TROPOSPHERIC REACTIONS OF THE HALOALKYL RADICALS
FORMED FROM HYDROXYL RADICAL REACTION WITH
A SERIES OF ALTERNATIVE FLUOROCARBONS

Roger Atkinson

Statewide Air Pollution Research Center
University of California
Riverside, California 92521
1. INTRODUCTION

The majority of the chlorofluorocarbons (CFCs) currently in use, such as CFC-11 (CFC13), 12 (CF2Cl2) and 113 (CF2CICFC13), are chemically non-reactive in the troposphere, and transport to the stratosphere, with subsequent photolysis there, then becomes the only significant removal process from the troposphere (see, for example, Molina and Rowland, 1974; WMO, 1986; Hammitt et al., 1987). As replacements for these CFCs, compounds are now being sought which will be removed to a large extent in the troposphere, thus avoiding or minimizing the input of chlorine and other halogens into the stratosphere.

In the present assessment, the hydrogen-containing halocarbons being considered as alternates to the presently used chlorofluorocarbons are the hydrochlorofluorocarbons (HCFCs) 123 (CF3CHCl2), 141b (CFCIC2H5), 142b (CF2ClCICH3), 22 (CHF2Cl) and 124 (CF3CHFCI) and the hydrofluorocarbons (HFCs) 134a (CF3CH2F), 152a (CHF2CH3) and 125 (CF3CHF2). All of these HCFCs and HFCs will react with the hydroxyl (OH) radical in the troposphere, giving rise to haloalkyl (R') radicals which then undergo a complex series of reactions in the troposphere. These reactions of the haloalkyl radicals formed from the initial OH radical reactions with the HCFCs and HFCs under tropospheric conditions are the focus of the present article. The haloalkyl (R') radicals formed from the OH radical reactions with the HCFCs and HFCs listed above are as follows:

<table>
<thead>
<tr>
<th>HCFC or HFC</th>
<th>Haloalkyl Radical, R</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF3CHCl2</td>
<td>CF3CCl2</td>
</tr>
<tr>
<td>CFCl2CH3</td>
<td>CFCl2CH2</td>
</tr>
<tr>
<td>CF2ClCH3</td>
<td>CF2ClCH2</td>
</tr>
<tr>
<td>CHF2Cl</td>
<td>CF2Cl</td>
</tr>
<tr>
<td>CF3CHFCI</td>
<td>CF3CFCl</td>
</tr>
<tr>
<td>CF3CH2F</td>
<td>CF3CHF</td>
</tr>
<tr>
<td>CHF2CH3</td>
<td>CHF2CH2 and CH3CF2</td>
</tr>
<tr>
<td>CF3CHF2</td>
<td>CF3CF2</td>
</tr>
</tbody>
</table>

Of these radicals, only for the CF2Cl radical formed from CHF2Cl (HCFC-22) are experimental data available concerning certain of the reactions which are expected to take place under tropospheric conditions. It is therefore necessary to postulate the reactions of these haloalkyl radicals based upon the current state of knowledge of the tropospheric reactions of analogous alkyl and haloalkyl radicals and of the corresponding alkyl peroxy (RO'2) and alkoxy (RO') radicals formed from, or subsequent to, these alkyl and haloalkyl radical reactions. At the present time, experimental and theoretical data are available for certain of the tropospheric reactions of several C1-C5 alkyl and C1 haloalkyl radicals which are expected to be common to the haloalkyl radicals dealt with in this article. These reactions, together with the kinetic data available, are dealt with in Appendix A (Section 4). Since several of these reactions of R', RO2 and RO' radicals have recently been reviewed and evaluated by the National Aeronautics and Space Administration and the International Union of Pure and Applied Chemistry data evaluation panels (NASA, 1987; IUPAC, 1989), in most cases the recommendations from these data evaluations are cited rather than the original
DEGRADATION MECHANISMS

literature. Furthermore, since the IUPAC panel (IUPAC, 1989) considered a wider range of relevant reactions than did the NASA (1987) panel, and the differences (if any) between the recommended kinetic expressions from these data evaluations are relatively minor (<50% for the temperature and pressure conditions encountered in the troposphere), the recommendations of the IUPAC (1989) evaluation are used in this article. The reactions of the individual haloalkyl radicals formed from the HCFCs and HCFs are dealt with in Section 2, using the data base for analogous alkyl and haloalkyl radicals (Section 4; Appendix A) to provide estimates of the reaction pathways and the rate constants for these reactions.

In this article, all rate constants are given in cm molecule s units, and pressures are given in Torr (1 Torr = 133.3 Pa). For reactions which are in the fall-off region between first- and second-order kinetics or between second- and third-order kinetics, the Troe fall-off expression (Troe, 1979) is used,

\[
k = \left( \frac{k_o[M]}{1 + k_o[M]/k_{oo}} \right) F \left\{ 1 + \left[ \log(k_o[M]/k_{oo}) \right]^2 \right\}^{-1}
\]

where \(k_o\) is the limiting low-pressure rate constant, \(k_{oo}\) is the limiting high-pressure rate constant, \([M]\) is the concentration of diluent gas (air, \(N_2\) or \(O_2\) in this article, unless otherwise specified) and \(F\) is the broadening factor. The rate constants \(k_o\) and \(k_{oo}\) are generally assumed to have \(T^n\) temperature dependences, while the temperature dependence of \(F\) is given by \(F = e^{-T/T^*}\), where \(T^*\) is a constant (Troe, 1979; Baulch et al., 1982).

2. TROPOSPHERIC DEGRADATIONS OF SELECTED HALOGENATED ALKYL RADICALS

In this section, the tropospheric reaction schemes subsequent to OH radical reaction with the alternative HCFCs and HFCs being considered are formulated. While the quantitative assessment of the concentrations of the intermediate species and of chemically reactive and non-reactive products requires the use of atmospheric computer models which include time- and altitude-dependent radiation fluxes and OH, \(HO_2\), \(CH_3O_2\) and other \(RO_2\) radicals, \(NO\), \(NO_x\), \(O_3\), \(H_2O\), \(O_2\), and \(N_2\) concentrations, approximate concentrations of these species are used in this section to permit the qualitative assessment of intermediate and product lifetimes. Based upon the tropospheric concentrations given in WMO (1986) for \(NO\), \(NO_x\), \(CH_4\) and \(CO\), the tropospheric \(O_3\) concentrations given by Logan (1985), an average daytime OH radical concentration of \(1.5 \times 10^6\) molecule cm\(^{-3}\) [equivalent to a diurnally-averaged concentration of \(7.5 \times 10^5\) molecule cm\(^{-3}\)] (Prinn et al., 1987) and an approximate consideration of tropospheric \(CH_4\) and \(CO\) chemistry, the \(HO_2\) and \(CH_3O_2\) concentrations were calculated. The concentration of the relevant species are given in Table 1 for the lower and upper levels of the troposphere. The ground level solar flux data given by Hendry and Kenley (1979) were used to approximately estimate lifetimes with respect to photolysis.

The reaction schemes presented are based upon the discussion and review of the literature data for analogous reactions given in Section 4 below. In general, no detailed discussion is given in this section, unless required to assess the relative importance of possible reaction pathways or to point out that the present data base does not permit a judgment to be made. The discussion dealing with the \(CF_3CCl_2\) radical in Section 2.1 below applies to many of the haloalkyl radical reaction schemes, and is not repeated in detail in the sections following.
Table 1. Daytime species concentrations used in the assessment of reaction routes and species lifetimes

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration (molecule cm(^{-3}))</th>
<th>Lower Troposphere</th>
<th>Upper Troposphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>(M (N_2 + O_2))</td>
<td>2.5 x 10(^{19})</td>
<td>4.5 x 10(^{18})</td>
<td></td>
</tr>
<tr>
<td>(O_2)</td>
<td>5 x 10(^{18})</td>
<td>9 x 10(^{17})</td>
<td></td>
</tr>
<tr>
<td>(O_3)</td>
<td>7 x 10(^{11})</td>
<td>4 x 10(^{11})</td>
<td></td>
</tr>
<tr>
<td>(NO)</td>
<td>2.5 x 10(^{8})</td>
<td>2.5 x 10(^{8})</td>
<td></td>
</tr>
<tr>
<td>(NO_2)</td>
<td>2.5 x 10(^{8})</td>
<td>2.5 x 10(^{8})</td>
<td></td>
</tr>
<tr>
<td>(OH)</td>
<td>1.5 x 10(^{6})</td>
<td>1.5 x 10(^{6})</td>
<td></td>
</tr>
<tr>
<td>(HO_2)</td>
<td>10(^9)</td>
<td>10(^8)</td>
<td></td>
</tr>
<tr>
<td>(CH_3O_2)</td>
<td>2.5 x 10(^{8})</td>
<td>6 x 10(^{6})</td>
<td></td>
</tr>
</tbody>
</table>

2.1. The CF\(_3\)CCl\(_2\) Radical formed from HCFC-123 (CF\(_3\)CHCl\(_2\))

A. CF\(_3\)CCl\(_2\). The CF\(_3\)CCl\(_2\) radical will react solely with \(O_2\) to form the peroxo radical CF\(_3\)CCl\(_2\)O\(^2\)

\[
M + CF_3CCl_2 + O_2 \rightarrow CF_3CCl_2O_2^+ 
\]

with a rate constant \(k \geq 5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\). This results in a tropospheric lifetime of the CF\(_3\)CCl\(_2\) radical of \(< 2 \times 10^{-6} \text{ s}\).

B. CF\(_3\)CCl\(_2\)O\(^2\). The expected reactions of this peroxo radical are,

\[
CF_3CCl_2O_2^+ + NO \rightarrow CF_3CCl_2O^+ + NO_2 \quad \text{(a)} 
\]

\[
M + CF_3CCl_2O_2^+ + NO_2 \rightarrow CF_3CCl_2OOONO_2 \quad \text{(b)} 
\]

\[
CF_3CCl_2O_2^+ + HO_2 \rightarrow CF_3CCl_2OOH + O_2 \quad \text{(c)} 
\]

\[
CF_3CCl_2O_2^+ + CH_3O_2 \rightarrow CF_3CCl_2O^+ + CH_3O^+ + O_2 \quad \text{(d1)} 
\]

\[
CF_3CCl_2O_2^+ + CH_3O_2 \rightarrow CF_3CCl_2OH + HCHO + O_2 \quad \text{(d2)} 
\]

with rate constants (cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) units) of \(k_a \sim 1.5 \times 10^{-11} \left(\text{T}/300\right)^{-1.2}\), \(k_b \sim 1.0 \times 10^{-11}\), \(k_c = 3.4 \times 10^{-13} \text{ e}^{800/T}\), and \(k_{d1} + k_{d2} \sim 2 \times 10^{-13}\). Based on the approximate concentrations of NO, NO\(_2\), HO\(_2\),
DEGRADATION MECHANISMS

and CH$_3$O$^-$ given in Table 1, the decay rates (s$^{-1}$) of the CF$_3$CCl$_2$O$_2^-$ radical with respect to reactions (a) through (d) for the lower and upper troposphere, respectively, are: reaction (a), 3.8 x 10$^{-3}$ and 5.4 x 10$^{-3}$; reaction (b), 2.5 x 10$^{-3}$ and 2.5 x 10$^{-3}$; reaction (c), 5 x 10$^{-3}$ and 1.3 x 10$^{-3}$; and reaction (d), 5 x 10$^{-5}$ and 1.2 x 10$^{-7}$.

