<td>HCO$_3^-$/CO$_3^{2-}$</td>
<td>10.33</td>
<td>1</td>
</tr>
<tr>
<td>HCl/Cl$^-$</td>
<td>-6.1</td>
<td>1</td>
</tr>
<tr>
<td>HF/F$^-$</td>
<td>3.18</td>
<td>1</td>
</tr>
<tr>
<td>HC(O)OH/HC(O)O$^-$</td>
<td>3.75</td>
<td>1</td>
</tr>
<tr>
<td>CH$_3$C(O)OH/CH$_3$C(O)O$^-$</td>
<td>4.76</td>
<td>1</td>
</tr>
<tr>
<td>CCl$_3$C(O)OH/CCl$_3$C(O)$^+$</td>
<td>0.64</td>
<td>1</td>
</tr>
<tr>
<td>CF$_3$C(O)OH/CF$_3$C(O)O$^-$</td>
<td>0.25</td>
<td>1</td>
</tr>
<tr>
<td>CH$_3$C(O)OOH/CH$_3$C(O)OO$^-$</td>
<td>8.20</td>
<td>1</td>
</tr>
<tr>
<td>CICH$_2$C(O)OOH/CICH$_2$C(O)OO$^-$</td>
<td>7.2</td>
<td>2</td>
</tr>
<tr>
<td>CH$_3$OOH/CH$_3$OO$^-$</td>
<td>11.5</td>
<td>2</td>
</tr>
<tr>
<td>CF$_3$OOH/CF$_3$OO$^-$</td>
<td>6.4</td>
<td>3</td>
</tr>
<tr>
<td>CH$_3$CH$_2$OH/CH$_3$CH$_2$O$^-$</td>
<td>15</td>
<td>4</td>
</tr>
<tr>
<td>CF$_3$CH$_2$OH/CF$_3$CH$_2$O$^-$</td>
<td>12.37</td>
<td>4</td>
</tr>
<tr>
<td>HO$_2$/O$_2^-$</td>
<td>4.69</td>
<td>5</td>
</tr>
</tbody>
</table>

1. Lange, 1979
2. Richardson, 1983
5. Bielski, 1978
Table AIV. One-Electron Redox Potentials

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

*in water, versus the normal hydrogen electrode

1. Berdnikov and Bazhin, 1970
2. Schwarz and Dodson, 1984
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

D. A. Fisher, Charles H. Hales and David L. Filkin
E. I. du Pont de Nemours & Company
Wilmington, DE

Malcolm K. W. Ko and N. Dak Sze
Atmospheric And Environmental Research, Inc.
Cambridge, MA

Peter S. Connell and Donald J. Wuebbles
Lawrence Livermore National Laboratory
Livermore, CA

Ivar S. A. Isaksen and Frode Stordal
Institute for Geophysics
University of Oslo
Oslo, Norway
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 atmospheres 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 $(0.049 \pm 0.015)/0.93 = 0.053 \pm 0.015$. 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 $Br_x$ 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 $Cl_y$ 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 chemistry 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.
STRATOSPHERIC OZONE

Range of Ozone Depletion Potentials (ODP) determined by one-dimensional and two-dimensional models, assuming scaling for HCFC ODPs by CH$_3$CCL$_3$ observed lifetime (6.3 years).

<table>
<thead>
<tr>
<th>Species</th>
<th>1-D Models*</th>
<th>2-D Models**</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFC-11</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>CFC-12</td>
<td>0.9-1.0</td>
<td>0.9</td>
</tr>
<tr>
<td>CFC-113</td>
<td>0.8-0.9</td>
<td>0.8-0.9</td>
</tr>
<tr>
<td>CFC-114</td>
<td>0.6-0.8</td>
<td>0.6-0.8</td>
</tr>
<tr>
<td>CFC-115</td>
<td>0.4-0.5</td>
<td>0.3-0.4</td>
</tr>
<tr>
<td>HCFC-22</td>
<td>0.4-0.05</td>
<td>0.04-0.06</td>
</tr>
<tr>
<td>HCFC-123</td>
<td>0.013-0.016</td>
<td>0.013-0.022</td>
</tr>
<tr>
<td>HCFC-124</td>
<td>0.016-0.018</td>
<td>0.017-0.024</td>
</tr>
<tr>
<td>HFC-125</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>HFC-134a</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>HCFC-141b</td>
<td>0.07-0.08</td>
<td>0.09-0.11</td>
</tr>
<tr>
<td>HCFC-142b</td>
<td>0.05-0.06</td>
<td>0.05-0.06</td>
</tr>
<tr>
<td>HFC-134a</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>HFC-152a</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CCl$_4$</td>
<td>1.0-1.2</td>
<td>1.0-1.2</td>
</tr>
<tr>
<td>CH$_3$CCL$_3$</td>
<td>0.10-0.12</td>
<td>0.13-0.16</td>
</tr>
</tbody>
</table>

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