These calculated reaction rates for the CF$_3$CCl$_2$O$_2^-$ radical suggest that reaction with RO$_2^-$ radicals will be of negligible importance, but that the reactions with NO, NO$_2$ and the HO$_2$ radical will be of approximately comparable importance and must be considered. The lifetime of the CF$_3$CCl$_2$O$_2^-$ radical is expected to be $\sim$10$^2$ s. The products of reactions (a), (b) and (c) are the CF$_3$CCl$_2$O$^-$ radical, the peroxytrate CF$_3$CCl$_2$OONO$_2$ and the hydroperoxide CF$_3$CCl$_2$OOH, respectively. Formation of the nitrate, CF$_3$CCl$_2$ONO$_2$, from the NO reaction (a) is expected to account for < 2% of the CF$_3$CCl$_2$O$^-$ radical yield.

C. CF$_3$CCl$_2$OONO$_2^-$ Under tropospheric conditions, this haloalkyl peroxytrate will undergo thermal decomposition and photolysis. The thermal decomposition reaction

\[
\text{M} \quad \text{CF}_3\text{CCl}_2\text{OONO}_2 \rightarrow \text{CF}_3\text{CCl}_2\text{O}_2^- + \text{NO}_2
\]

is expected to have a rate constant of $\sim$1 x 10$^{15}$ e$^{-11000/T}$ s$^{-1}$ at the high-pressure limit, leading to calculated loss rates of 0.1 s$^{-1}$ at 298 K and 2 x 10$^{-7}$ s$^{-1}$ at 220 K (the rate constants are expected to be close to the high pressure limit). As noted in Section 4.4, the effective lifetime of the peroxytrate may be longer than calculated from the thermal decomposition rate constant due to reformation from the reverse reaction.

Photolysis of CF$_3$CCl$_2$OONO$_2$ can occur by two channels

\[
\text{CF}_3\text{CCl}_2\text{OONO}_2 + \text{hv} \rightarrow \text{CF}_3\text{CCl}_2\text{O}_2^- + \text{NO}_2
\]

\[
\text{CF}_3\text{CCl}_2\text{OONO}_2 + \text{hv} \rightarrow \text{CF}_3\text{CCl}_2\text{O}^- + \text{NO}_3
\]

and the relative importance of these photolysis pathways is not known for any ROONO$_2$ species (IUPAC, 1989). It is expected that the photodissociation quantum yield is unity. Assuming that the absorption cross-section is similar to those of HOOONO$_2$, CH$_3$OOONO$_2$, CFCl$_2$OONO$_2$ and CC$_2$OONO$_2$ (Morel et al., 1980; NASA, 1987; IUPAC, 1989), the lifetime in the lower troposphere with respect to photodissociation is calculated to be $\sim$5 days.

Hence, in the lower troposphere the dominant loss process of CF$_3$CCl$_2$OONO$_2$ will be thermal decomposition, with a lifetime of $\sim$10 s. Thermal decomposition becomes slower with increasing altitude (decreasing temperature), and becomes sufficiently slow in the upper troposphere that photolysis is expected to dominate there, with a lifetime of $\sim$5 days. The products of these reactions are the CF$_3$CCl$_2$O$_2^-$ radical and, possibly, the CF$_3$CCl$_2$O$^-$ radical (from photolysis). The reactions of the peroxy radical have been dealt with above, and the haloalkoxy radical reactions are dealt with below.

D. CF$_3$CCl$_2$OOH. As for methyl hydroperoxide (CH$_3$OOH), the gas-phase tropospheric reactions of CF$_3$CCl$_2$OOH are expected to be photolysis and reaction with the OH radical. Photolysis is expected to proceed by
DEGRADATION MECHANISMS

\[ \text{CF}_3\text{CCl}_2\text{OOH} + h\nu \rightarrow \text{CF}_3\text{CCl}_2\text{O}^- + \text{OH} \]

Assuming an absorption cross-section similar to that for CH$_3$OOH and a photodissociation quantum yield of unity (Baulch et al., 1982; NASA, 1987), then the lifetime of CF$_3$CCl$_2$OOH with respect to photolysis is calculated to be \( \sim 6 \) days in the lower troposphere.

Reaction of CF$_3$CCl$_2$OOH with the OH radical will lead to formation of the CF$_3$CCl$_2$O$^-$ radical

\[ \text{OH} + \text{CF}_3\text{CCl}_2\text{OOH} \rightarrow \text{H}_2\text{O} + \text{CF}_3\text{CCl}_2\text{O}^- \]

The rate constant for this process can be estimated from the data for the corresponding OH radical reactions with (CH$_3$)$_3$COOH (Anastasi et al., 1978) and CH$_3$OOH (Vaghjiani and Ravishankara, 1989) [noting that the OH radical reaction with CH$_3$OOH also proceeds to a significant extent by H atom abstraction from the -CH$_3$ group (Vaghjiani and Ravishankara, 1989; Atkinson, 1989b)]. At 298 K both reactions to yield H$_2$O + RO$_2^-$ have rate constants of \((3-4) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) (Atkinson, 1989b). With the temperature dependence determined by Vaghjiani and Ravishankara (1989) for this reaction channel, this yields

\[ k(\text{OH} + \text{ROOH} \rightarrow \text{H}_2\text{O} + \text{RO}_2^-) = 1.7 \times 10^{-12} e^{220/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

The calculated OH radical reaction rates during daylight hours of \((5-7) \times 10^{-6} \text{ s}^{-1}\) throughout the troposphere are a factor of \(~2\) higher than the expected photolysis rate. Clearly, both OH radical reaction and photolysis must be considered as gas-phase removal processes, with a lifetime of CF$_3$CCl$_2$OOH with respect to these processes of \(~2\) to 3 days. These reactions again lead to the formation of the peroxy and haloalkoxy radicals.

In addition to these gas-phase tropospheric removal processes, physical removal processes may occur, leading to the incorporation of CF$_3$CCl$_2$OOH in cloud, rain and fog water.

E. CF$_3$CCl$_2$O$^-$. Based upon the discussion in Section 4.3, the reactions of the CF$_3$CCl$_2$O$^-$ radical which need to be considered are

\[ \text{CF}_3\text{CCl}_2\text{O}^- \rightarrow \text{CF}_3\text{C(O)Cl} + \text{Cl} \]  \hspace{1cm} (a)
\[ \text{CF}_3\text{CCl}_2\text{O}^- \rightarrow \text{CF}_3 + \text{COCI} \]  \hspace{1cm} (b)

The value of \( \Delta H_f(\text{CF}_3\text{C(O)Cl}) \), and of most of the other halogenated acetyl halides of interest in this article, must be estimated. The bond additivity method of Benson (1976), in which \( \Delta H_f(XYZC(O)B) \) is obtained from the contributions of C-X, C-Y, C-Z, >CO-C and >CO-B bonds, is one method. The partial bond contributions are given on page 25 of Benson (1976), with the exception that the literature heats of formation of HC(O)Cl (Dewar and Rzepa, 1983) and CH$_3$C(O)Cl (Wagman et al., 1982) require that the >CO-Cl bond contribution be -34 kcal mol$^{-1}$ instead of -27.0 kcal mol$^{-1}$ as cited. A modification to the group additivity method of Benson (1976) is also used here, in which the contributions from \( \Delta H_f(C-(X)(Y)(Z)(C)) \) and \( \Delta H_f(C-(=O)(B)) \) are summed. Heats of formation of the C(O)H, C(O)Cl and C(O)F groups can be calculated from the literature data for CH$_3$CHO (IUPAC, 1989), CH$_3$C(O)Cl (Wagman et al., 1982) and CH$_3$C(O)F (Wagman et al., 1982) as -29.5, -48.1 and -94.8 kcal mol$^{-1}$, respectively.
DEGRADATION MECHANISMS

The sum of the heats of formation of the products of pathways (a) and (b) are then: $\text{CF}_3\text{C(O)Cl} + \text{Cl} - 177 \text{ kcal mol}^{-1}$ $[\Delta H_f(\text{CF}_3\text{C(O)Cl}) = -206 \text{ kcal mol}^{-1}$ by both the above methods]; and $\text{CF}_3 + \text{COCl}_2, -166.5 \text{ kcal mol}^{-1}$. Cl atom elimination [channel (a)] is then expected to dominate, with the concurrent formation of $\text{CF}_3\text{C(O)Cl}$. This conclusion is in agreement with the discussion given in Section 4.3.B, based upon the experimental data of Sanhueza and Heicklen (1975) and Sanhueza et al. (1976) for analogous halogenated alkoxy radicals.

F. Cl. The chlorine atom will react with organic compounds in the troposphere. The reaction with methane,

$$\text{Cl} + \text{CH}_2 \rightarrow \text{HCl} + \text{CH}_3$$

which has a rate constant (IUPAC, 1989) of $k = 9.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (1.0 $\times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K), will dominate under "clean" tropospheric conditions. Reactions with other organic compounds, mainly the higher alkanes such as ethane, propane and the butanes, will be more important in more polluted areas and will dominate over the reaction with $\text{CH}_4$ in polluted urban areas.

$$\text{Cl} + \text{RH} \rightarrow \text{HCl} + \text{R}$$

For the alkanes, the room temperature rate constants for these Cl atom reactions are $\sim 1 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, within a factor of approximately 2 (Lewis et al., 1980; Atkinson and Aschmann, 1985; Wallington et al., 1988a). Reactions of the Cl atom with alkenes and/or aromatic hydrocarbons will be of generally less importance because of the lower ambient concentrations of these organics. In particular, benzene exhibits only a low reactivity towards the Cl atom (Atkinson and Aschmann, 1985; Wallington et al., 1988b), and the reactions of the Cl atom with the aromatic hydrocarbons probably proceed by H atom abstraction from the substituent alkyl groups (Wallington et al., 1988b), again leading to HCl formation. The net result of the reactions of the Cl atom with organic compounds will be the dominant formation of HCl and an alkyl-type radical. These alkyl or related radicals will then undergo reaction sequences similar to those discussed in Section 4, resulting in the chlorine atom-initiated photooxidations of these organic compounds.

G. $\text{CF}_3\text{C(O)Cl}$. This compound, trifluoroacetyl chloride, is not expected to react with the OH radical to any significant extent (Atkinson, 1987), with an expected room temperature rate constant $< 10^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. Photolysis and/or incorporation into cloud, fog and rain water are then expected to be the major tropospheric removal processes for this compound.

H. HCl. Under tropospheric conditions, HCl does not photolyze (NASA, 1987), and the removal processes are then reaction with the OH radical and wet deposition (or rain-out). The OH radical reaction

$$\text{OH} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{Cl}$$

has a rate constant (IUPAC, 1989) of $k = 2.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (8.1 $\times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K). This leads to a lifetime of HCl with respect to reaction with the OH radical of $\sim 20$ days in the lower troposphere, and longer at higher, and colder, altitudes. Rain out of HCl is then expected to dominate as a loss process.
DEGRADATION MECHANISMS

I. COCl₂. Although COCl₂ is not expected to be the dominant reaction product of the tropospheric degradation of HCFC-123, its tropospheric reactions need to be considered. Reaction with the OH radical is calculated to be of no importance as a tropospheric loss process (Atkinson, 1987). At wavelengths > 220 nm, COCl₂ has an absorption maximum at 232 nm, with the absorption cross-section decreasing with increasing wavelength out to 280 nm (Baulch et al., 1982). From the cross-sections given by Baulch et al. (1982) and assuming a quantum yield of unity for photodissociation to CO + 2Cl (Baulch et al., 1982), photolysis in the troposphere will be slow, with a lifetime with respect to this process of > 50 days. Physical removal leading to incorporation into rain, cloud and fog water may then be a major tropospheric loss process for this compound.

J. CF₃. The tropospheric reactions of this radical are dealt with in Section 2.9 below.

The tropospheric degradation scheme for the CF₃CCl₂ radical is then as follows:

\[
\begin{align*}
\text{CF}_3\text{CCl}_2 & \xrightarrow{O_2} \text{CF}_3\text{CCl}_2\text{OOH} \\
\text{CF}_3\text{CCl}_2\text{OOH} & \xrightarrow{\text{HO}_2} \text{CF}_3\text{CCl}_2\text{O}_2 & \xrightarrow{\text{NO}_2} \text{CF}_3\text{CCl}_2\text{OONO}_2 \\
\text{CF}_3\text{CCl}_2\text{O}_2 & \xrightarrow{\text{NO}} \text{CF}_3\text{CCl}_2\text{O}^- \\
\text{CF}_3\text{CCl}_2\text{O}^- & \xrightarrow{\text{hv}} \text{CF}_3\text{C(O)Cl} + \text{Cl} \\
\text{CF}_3\text{C(O)Cl} & \xrightarrow{\text{RH}} \text{HCl}
\end{align*}
\]

2.2. The CFCl₃CH₂ Radical formed from HCFC-141b (CFCl₃CH₃).

A. CFCl₃CH₂. The CFCl₃CH₂ radical will react solely with O₂,

\[
\text{CFCl}_3\text{CH}_2 + \text{O}_2 \rightarrow \text{CFCl}_3\text{CH}_2\text{O}_2
\]
DEGRADATION MECHANISMS

with a rate constant of \( k \geq 5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \). The tropospheric lifetime of the CFCl_2CH_2 radical will thus be \(< 2 \times 10^{-6} \text{ s}\).

B. CFCl_2CH_2O^- . As discussed in Section 2.1, the CFCl_2CH_2O^- radical will react with NO, NO_2 and the HO_2 radical.

\[
\text{CFCl}_2\text{CH}_2\text{O}^- + \text{NO} \rightarrow \text{CFCl}_2\text{CH}_2\text{O}^- + \text{NO}_2
\]

\[
\text{M} \rightarrow \text{CFCl}_2\text{CH}_2\text{OONO}_2
\]

\[
\text{CFCl}_2\text{CH}_2\text{O}^- + \text{HO}_2 \rightarrow \text{CFCl}_2\text{CH}_2\text{OOH} + \text{O}_2
\]

with the HO_2 radical reaction possibly also leading to other products [see Jenkin et al. (1988) and Section 4.2.C]. The rate constants for these NO, NO_2 and HO_2 reactions are (in cm^3 molecule^{-1} s^{-1} units): \( \sim 1.5 \times 10^{-11}\text{ }\text{cm}^3\text{ molecule}^{-1}\text{ }\text{s}^{-1}\), \( \sim 1.0 \times 10^{-11}\text{ }\text{cm}^3\text{ molecule}^{-1}\text{ }\text{s}^{-1}\), and \( 3.4 \times 10^{-13}\text{ }\text{cm}^3\text{ molecule}^{-1}\text{ }\text{s}^{-1}\), respectively. With the concentrations of the reactive species given in Table 1, the lifetime of the CFCl_2CH_2O^- radical is \( \sim 10^2 \text{ s}\). Formation of the nitrate, CFCl_2CH_2ONO_2, from the NO reaction is assumed to be unimportant (\(< 2\%\) of the total reaction products).

C. CFCl_2CH_2OOH. The reactions to be considered are thermal decomposition

\[
\text{M} \rightarrow \text{CFCl}_2\text{CH}_2\text{OOH} \rightarrow \text{CFCl}_2\text{CH}_2\text{O}^- + \text{NO}_2
\]

with a rate constant at the high-pressure limit of \( \sim 1 \times 10^{15} \text{ }\text{cm}^3\text{ molecule}^{-1}\text{ }\text{s}^{-1}\), and photolysis

\[
\text{CFCl}_2\text{CH}_2\text{OOH} + \text{hv} \rightarrow \text{CFCl}_2\text{CH}_2\text{O}^- + \text{NO}_2
\]

\[
\text{CFCl}_2\text{CH}_2\text{OOH} + \text{hv} \rightarrow \text{CFCl}_2\text{CH}_2\text{O}^- + \text{NO}_3
\]

which is calculated to have a rate of \( \sim 2 \times 10^{-6} \text{ s}^{-1}\). As discussed in Section 2.1.C above, in the lower troposphere thermal decomposition will dominate, with photolysis becoming the dominant loss process in the upper troposphere.

D. CFCl_2CH_2OOH. The gas-phase removal reactions of this hydroperoxide are photolysis

\[
\text{CFCl}_2\text{CH}_2\text{OOH} + \text{hv} \rightarrow \text{CFCl}_2\text{CH}_2\text{O}^- + \text{OH}
\]

which is calculated to have a rate of \( \sim 2 \times 10^{-6} \text{ s}^{-1}\) in the lower troposphere, and reaction with the OH radical.

\[
\text{OH} + \text{CFCl}_2\text{CH}_2\text{OOH} \rightarrow \text{H}_2\text{O} + \text{CFCl}_2\text{CH}_2\text{O}^-.
\]

The rate constant for this reaction pathway is expected to be \( k \sim 1.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\). Abstraction of an H atom from the -CH_2- group to form the CFCl_2CHOOH radical is calculated to be a minor reaction pathway, accounting for \( \sim (5-15)\%\) of the overall reaction (Atkinson, 1987), which, however, cannot be neglected. Formation of the CFCl_2CHOOH radical is expected to be followed by
rapid decomposition to yield an OH radical and CFCl₂CHO

\[ \text{CFCl}_2\text{CHO} = \text{CFCl}_2\text{CHO} + \text{OH} \]

Reaction with the OH radical and photolysis of CFCl₂CH₂OOH are calculated to occur at comparable rates in the troposphere, with a lifetime of CFCl₂CH₂OOH of ~2 to 3 days. Physical removal processes leading to incorporation of CFCl₂CH₂OOH into rain, cloud and fog water may also be important.

E. \text{CFCl}_2\text{CH}_2\text{O}^\cdot\). Based on the discussion in Section 4.3, the reactions of this radical which need to be considered are

\[ \text{CFCl}_2\text{CH}_2\text{O}^\cdot + \text{O}_2 \rightarrow \text{CFCl}_2\text{CHO} + \text{HO}_2 \] (a)

\[ \text{CFCl}_2\text{CH}_2\text{O}^\cdot \rightarrow \text{CFCl}_2 + \text{HCHO} \] (b)

with H atom elimination being totally negligible. The sum of the heats of formation of the products of reactions (a) and (b) are -92.1 kcal mol⁻¹ and -48.9 kcal mol⁻¹, respectively. On the basis of the difference in these heats of formation of 43 kcal mol⁻¹, it is expected that pathway (a) will dominate at room temperature, and more so at the lower temperatures of the upper troposphere (taking into account the lower \text{O}_2 concentrations). Again, this expectation is in agreement with the conclusions of Sanhueza et al. (1976). The decomposition to HCHO and the \text{CFCl}_2 radical cannot be ruled out at the present time, however. The reactions of the \text{CFCl}_2 radical will be totally analogous to those of the \text{CF}_2\text{Cl} radical discussed in Section 2.4 below, except that the \text{CFCl}_2\text{O}^\cdot radical will eliminate a Cl atom to yield \text{COFCl} (instead of the \text{COF}_2 formed from the \text{CF}_2\text{ClO}^\cdot radical).

Assuming that the rate constant for the reaction (a) is identical to that for the ethoxy radical of \( k_a = 3.7 \times 10^{-14} \ e^{-460/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \), the lifetime of the \text{CFCl}_2\text{CH}_2\text{O}^\cdot radical will be ~2 x 10⁻⁴ to 2 x 10⁻⁵ s in the troposphere.

F. \text{CFCl}_2\text{CHO}. The possible tropospheric reactions of dichlorofluoroacetaldehyde are reaction with OH and \text{NO}_3 radicals and \text{O}_3, and photolysis. By analogy with \text{CH}_3\text{CHO}, for which the \text{O}_3 reaction rate constant at room temperature is < 10⁻²⁰ cm³ molecule⁻¹ s⁻¹ (Atkinson and Carter, 1984), reaction with \text{O}_3 is expected to be of totally negligible importance as a loss process. Reaction with the \text{NO}_3 radical is expected to be no faster than the corresponding reaction with \text{CH}_3\text{CHO} [k = 1.4 \times 10⁻¹² \ e^{-1860/T} \text{ cm}³ \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K} (\text{IUPAC}, 1989)]

Thus, photolysis and OH radical reaction remain to be considered. The OH radical reaction will proceed by

\[ \text{OH} + \text{CFCl}_2\text{CHO} \rightarrow \text{H}_2\text{O} + \text{CFCl}_2\text{CO} \]

Assuming that the substituent group factor for the -\text{CFCl}_2 group is similar to those for the -\text{CCl}_3, -\text{CF}_3 and -\text{CF}_2\text{Cl} groups (Atkinson, 1987), the estimation technique of Atkinson (1987) allows an approximate room temperature rate constant of ~(0.5-2) x 10⁻¹² cm³ molecule⁻¹ s⁻¹ to be calculated. A rate constant...
DEGRADATION MECHANISMS

of this magnitude leads to a lifetime of CFCl₂CHO with respect to OH radical reaction of ~15 days (to within ± a factor of ~2).

The photolysis rate is not known, but is expected to be less than that of CH₃CHO, which leads to a lifetime with respect to photolysis of ≥ 5-10 days. In the absence of data for the absorption cross-sections, photodissociation quantum yields and photodissociation products of CFCl₂CHO, it is assumed that the OH radical reaction, while relatively slow, is the dominant tropospheric loss process, leading to the formation of the CFCl₂CO radical.

G. CFCl₂CO. This acyl radical will rapidly add O₂, with a rate constant of ~10⁻¹² cm³ molecule⁻¹ s⁻¹ (Atkinson, 1989a).

\[
\text{CFCl}_2\dot{\text{CO}} + \text{O}_2 \rightarrow \text{CFCl}_2\text{C(O)O}_2^\cdot
\]

This will be the sole reaction of the CFCl₂CO radical, which will have a lifetime of < 10⁻⁶ s⁻¹ in the troposphere.

H. CFCl₂C(O)O₂⁺. Analogous to the alkyl and haloalkyl peroxy (RO₂⁺) radicals and the acetyl peroxy (CH₃C(O)O₂⁺) radical, this acyl peroxy radical will react with NO and NO₂.

\[
\text{CFCl}_2\text{C(O)O}_2^\cdot + \text{NO} \rightarrow \text{CFCl}_2\text{CO}_2^\cdot + \text{NO}_2
\]

\[
\text{CFCl}_2 + \text{CO}_2
\]

\[
\text{CFCl}_2\text{C(O)O}_2^\cdot + \text{NO}_2 \rightarrow \text{CFCl}_2\text{C(O)OONO}_2
\]

Assuming identical rate constants for these NO and NO₂ reactions to those for the analogous reactions with the acetyl peroxy radical, rate constants of 5.1 x 10⁻¹² e²⁰⁰/T cm³ molecule⁻¹ s⁻¹ for the NO reaction and 8 x 10⁻¹² cm³ molecule⁻¹ s⁻¹ for the NO₂ reaction (at the high pressure limit, which should be a good approximation) are obtained (Atkinson, 1989a). The reaction with NO leads to the formation of the CFCl₂ radical, while the NO₂ reaction forms an analog to peroxyacetyl nitrate (PAN).

In addition, reaction with the HO₂ radical and, at least in the lower troposphere, with CH₃O₂⁺ radicals cannot be ruled out as being of importance. The reaction of the CH₃C(O)O₂⁺ radical with HO₂ has been reported to lead to the formation of CH₃C(O)OOH + O₂ and CH₃COOH + O₃ in an approximately 3:1 ratio at room temperature (Niki et al., 1985) [see also Moortgat et al., 1987]. The reaction of the CH₃C(O)O₂⁺ radical with the CH₃O₂⁺ radical is rapid, with a rate constant of 1.1 x 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ at 298 K, forming CH₃O⁺ + CH₃CO₂⁺ + O₂ and CH₃COOH + HCHO + O₂ in equal yield at room temperature (IUPAC, 1989; Moortgat et al., 1989).

The analogous products would then be CFCl₂CO₂⁺, which should rapidly decompose to CFCl₂ + CO₂, CFCl₂COOH and CFCl₂C(O)OOH. The reactions of the CFCl₂ radical are dealt with below in Section 2.4. By analogy with CH₃COOH, the acid CFCl₂COOH is expected to react only slowly with the OH
radical (Atkinson, 1989b), with a lifetime with respect to OH radical reaction of ~25 days, and the major tropospheric loss process for CFCl2COOH and CFCl2C(O)OOH will be by wet deposition and rain-out.

I. CFCl2C(O)OONO2. This halogenated peroxy acylnitrate is expected to react in an analogous manner to PAN, with thermal decomposition and photolysis being the likely tropospheric homogeneous gas-phase loss processes (reaction with the OH radical being of no importance). The rate constant for the thermal decomposition

\[
M
\xrightarrow{\text{CFCl}_2\text{C(O)OONO}_2} \text{CFCl}_2\text{C(O)O}_2^- + \text{NO}_2
\]

is expected to be similar to that for PAN, with \( k = 2.2 \times 10^{16} \exp{-13435/T} \) S\(^{-1}\) at the high-pressure limit (IUPAC, 1989). While the thermal decomposition rate constant for PAN is in the fall-off region at atmospheric pressure and below at room temperature, the thermal decomposition rate constant for CFCl2C(O)OONO2 should be close to the high pressure limit throughout the troposphere. The lifetime of CFCl2C(O)OONO2 with respect to thermal decomposition will then increase with altitude, from ~1 hr at ground level (298 K) to ~45 yr in the upper troposphere (220 K).

PAN has a weak absorption which extends out to 300 nm, with a cross-section of 1 x 10\(^{-21}\) cm\(^2\) (IUPAC, 1989). Photolysis of CFCl2C(O)OONO2, presumably to the same products as arise from its thermal decomposition, will then be slow, but may compete with or dominate over thermal decomposition in the upper troposphere. It appears that in the upper troposphere CFCl2C(O)OONO2 will act as a long-lived intermediate species in the degradation of HCFC-141b.

A portion of the tropospheric degradation scheme for HCFC-141b is shown below.

2.3. The CF2ClCH2 Radical formed from HCFC-142b (CF2ClCH2).

The reactions undergone by the CF2ClCH2 radical in the troposphere are expected to be totally analogous to the reactions of the CFCl2CH2 radical discussed above in Section 2.2. However, the possible reactions of the CF2ClCH2O' radical which is formed during the overall reaction scheme need to be evaluated, as follows.

A. CF2ClCH2O'. The likely reaction pathways are (see Section 2.2.E above)

\[
\begin{align*}
\text{CF}_2\text{ClCH}_2\text{O}' + \text{O}_2 & \rightarrow \text{CF}_2\text{ClCHO} + \text{HO}_2 \quad \text{(a)} \\
\text{CF}_2\text{ClCH}_2\text{O}' & \rightarrow \text{CF}_2\text{Cl} + \text{HCHO} \quad \text{(b)}
\end{align*}
\]

The calculated sum of the heats of formation of the products of reactions (a) and (b) are then -135 kcal mol\(^{-1}\) for pathway (a) (uncertain to at least ±3 kcal mol\(^{-1}\)) and -90.3 kcal mol\(^{-1}\) for pathway (b). This again suggests, as for the case for the CFCl2CH2O' radical in Section 2.2.E., that pathway (a) will dominate, leading to the formation of CF2ClCHO.

A portion of the tropospheric degradation scheme of the CF2ClCH2 radical, leading to the formation of the CF2Cl radical, is shown below.
DEGRADATION MECHANISMS

\[
\begin{align*}
\text{CFC}_2\text{CH}_2 & \\
\rightarrow & \\
\text{O}_2 & \\
\text{CFC}_2\text{CH}_2\text{OOH} & \xrightleftharpoons{\text{OH}} \text{CFC}_2\text{CH}_2\text{O}_2 & \xrightarrow{\text{NO}_2} \text{CFC}_2\text{CH}_2\text{OOONO}_2 \\
\downarrow & \\
\text{NO} & \rightarrow \text{NO}_2 & \xrightarrow{\text{hv}} \\
\text{CFC}_2\text{CH}_2\text{O}^- & \\
\downarrow & \\
\text{O}_2 & \\
\text{CFC}_2\text{CHO} & \\
\downarrow & \\
\text{OH} & \\
\text{CFC}_2\text{CO} & \\
\downarrow & \\
\text{O}_2 & \\
\text{CFC}_2\text{COOH} & \xrightarrow{\text{CH}_3\text{O}_2} \text{CFC}_2\text{C(O)OOH} & \xrightarrow{\text{NO}_2} \text{CFC}_2\text{C(O)OOONO}_2 \\
\downarrow & \\
\text{NO} & \rightarrow \text{NO}_2 & \xrightarrow{\text{hv}} \\
\cdot & \\
\text{CFC}_2 & \\
\end{align*}
\]
DEGRADATION MECHANISMS

\[ \text{CF}_2\text{ClCH}_2 \]
\[ \rightarrow \text{O}_2 \]

\[ \text{CF}_2\text{ClCH}_2\text{OOH} \]
\[ \xrightarrow{\text{HO}_2} \text{CF}_2\text{ClCH}_2\text{O}^\cdot \]
\[ \xrightarrow{\text{NO}} \text{CF}_2\text{ClCH}_2\text{OONO}_2 \]
\[ \xrightarrow{\text{hv}} \text{NO}_2 \]

\[ \text{CF}_2\text{ClCH}_2\text{O}^\cdot \]
\[ \rightarrow \text{O}_2 \]

\[ \text{CF}_2\text{ClCHO} \]
\[ \rightarrow \text{OH} \]

\[ \text{CF}_2\text{ClCO} \]
\[ \rightarrow \text{O}_2 \]

other products (CF\text{\textsubscript{2}}C\text{\textsubscript{1}}COOH, CF\text{\textsubscript{2}}C\text{\textsubscript{1}}C(0)OOH)

\[ \xrightarrow{\text{HO}_2} \text{CF}_2\text{ClC(0)O}_2 \]
\[ \xrightarrow{\text{NO}_2} \text{CF}_2\text{ClC(0)OOONO}_2 \]

\[ \xrightarrow{\text{NO}} \text{NO}_2 \]

\[ \cdot \text{CF}_2\text{Cl} \]
DEGRADATION MECHANISMS

As noted above, the tropospheric reactions of the \( \text{CFCl}_2\text{C} \text{H}_2 \) and \( \text{CF}_2\text{ClC} \text{H}_2 \) radicals formed from HCFC-141b and HCFC-142b, respectively, are expected to be totally analogous, except that the \( \text{CFCl}_2 \) radical is formed subsequent to the reactions of the \( \text{CFCl}_2\text{C} \text{H}_2 \) radical, while the \( \text{CF}_2\text{Cl} \) radical is the subsequent product from the \( \text{CF}_2\text{ClC} \text{H}_2 \) radical.

2.4. The \( \text{CF}_2\text{Cl} \) Radical formed from HCFC-22 (CHF_2Cl)

In addition to being the primary product of the OH radical reaction with CHF_2Cl, the \( \text{CF}_2\text{Cl} \) radical is also expected to be formed from the reactions subsequent to the OH radical reaction with HCFC-142b. The analogous radical \( \text{CFCl}_2 \) is expected to be formed subsequent to the OH radical reaction with HCFC-141b, and the reaction sequence discussed in this section for the \( \text{CF}_2\text{Cl} \) radical is also applicable for the \( \text{CFCl}_2 \) radical, with the differences being noted at the appropriate points.

A. \( \text{CF}_2\text{Cl} \). No experimental data are available for this particular radical. Experimental data are available for the analogous \( \text{CFCl}_2 \) radical reaction (Caralp and Lesclaux, 1983), and the IUPAC (1989) recommended values of \( k_0 \), \( k_m \) and \( F \) for the reaction of the \( \text{CFCl}_2 \) radical with \( \text{O}_2 \) are given in Table 2 (see Section 4). Both the \( \text{CF}_2\text{Cl} \) and \( \text{CFCl}_2 \) radicals rapidly add \( \text{O}_2 \) to form the \( \text{CF}_2\text{ClO}_2 \) and \( \text{CFCl}_2\text{O}_2 \) peroxy radicals, respectively,

\[
\text{CF}_2\text{Cl} + \text{O}_2 \rightarrow \text{CF}_2\text{ClO}_2 \\
\text{CFCl}_2 + \text{O}_2 \rightarrow \text{CFCl}_2\text{O}_2
\]

with rate constants of \( \geq 5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) under the temperature and pressure conditions in the troposphere. The lifetimes of the \( \text{CF}_2\text{Cl} \) and \( \text{CFCl}_2 \) radicals will then be \( < 2 \times 10^{-6} \text{ s} \) in the troposphere.

B. \( \text{CF}_2\text{ClO}_2 \). This peroxy radical can, as described above in Section 2.1, react with NO, NO_2 and the \( \text{HO}_2 \) radical under tropospheric conditions.

\[
\text{CF}_2\text{ClO}_2 + \text{NO} \rightarrow \text{CF}_2\text{ClO}^- + \text{NO}_2 \quad (a)
\]

\[
\text{CF}_2\text{ClO}_2 + \text{NO}_2 \rightarrow \text{CF}_2\text{ClOOONO}_2 \quad (b)
\]

\[
\text{CF}_2\text{ClO}_2 + \text{HO}_2 \rightarrow \text{CF}_2\text{ClOOH} + \text{O}_2 \quad (c)
\]

The reactions of the \( \text{CFCl}_2\text{O}_2 \) radical are totally analogous. Experimental rate constant data are available for the reactions of the \( \text{CF}_2\text{ClO}_2 \) radical with NO (Dognon et al., 1985), and for the reactions of the \( \text{CFCl}_2\text{O}_2 \) radical with NO (Lesclaux and Caralp, 1984; Dognon et al., 1985) and NO_2 (Lesclaux and Caralp, 1984; Lesclaux et al., 1986; Caralp et al., 1988). The IUPAC (1989) recommendations for these NO and NO_2 reactions (based upon these data) are given in Tables 3 and 4, respectively (see Section 4). As discussed in Section 4.2, the rate constants for the reactions (a), (b) and (c) are (in \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} units), \( k_a = 1.5 \times 10^{-11} (T/300)^{1.4} \), \( k_b \sim 9 \times 10^{-12} \) under tropospheric conditions, and \( k_c \sim 3.4 \times 10^{-13} \text{ e}^{800/T} \). As discussed in Section 2.1 above, all three of these reactions are expected to occur under tropospheric conditions, leading to the formation of the \( \text{CF}_2\text{ClO}^- \) radical, \( \text{CF}_2\text{ClOOONO}_2 \) and \( \text{CF}_2\text{ClOOH} \).
DEGRADATION MECHANISMS

Formation of the nitrate, CF₂ClONO₂, from the reaction of the CF₂ClO₂ radical with NO is expected to be of negligible importance. Analogous products will be formed from the CFCI₂O₂ radical reactions.

C. CF₂ClOO.NO₂. As in Sections 2.1 and 2.2 above, this peroxynitrate can undergo thermal decomposition or photolyze. The thermal decomposition

\[ \text{CF}_2\text{ClOONO}_2 \rightarrow \text{CF}_2\text{ClO}_2 + \text{NO}_2 \]

rate data have been evaluated by IUPAC (1989), and the recommended rate expressions for this reaction and the analogous thermal decomposition of CFCI₂OONO₂ are given in Table 10 (Section 4). The lifetimes of these two peroxynitrates with respect to thermal decomposition increase from \( \sim 15 \) s in the lower troposphere to \( \sim (2-3) \times 10^7 \) s (\( \sim 290 \) days) in the upper troposphere.

No absorption cross-section data are available for CF₂ClOO:NO₂. However, data are available for CFCI₂ONO₂ (Morel et al., 1980) for wavelengths out to 280 nm. Extrapolation of these cross-sections to longer wavelengths leads to the expectation (Section 4.4.B) that photolysis

\[ \text{CF}_2\text{ClOONO}_2 + \text{hv} \rightarrow \text{CF}_2\text{ClO}_2 + \text{NO}_2 \]

\[ \text{CF}_2\text{ClOONO}_2 + \text{hv} \rightarrow \text{CF}_2\text{ClO}^- + \text{NO}_3 \]

will dominate in the upper troposphere, with a lifetime with respect to this process of \( \sim 5 \) days. The photolysis products are not known, but are expected to be mainly the peroxy radical plus NO₂.

D. CF₂ClOOH. The homogeneous gas-phase tropospheric loss processes for CF₂ClOOH and CFCI₂OOH are photolysis and reaction with the OH radical. As discussed in Section 2.1 above, photolysis

\[ \text{CF}_2\text{ClOOH} + \text{hv} \rightarrow \text{CF}_2\text{ClO}^- + \text{OH} \]

is expected to have a lifetime of \( \sim 6 \) days in the lower troposphere. The OH radical reaction can only proceed to regenerate the peroxy radical

\[ \text{OH} + \text{CF}_2\text{ClOOH} \rightarrow \text{H}_2\text{O} + \text{CF}_2\text{ClO}_2 \]

and the rate constant for this reaction is estimated to be \( k = 1.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \). Reaction with the OH radical and photolysis are expected to occur at comparable rates in the troposphere, leading to a lifetime of CF₂ClOOH with respect to these reactions of 2 to 3 days. Incorporation into aqueous systems may also be important. The reactions of CFCI₂OOH are expected to be totally analogous.

E. CF₂ClO⁻. As discussed in Section 4.3.B., the CF₂ClO⁻ radical will undergo decomposition to yield COF₂ and a Cl atom (Table 8).

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

The CFCI₂O⁻ radical decomposes in an analogous manner

\[ \text{CFCI}_2\text{O}^- \rightarrow \text{COFCI} + \text{Cl} \]
DEGRADATION MECHANISMS

The lifetimes of these halomethoxy radicals are calculated (Table 8) to be <0.1 s throughout the troposphere, and reactions with NO and NO₂ will be unimportant.

F. COF₂ and COFCI. Neither of these compounds are expected to react with the OH radical at tropospherically significant rate constants (Atkinson, 1987). Furthermore, photolysis of these species in the troposphere will be of essentially no importance (NASA, 1987). Physical removal processes leading to incorporation into rain, cloud or fog water, with subsequent hydrolysis to form HF and (for COFCI) HCl, are then expected to be the major tropospheric loss processes for these carbonyl halides.

The reaction scheme for the CF₂Cl radical is shown below

\[
\begin{align*}
\text{CF}_2\text{Cl} & \quad \xrightarrow{O_2} \quad \text{CF}_2\text{ClO}^- \quad \xrightarrow{O_2} \quad \text{CF}_2\text{ClOONO}_2 \\
\text{CF}_2\text{ClO}^- & \quad \xrightarrow{\text{OH}} \quad \text{CF}_2\text{ClOOH} \quad \xrightarrow{\text{OH}} \quad \text{CF}_2\text{ClO}^- \\
\text{CF}_2\text{ClO}^- & \quad \xrightarrow{\text{NO}} \quad \text{CF}_2\text{ClO}^- \quad \xrightarrow{\text{NO}_2} \quad \text{CF}_2\text{ClOONO}_2 \\
\text{CF}_2\text{ClO}^- & \quad \xrightarrow{\text{hv}} \quad \text{CF}_2\text{ClO}^- \\
\text{CF}_2\text{ClO}^- & \quad \xrightarrow{\text{hv}} \quad \text{COF}_2 + \text{Cl} 
\end{align*}
\]

The reaction scheme for the CFCl₂ radical is totally analogous, except that the final products are COFCI and a Cl atom.

2.5. The CF₃CFCl Radical formed from HCFC-124 (CF₃CHFCl)

The tropospheric reactions of this radical will be totally analogous to those of the CF₃CCl₂ radical formed from HCFC-123, discussed in Section 2.1. The reactions of the CF₃CFClO⁻ radical which is formed during the degradation need to be evaluated.
DEGRADATION MECHANISMS

A. CF₃CFClO. The likely reactions of this radical are

\[
\text{CF}_3\text{CFClO}^{-} \rightarrow \text{CF}_3\text{C(O)F} + \text{Cl} \quad (a)
\]

\[
\text{CF}_3\text{CFClO}^{-} \rightarrow \cdot\text{CF}_3 + \text{COFCl} \quad (b)
\]

The heats of formation of the products of reaction pathways (a) and (b) are: \(\text{CF}_3\text{C(O)F} + \text{Cl}\) from pathway (a), -222.1 kcal mol\(^{-1}\) (\(\Delta H_f(\text{CF}_3\text{C(O)F}) = -251.1\) kcal mol\(^{-1}\) with an uncertainty of at least 2 kcal mol\(^{-1}\)); and \(\cdot\text{CF}_3 + \text{COFCl}\) from reaction pathway (b), -216.0 kcal mol\(^{-1}\). As expected (Section 4.3.B), the Cl atom elimination pathway (a) is preferred, leading to \(\text{CF}_3\text{C(O)F}\) and a Cl atom.

B. CF₃C(O)F. Trifluoroacetyl fluoride is not expected to react with the OH radical with any tropospherically significant rate constant (Atkinson, 1987) since there are no H atoms to abstract. While no data exist concerning photolysis of \(\text{CF}_3\text{C(O)F}\) to \(\cdot\text{CF}_3 + \text{FCO}\) or to \(\text{CF}_4 + \text{CO}\), photodissociation to \(\cdot\text{CF}_3 + \text{FCO}\) is expected to be negligible in the troposphere since the threshold wavelength for this process is calculated to be 296 nm (96.5 kcal mol\(^{-1}\)). This then leaves physical processes as the main removal route, with wet deposition/incorporation into cloud, fog and rain water with subsequent hydrolysis (to \(\text{CF}_3\text{COOH} + \text{HF}\)) being expected to dominate.

The expected reaction scheme for the CF₃CFCl radical is shown below

2.6. The CF₃CHF Radical formed from HFC-134a (CF₃CH₂F).

The tropospheric reactions of the CF₃CHF radical are expected to be generally similar to those of the
DEGRADATION MECHANISMS

CF₂ClCH₂ and CFC₁₂CH₂ radicals discussed above in Sections 2.2 and 2.3.

A. CF₂CHF. Reaction with O₂ to form the peroxy radical will be the sole reaction of this radical in the troposphere.

\[ M \]
\[ \text{CF}_2\text{CHF} + \text{O}_2 \rightarrow \text{CF}_2\text{CHFO}_2 \]

The rate constant is expected to be \( > 5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) at the temperatures and pressures encountered in the troposphere, leading to a lifetime of the CF₂CHF radical of \( < 2 \times 10^{-6} \text{ s} \).

B. CF₂CHFO₂. The tropospherically important reactions of the CF₂CHFO₂ radical are expected to be with NO, NO₂ and the HO₂ radical:

\[ \text{CF}_2\text{CHFO}_2 + \text{NO} \rightarrow \text{CF}_2\text{CHFO}^\cdot + \text{NO}_2 \quad \text{(a)} \]
\[ M \]
\[ \text{CF}_2\text{CHFO}_2 + \text{NO}_2 \rightarrow \text{CF}_2\text{CHFOONO}_2 \quad \text{(b)} \]
\[ \text{CF}_2\text{CHFO}_2 + \text{HO}_2 \rightarrow \text{CF}_2\text{CHFOOH} + \text{O}_2 \quad \text{(c)} \]

The rate constants for these reactions are estimated (in cm³ molecule⁻¹ s⁻¹ units) to be \( k_a \sim 1.5 \times 10^{-11} (T/300)^{-1.2} \), \( k_b \sim 1.0 \times 10^{-11} \), and \( k_c \sim 3.4 \times 10^{-13} \text{ e}^{0.007/T} \), respectively. With the tropospheric concentrations of NO, NO₂ and the HO₂ radical as given in Table 1, all three of these reactions are of comparable importance, and the reactions of the products formed must be considered further. The lifetime of the CF₂CHFO₂ radical is calculated to be \( \sim 10^2 \text{ s} \).

C. CF₂CHFOONO₂. This species is expected to undergo thermal decomposition and photolysis. Thermal decomposition

\[ M \]
\[ \text{CF}_2\text{CHFOONO}_2 \rightarrow \text{CF}_2\text{CHFO}_2 + \text{NO}_2 \]

is expected to have a rate constant at the high-pressure limit of \( \sim 1 \times 10^{15} \text{ e}^{-10000/T} \text{ s}^{-1} \), leading to lifetimes of this peroxynitrate, with respect to thermal decomposition, of \( \sim 10 \text{ s} \) in the lower troposphere (298 K) and \( \sim 10^7 \text{ s} \) in the upper troposphere (220 K). The peroxy radical CF₂CHFO₂ is reformed. Photolysis

\[ \text{CF}_2\text{CHFOONO}_2 + \text{hv} \rightarrow \text{CF}_2\text{CHFO}_2 + \text{NO}_2 \]
\[ \text{CF}_2\text{CHFOONO}_2 + \text{hv} \rightarrow \text{CF}_2\text{CHFO}^\cdot + \text{NO}_3 \]

is expected to be slow, with a lifetime of the peroxynitrate due to photolysis of \( \sim 5 \text{ days} \). Which of the two photolysis pathways occurs is not known. Thus, in the lower and middle troposphere thermal decomposition should dominate, while in the upper troposphere photolysis is expected to be the dominant removal process of CF₂CHFOONO₂.
DEGRADATION MECHANISMS

D. CF₃CHFOOH. As for the hydroperoxides considered in the sections above, photolysis and reaction with the OH radical are expected to be the only significant homogeneous gas-phase removal processes. Photolysis

\[ \text{CF₃CHFOOH} + \text{hv} \rightarrow \text{CF₃CHFO}^\cdot + \text{OH} \]

forms the haloalkoxy radical CF₃CHFO^\cdot. Based upon the absorption cross-section for CH₃OOH (NASA, 1987), the lifetime of CF₃CHFOOH with respect to photolysis is estimated to be \( \sim 6 \) days in the lower troposphere.

The OH radical reaction will proceed mainly by

\[ \text{OH} + \text{CF₃CHFOOH} \rightarrow \text{H₂O} + \text{CF₃CHFO}_2^\cdot \]

with an estimated rate constant of \( \sim 1.7 \times 10^{-12} \) \( \text{e}^{220/T} \) cm³ molecule⁻¹ s⁻¹. The reaction to form the CF₃CFOOH radical

\[ \text{OH} + \text{CF₃CHFOOH} \rightarrow \text{H₂O} + \text{CF₃CFOOH} \]

is expected to of minor importance [<5% of the overall reaction (Atkinson, 1987)].

Photolysis and OH radical reaction are expected to be of comparable importance as tropospheric loss processes for CF₃CHFOOH, with a lifetime due to these processes of 2-3 days. Physical removal of CF₃CHFOOH from the gas phase into rain, cloud and fog water and aerosols may also be important.

E. CF₃CHFO'. The possible reactions of this haloalkoxy radical are

\[ \text{CF₃CHFO}^\cdot + \text{O}_2 \rightarrow \text{CF₃C(O)F} + \text{HO}_2 \] \hspace{1cm} (a)

\[ \text{CF₃CHFO}^\cdot \rightarrow \text{CF₃C(O)F} + \text{H} \] \hspace{1cm} (b)

\[ \text{CF₃CHFO}^\cdot \rightarrow \text{CF₃} + \text{HC(O)F} \] \hspace{1cm} (c)

\[ \text{CF₃CHFO}^\cdot \rightarrow \text{CF₃CHO} + \text{F} \] \hspace{1cm} (d)

The sum of the heats of formation of the products from these reactions are (with \( \Delta H_f(\text{CF₃C(O)F}) = -251.1 \) kcal mol⁻¹ being calculated, with an uncertainty of at least \( \pm 2 \) kcal mol⁻¹): CF₃C(O)F + HO₂ from reaction (a), -247.6 kcal mol⁻¹; CF₃C(O)F + H from reaction (b), -199.0 kcal mol⁻¹; CF₃ + HC(O)F from reaction (c), -205.3 kcal mol⁻¹ (with \( \Delta H_f(\text{HC(O)F}) = -90.9 \) kcal mol⁻¹ calculated from bond additivity (Benson, 1976) being in good agreement with the value of -91.8 kcal mol⁻¹ obtained by Goldstein et al. (1983) from MINDO calculations); and CF₃CHO + F from reaction (d), -168.0 kcal mol⁻¹. Clearly, H atom [reaction (b)] and F atom [reaction (d)] elimination will be of negligible importance, as expected from the discussion in Section 4.3.B. This leaves reaction with O₂ and C-C bond cleavage as the likely reaction routes of the CF₃CHFO radical. The difference in the sums of the heats of formation of the products of these two reactions, \( \Delta(\Delta H_f) \), of 42.3 kcal mol⁻¹, with at least \( \pm 2-3 \) kcal mol⁻¹ uncertainty, indicates that both reactions may be of comparable importance at room temperature (with the reaction with O₂ presum-
DEGRADATION MECHANISMS

ably having a smaller temperature dependence than that for the C-C bond cleavage and hence becoming more important in the upper, colder, troposphere).

Thus, the formation of both CF₃C(O)F and of CF₃ + HC(O)F must be considered.

F. CF₃C(O)F. As discussed in Section 2.5 above, the reaction of OH radical with CF₃C(O)F will be unimportant as a tropospheric loss process, and photolysis is also expected to be slow or negligible. The removal of CF₃C(O)F by chemical pathways is thus expected to be slow, and physical removal by wet deposition and incorporation into cloud, rain and fog water will be the dominant tropospheric removal process, with the expectation of subsequent hydrolysis in aqueous media to HF + CF₃COOH.

G. HC(O)F. The expected tropospheric removal routes for formyl fluoride are photolysis, reaction with the OH radical and wet deposition. Reaction with the OH radical

\[
\text{OH} + \text{HC(O)F} \rightarrow \text{H}_2\text{O} + \text{FCO}
\]

is calculated (Atkinson, 1987) to have a rate constant at room temperature of \(\sim 1.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\), and the magnitude of this rate constant is reasonably consistent (being high, in fact) with the C-H bond strength of \(\sim 102 \text{ kcal mol}^{-1}\) in HC(O)F. An OH radical reaction rate constant of this magnitude leads to a lifetime of HC(O)F with respect to OH radical reaction of \(\sim 10\) days. Photolysis is also expected to be slow in the troposphere (due to the high C-H bond dissociation energy), although no experimental data are available. This leaves wet deposition with subsequent hydrolysis to HF as the most likely tropospheric removal process.

H. CF₃. The reactions of this radical are dealt with in Section 2.9 below.

The expected reaction scheme in the troposphere for the CF₃CHF radical is shown below
2.7. The CHF₂CH₂ Radical formed from HFC-152a (CHF₂CH₃).

The expected reactions of the CHF₂CH₂ radical are essentially identical to those of the CF₂ClCH₂ and CFC₁₂CH₂ radicals discussed above in Sections 2.2. and 2.3. The fate of the resulting haloalkoxy radical CHF₂CH₂O⁻ needs to be considered, as follows.

A. CHF₂CH₂O⁻. The reactions of this radical which need to be considered are,

\[ \text{CHF}_2\text{CH}_2\text{O}^- + \text{O}_2 \rightarrow \text{CHF}_2\text{CHO} + \text{HO}_2 \]  
(a)

\[ \text{CHF}_2\text{CH}_2\text{O}^- \rightarrow \cdot \text{CHF}_2 + \text{HCHO} \]  
(b)

with H atom elimination to yield CHF₂CHO + H being of no importance. The sum of the heats of formation of the products from reactions (a) and (b) are: CHF₂CHO + HO₂ from reaction (a), \(-134.1 \text{ kcal mol}^{-1}\) [using the bond additivity method of Benson (1976) to calculate \(\Delta H_f(\text{CHF}_2\text{CHO})\)]; and \(\cdot \text{CHF}_2 + \text{HCHO}\) from reaction (b), \(-84.2 \text{ kcal mol}^{-1}\) [\(\Delta H_f(\text{CHF}_2)\) being obtained from McMillen and Golden (1982) and Pickard and Rodgers (1983)]. The difference in these heats of formation of the products of 50 kcal mol\(^{-1}\) indicates that reaction (a) to form CHF₂CHO + HO₂ will be the totally dominant reaction pathway for the CHF₂CH₂O radical throughout the troposphere, as expected from the discussion in Section 4.3.

B. CHF₂CHO. Difluoroacetaldehyde will react in a similar manner to CF₂ClCHO and CFC₁₂CHO discussed above in Sections 2.2 and 2.3. The OH radical reaction

\[ \text{OH} + \text{CHF}_2\text{CHO} \rightarrow \text{H}_2\text{O} + \text{CHF}_2\cdot\text{CO} \]

will proceed as shown, with an estimated rate constant of \(\sim 1.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) at room temperature (Atkinson, 1987). The reaction pathway involving H atom abstraction from the -CHF₂ group to form the CF₂CHO radical has an estimated room temperature rate constant of \(\sim 1.4 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) (Atkinson, 1987), and is hence of negligible importance. It should be noted that no data are available concerning the photolysis of CHF₂CHO under tropospheric conditions.

The subsequent reactions of the CHF₂ÇO radical will be as discussed in Section 2.2 above [H atom abstraction by the OH radical from the -CHF₂ group will be of no importance during the subsequent reactions of this CHF₂ÇO radical]. The reaction scheme for the CHF₂ÇH₂ radical is thus as shown below.

The CHF₂C(Ö)O⁻ radical formed in the final stages of this reaction sequence is expected to rapidly unimolecularly decompose to CO₂ plus the ÇHF₂ radical. Under tropospheric conditions, this ÇHF₂ radical will undergo the sequence of reactions generally similar to those discussed above in Section 2.4 for the CF₂Cl radical, to yield the CHF₂O⁻ radical. The reactions of this radical are as follows.
DEGRADATION MECHANISMS

\[
\begin{align*}
\text{CHF}_2\text{CH}_2 & \\
\downarrow & \downarrow O_2 \\
\text{CHF}_2\text{CH}_2\text{OOH} & \overset{\text{HO}_2}{\rightleftharpoons} \text{CHF}_2\text{CH}_2\text{O}^- & \overset{\text{NO}_2}{\rightarrow} \text{CHF}_2\text{CH}_2\text{OONO}_2 \\
\overset{\text{hv}}{\rightarrow} & \text{CHF}_2\text{CH}_2\text{O}^- & \overset{\text{hv}}{\rightarrow} \text{NO}_2 \\
\text{NO} & \overset{\rightarrow}{\text{NO}_2} \\
\text{CHF}_2\text{CH}_2\text{O}^- & \downarrow O_2 \\
\text{CHF}_2\text{CHO} & \\
\downarrow & \downarrow \text{OH} \\
\text{CHF}_2\text{CO} & \\
\downarrow & \downarrow O_2 \\
\text{other products} & \overset{\text{HO}_2}{\rightleftharpoons} \text{CHF}_2\text{C(O)OO}^- \overset{\text{NO}_2}{\rightarrow} \text{CHF}_2\text{C(O)OOONO}_2 \\
\overset{\text{NO}}{\rightarrow} & \text{NO}_2 \\
\text{CHF}_2\text{C(O)O}^- & \downarrow \\
\text{CHF}_2 + \text{CO}_2
\end{align*}
\]
C. CHF₂O⁻. Reaction with O₂ will be the only important reaction pathway

\[
\text{CHF}_2\text{O}^- + \text{O}_2 \rightarrow \text{COF}_2 + \text{HO}_2
\]

under tropospheric conditions (Table 8). The tropospheric loss processes for COF₂ have been dealt with in Section 2.4 above.

2.8. The CH₃CF₂ Radical formed from HFC-152a (CHF₂CH₃).

The reactions of the CH₃CF₂ radical in the troposphere will be generally similar to those of the CF₃CCl₂ and CF₃CFCl radicals dealt with in Sections 2.1 and 2.5 above. The reactions of the CH₃CF₂ radical leading to the formation of the CH₃CF₂O⁻ radical are then as shown below

The reactions of CH₃CF₂OONO₂ and CH₃CF₂OOH with the OH radical by H atom abstraction from the -CH₃ group are calculated to be of negligible importance, with a room temperature rate constant for this
DEGRADATION MECHANISMS

H atom abstraction process of $< 1 \times 10^{-13} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ being expected (Atkinson, 1987). The subsequent reactions of the haloalkoxy radical $\text{CH}_3\text{CF}_2\text{O}^-$ need to be considered, as discussed below.

A. $\text{CH}_3\text{CF}_2\text{O}^-$. The reactions of this radical which can occur are

$$\text{CH}_3\text{CF}_2\text{O}^- \rightarrow \text{CH}_3 + \text{COF}_2 \quad (a)$$
$$\text{CH}_3\text{CF}_2\text{O}^- \rightarrow \text{CH}_3\text{C(O)}\text{F} + \text{F} \quad (b)$$

Reaction pathway (a) is calculated to be 32 kcal mol$^{-1}$ more exothermic than pathway (b), and hence the unimolecular decomposition of the $\text{CH}_3\text{CF}_2\text{O}^-$ radical to $\text{CH}_3 + \text{COF}_2$ will totally dominate as a loss process. This conclusion is then in agreement with the discussion in Section 4.3.B below. The tropospheric loss processes of $\text{COF}_2$ have been dealt with in Section 2.4 above. The methyl radical will react as discussed in Section 4 below and by Ravishankara (1988), to yield compounds such as $\text{CH}_3\text{OOH}$, $\text{CH}_3\text{OONO}_2$ and $\text{HCHO}$, which react further to ultimately form $\text{CO}$, $\text{CO}_2$ and $\text{H}_2\text{O}$.

2.9. The CF$_3$CF$_2$ Radical formed from HFC-125 (CF$_3$CHF$_2$).

The tropospheric reactions of this radical are analogous to those of the CF$_3$CCl$_2$, CF$_3$CFCl and CH$_3$CF$_2$ radicals dealt with in Sections 2.1, 2.5 and 2.8, respectively. The reaction sequence leading to the formation of the CF$_3$CF$_2$O$^-$ haloalkoxy radical will be as shown below.

A. CF$_3$CF$_2\dot{O}^-$. The reactions of the CF$_3$CF$_2\dot{O}^-$ radical are expected to be (reaction with NO and NO$_2$ are expected to be too slow at the NO and NO$_2$ concentrations encountered in the troposphere):

$$\text{CF}_3\text{CF}_2\text{O}^- \rightarrow \text{CF}_3 + \text{COF}_2 \quad (a)$$
$$\text{CF}_3\text{CF}_2\text{O}^- \rightarrow \text{CF}_3\text{C(O)}\text{F} + \text{F} \quad (b)$$
DEGRADATION MECHANISMS

Reaction pathway (a) is calculated to be 33.5 kcal mol\(^{-1}\) more exothermic than pathway (b), and hence unimolecular decomposition of the CF\(_3\)CF\(_2\)O\(^{+}\) radical to yield CF\(_3\) + COF\(_2\) will be totally dominant. This conclusion is in agreement with the general discussion in Section 4.3.B below.

The tropospheric fate of COF\(_2\) has been dealt with above in Section 2.4.

B. CF\(_3\). As discussed in Section 4, reaction with O\(_2\) will be the sole tropospheric reaction of the CF\(_3\) radical

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

and the rate constant data for this reaction are given in Table 2. The reactions of the CF\(_3\)O\(^{+}\) radical with NO, NO\(_2\) and the HO\(_2\) radical, and the reactions of the CF\(_3\)OOONO\(_2\) and CF\(_3\)OOH species formed, are expected to be totally analogous to those of the CF\(_2\)Cl and CFCl\(_2\) radicals dealt with in Section 2.4 above. The rate constants for the reactions of the CF\(_3\)O\(^{+}\) radicals with NO and NO\(_2\) are given in Tables 3 and 4 (Section 4), respectively, and the rate data for the thermal decomposition of CF\(_3\)OOONO\(_2\) are expected to be similar to those for CF\(_2\)ClOOONO\(_2\), CFCl\(_2\)OOONO\(_2\) and CC\(_l\)OOONO\(_2\) given in Table 10 (Caralp et al., 1988).

C. Reaction of CF\(_3\)O\(^{+}\) with NO. The rate constant data for this reaction are given in Table 3. Dognon et al. (1985) observed a formation yield of NO\(_2\) from this reaction of 1.5 ± 0.5, strongly suggesting that the reaction proceeds by

\[
\text{CF}_3\text{O}_2^+ + \text{NO} \rightarrow \text{CF}_3\text{O}^+ + \text{NO}_2
\]

as for the other halomethyl peroxy radicals. This reaction is exothermic by 9 kcal mol\(^{-1}\) (Batt and Walsh, 1983; IUPAC, 1989).

However, from a low temperature matrix study of the reaction of the CF\(_3\) radical with O\(_2\) in the presence of NO, Clemitshaw and Sodeau (1987) obtained product data showing that under their experimental conditions, the reaction of CF\(_3\)O\(^{+}\) radicals with NO proceeded, presumably through the expected intermediate CF\(_3\)OOONO\(_2\), to yield COF\(_2\) and FNO\(_2\)

\[
\text{CF}_3\text{O}_2 + \text{NO} \rightarrow \text{COF}_2 + \text{FNO}_2
\]

which is exothermic by 38 kcal mol\(^{-1}\) (Batt and Walsh, 1983; IUPAC, 1989).

If, as expected, CF\(_3\)O\(^{+}\) is formed from the reaction of the CF\(_3\)O\(^{+}\) radical with NO, as well as from the photolysis of CF\(_3\)OOH, the subsequent reactions of this radical under tropospheric conditions are not understood. F atom elimination to yield COF\(_2\) + F is endothermic by 24 kcal mol\(^{-1}\) and is hence extremely slow (Table 8). The expected reactions of the CF\(_3\)O\(^{+}\) radical would then be with NO

\[
\text{M} + \text{CF}_3\text{OO}^+ + \text{NO} \rightarrow \text{CF}_3\text{ONO}
\]

to form the nitrite, which is expected to rapidly photolyze back to the CF\(_3\)O\(^{+}\) radical and NO, and with NO\(_2\)
DEGRADATION MECHANISMS

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

to form the nitrate. The tropospheric chemistry of this nitrate is not known, but unimolecular decomposition to \( \text{COF}_2 + \text{FNO}_2 \), photolysis and wet and/or dry deposition are the likely tropospheric removal pathways.

However, photolysis of \( \text{CF}_3\text{Br} \) in the presence of \( \text{O}_2 \) gave rise to the formation of \( \text{COF}_2 \) with a unit formation yield (Withnall and Sodeau, 1986), showing that under the conditions employed the \( \hat{\text{CF}}_3 \) radicals ultimately formed only \( \text{COF}_2 \). These data then suggest that the \( \text{CF}_3\text{O}^- \) radicals formed from the \( \hat{\text{CF}}_3 \) radical reaction with \( \text{O}_2 \) do yield \( \text{COF}_2 \). Possible tropospheric reactions of the \( \hat{\text{CF}}_3 \) radical are shown schematically below.

\[
\begin{align*}
\hat{\text{CF}}_3 \\
\text{CF}_3\text{OOH} & \xrightleftharpoons[\text{OH}]{\text{HO}_2} \text{CF}_3\text{O}^- \\
\text{CF}_3\text{O}^- + \text{NO}_2 & \xrightarrow{\text{hv}} \text{CF}_3\text{ONO}_2 \\
\text{FNO}_2 + \text{COF}_2 & \xrightarrow{\text{hv}} \text{CF}_3\text{ONO}_2
\end{align*}
\]

Clearly, the reactions of the \( \text{CF}_3\text{O}^- \) radical under tropospheric conditions need to be investigated, and the formation of \( \text{CF}_3\text{O}^- \) from the reaction of \( \hat{\text{CF}}_3\text{O}^- \) with \( \text{NO} \) confirmed. While it may be anticipated that the final product of the tropospheric degradation of the \( \hat{\text{CF}}_3 \) radical is \( \text{COF}_2 \), the formation of other product species cannot be ruled out.

3. CONCLUSIONS

The expected gas-phase reactions of the haloalkyl radicals formed from the potential alternative fluorocarbons have been outlined and discussed in the Sections above. As noted in the Introduction, only for the \( \hat{\text{CF}}_2\text{Cl} \) radical formed from HCFC-22 are experimental data concerning its tropospheric reactions avail-
DEGRADATION MECHANISMS

able. For the remaining radicals formed from the initial OH radical reactions with the HCFCs and HFCs, the reaction sequences operating in the troposphere must to a very large extent be deduced by analogy. This leads to uncertainties concerning the proposed reaction mechanisms, which can only be minimized by experimental investigations of the kinetics and, especially, the products of the individual reaction steps under realistic temperature, pressure and diluent gas conditions. In particular, the experimental investigation of the products of the reactions of the various haloalkoxy (RO) radicals with NO would remove large areas of uncertainty concerning the ultimate products formed from these HCFCs and HFCs in the troposphere.

Additionally, the absorption cross-sections and photodissociation quantum yields and products (under atmospheric conditions) for the various acetyl halides (CX₃C(O)Y) and halogenated acetaldehydes (CX₃CHO) need to be determined. A quantitative understanding of physical removal processes for several of the product species, including the hydroperoxides, peroxyinitrates, carbonyl halides, acetyl halides and halogenated acetaldehydes, is also necessary before the lifetimes of these species in the troposphere, the potential for transport of these species to the stratosphere, and the impact of the HFCs and HCFCs on the ecosystem, can be completely assessed.

4. APPENDIX A: TROPOSPHERIC REACTIONS SUBSEQUENT TO ALKYL AND HALOALKYL RADICAL FORMATION

4.1. Alkyl and Haloalkyl (R') Radicals

Under tropospheric conditions, alkyl and haloalkyl (R') radicals react rapidly with O₂ to form the corresponding peroxy alkyl (RO₂') radicals.

\[
\text{M} + \text{RO}_2' + \text{O}_2 \rightarrow \text{RO}_2' + \text{RO}_2' + \text{O}_2
\]

For the methyl and ethyl radicals and the C₁ haloalkyl radicals, the rate constants at room temperature for these reactions with O₂ are in the fall-off region between second and third-order kinetics below atmospheric pressure. The low and high pressure rate constants k₁ and kₙ and the factor F at 298 K are given in Table 2, together with calculated rate constants at 298 K and 760 Torr total pressure and at 220 K and 100 Torr total pressure (temperatures and pressures corresponding approximately to the lower and upper levels of the troposphere, respectively). For the C₄ and C₅ alkyl radicals, rate constants have been determined only at 1-4 Torr total pressure, and it is expected that these measured rate constants are close to the high pressure values.

The kinetic data presented in Table 2 show that the rate constants for the C₁ alkyl and haloalkyl radicals are within a factor of ~2-3 of the limiting high-pressure rate constant kₙ at the temperatures and pressures applicable to the troposphere. The rate constants for the C₂ haloalkyl radicals are expected to be closer to the high pressure limit under these conditions and, based upon the data in Table 2, the alkyl and haloalkyl radicals will have bimolecular rate constants for reaction with O₂ of > 5 x 10⁻¹³ cm³ molecule⁻¹ s⁻¹ throughout the troposphere. Since the O₂ concentration in the troposphere is ≥10¹⁸ molecule cm⁻³, the lifetime of the alkyl and haloalkyl radicals are < 2 x 10⁻⁶ s and reaction with O₂ is the only tropospheric loss process for alkyl and haloalkyl radicals. It should be noted that, to date, there is no evidence that 1,2-migration of H or halogen atoms occurs following initial OH radical or Cl atom (Nelson et al., 1984) reaction with the haloalkanes.
DEGRADATION MECHANISMS

Table 2. Low- and high-pressure rate constants $k_0$ and $k_{oo}$ and the broadening coefficient $F$ (at 298 K), together with bimolecular rate constants $k$ at 300 K, 760 Torr total pressure and 220 K, 100 Torr total pressure, for the gas-phase reactions of alkyl and haloalkyl (R') radicals with $O_2$

<table>
<thead>
<tr>
<th>$\text{R'}$</th>
<th>$k_0 \text{(cm}^3 \text{molecule}^{-1} \text{s}^{-1})$ (T/300)</th>
<th>$k_{oo} \text{(cm}^3 \text{molecule}^{-1} \text{s}^{-1})$ (T/300)</th>
<th>$F$ (298 K)</th>
<th>$k$ (10$^{12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) 300 K 760 Torr 220 K 100 Torr</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$</td>
<td>8x10$^{-11}$ (T/300)$^{-1}$ (3.3 ± 1)</td>
<td>2.2 x 10$^{-12}$ (T/300)$^{-1}$ (3.8 ± 1)</td>
<td>0.27</td>
<td>1.0 0.76</td>
<td>IUPAC (1989)</td>
</tr>
<tr>
<td>C$_2$H$_5$</td>
<td>2.0x10$^{-28}$ (T/300)$^{-1}$ (3.8 ± 1)</td>
<td>5x10$^{-12}$</td>
<td>0.7</td>
<td>4.8 6</td>
<td>IUPAC (1989)</td>
</tr>
<tr>
<td>CH$_3$CH$_2$CH$_2$</td>
<td>6x10$^{-12}$</td>
<td>6x10$^{-12}$</td>
<td>6</td>
<td>6 IUPAC (1989)</td>
<td></td>
</tr>
<tr>
<td>(CH$_3$)$_2$CH</td>
<td>1.5x10$^{-11}$</td>
<td>1.5x10$^{-11}$</td>
<td>15</td>
<td>15 IUPAC (1989)</td>
<td></td>
</tr>
<tr>
<td>CH$_3$CH$_2$CH$_2$</td>
<td>(7.5 ± 1.4)x10$^{-12}$b (room temperature)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(CH$_3$)$_2$CCH</td>
<td>(1.66 ± 0.22)x10$^{-11}$b (room temperature)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(CH$_3$)$_2$CHCH</td>
<td>(2.9 ± 0.7)x10$^{-12}$b (298 ± 2 K)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(CH$_3$)$_2$CCH$_2$</td>
<td>(1.6 ± 0.3)x10$^{-12}$b (298 ± 2 K)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(CH$_3$)$_3$CH</td>
<td>2.1x10$^{-12}$ (T/300)$^{-1}$ (266-374 K)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF$_3$</td>
<td>1.9x10$^{-19}$ (T/300)$^{-1}$ (4.7 ± 1)</td>
<td>1x10$^{-11}$</td>
<td>0.4-0.5</td>
<td>7.9 8.2</td>
<td>IUPAC (1989)</td>
</tr>
<tr>
<td>CFCI$_2$</td>
<td>5x10$^{-20}$ (T/300)$^{-1}$ (3.8 ± 1)</td>
<td>6x10$^{-11}$</td>
<td>0.6</td>
<td>4.7 4.7</td>
<td>IUPAC (1989)</td>
</tr>
<tr>
<td>CCl$_3$</td>
<td>1.5x10$^{-18}$ (T/300)$^{-1}$ (4 ± 2)</td>
<td>5x10$^{-12}$</td>
<td>0.25</td>
<td>2.0 2.0</td>
<td>IUPAC (1989)</td>
</tr>
</tbody>
</table>

a Calculated from fall-off expression.  

For the reactions of alkyl radicals with $O_2$ in the fall-off region, the activated $RO_2^\cdot$ radical can decompose to the alkene and the $HO_2^\cdot$ radical

$$R' + O_2 = [RO_2^\cdot]^* \rightarrow HO_2 + \text{alkene}$$

in addition to back-decomposition to the reactants (Slagle et al., 1984, 1985; McAdam and Walker, 1987). Hence, at the high pressure limit peroxy radical formation is expected to be the sole reaction process.
4.2. Alkyl Peroxy and Haloalkyl Peroxy ($RO_2^-$) Radicals

Under tropospheric conditions, $RO_2^-$ radicals are expected to react with NO, NO$_2$, HO$_2$ radicals, $RO_2^-$ radicals and acyl peroxy (RCO$_2^-$) radicals, with the reaction with $RO_2^-$ radicals potentially including self-reaction as well as reaction with other alkyl peroxy radicals. The relative importance of these reactions as a loss process for $RO_2^-$ radicals depends on the rate constants for the individual reactions and the concentrations of NO, NO$_2$, HO$_2$ radicals and the various $RO_2^-$ and RCO$_2^-$ radicals. These reactions are dealt with below.

A. Reaction with NO. The available rate constant data for the gas-phase reactions of alkyl and haloalkyl peroxy ($RO_2^-$) radicals with NO, obtained using absolute measurement techniques, are given in Table 3. The rate constants of Adachi and Basco (1979a, 1982) are suspect due to possible interfering absorptions of the product species (Ravishankara et al., 1981). The rate constant of Plumb et al. (1982) for C$_2$H$_50_2$ is similar to that recommended by NASA (1987) and IUPAC (1989) for CH$_30_2$, leading to the expectation (Atkinson and Lloyd, 1984; Atkinson, 1989a) that the rate constants for the reactions of alkyl peroxy radicals with NO are identical to that for CH$_3$O$_2$:

$$k(RO_2^- + NO) = 4.2 \times 10^{-12} \, e^{180/T} \, \text{cm}^3 \, \text{molecule}^{-1} \, s^{-1} \, (R = \text{alkyl})$$

The rate constants for the reactions of the C$_1$ haloalkyl peroxy radicals with NO are approximately a factor of two higher at room temperature.

The reaction of CH$_3$O$_2$ with NO proceeds by

$$CH_3O_2 + NO \rightarrow CH_3O^+ + NO_2$$

(Pate et al., 1974; Ravishankara et al., 1981; Zellner et al., 1986; NASA, 1987), and Plumb et al. (1982) have shown that the reaction of C$_2$H$_5$O$_2$ radicals with NO yields NO$_2$ with a yield of $\geq 0.80$. However, for the larger alkyl peroxy radicals, the reaction pathway

$$RO_2^- + NO \rightarrow [ROONO] \rightarrow RONO_2$$

Table 3. Rate constants k at room temperature and temperature-dependent expressions for the gas-phase reactions of alkyl and haloalkyl peroxy ($RO_2^-$) radicals with NO

<table>
<thead>
<tr>
<th>$RO_2^-$</th>
<th>k(cm$^3$molecule$^{-1}$s$^{-1}$)</th>
<th>10$^{12}$ x k (cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
<th>at T (K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$O$_2$</td>
<td>4.2 x 10$^{-12}$ e$(180\pm180)/T$</td>
<td>7.6</td>
<td>298</td>
<td>NASA (1987), IUPAC (1989)</td>
</tr>
<tr>
<td>C$_2$H$_5$O$_2$</td>
<td>2.66±0.17</td>
<td></td>
<td>Room Temperature</td>
<td>Adachi and Basco (1979a)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.9±3.0</td>
<td>298</td>
<td>Plumb et al. (1982)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.5±0.4</td>
<td>Room Temperature</td>
<td>Adachi and Basco (1982)</td>
</tr>
<tr>
<td>(CH$_3$)$_2$CHO$_2^-$</td>
<td>1.6x10$^{-11}$ (T/300)$^{-1.2}$</td>
<td>16</td>
<td>298</td>
<td>IUPAC (1989)</td>
</tr>
<tr>
<td>(CH$_3$)$_2$CO$_2^-$</td>
<td>1.6x10$^{-11}$ (T/300)$^{-1.3}$</td>
<td>15</td>
<td>298</td>
<td>IUPAC (1989)</td>
</tr>
<tr>
<td>CF$_3$O$_2$</td>
<td>1.5x10$^{-11}$ (T/300)$^{-1.3}$</td>
<td>18</td>
<td>298</td>
<td>IUPAC (1989)</td>
</tr>
</tbody>
</table>
DEGRADATION MECHANISMS

becomes important (see, for example, Atkinson et al., 1987; Harris and Kerr, 1989; Carter and Atkinson, 1989), with the alkyl nitrate yield increasing with the number of carbon atoms at room temperature and atmospheric pressure for the reactions of secondary alkyl peroxy radicals with NO (Atkinson et al., 1982, 1987; Carter and Atkinson, 1989). For a given alkyl peroxy radical the formation of the alkyl nitrate is pressure and temperature dependent, with the formation yield increasing with increasing pressure and decreasing temperature (Atkinson et al., 1987; Harris and Kerr, 1989; Carter and Atkinson, 1989). The calculated yield of ethyl nitrate from the C2H4O2 + NO reaction is ~0.02 at 300 K and 760 Torr total pressure and ~0.006 at 220 K and 100 Torr total pressure. The data of Lesclaux and Caralp (1984) and Dognon et al. (1985) for the reactions of the CF3O2, CF2ClO2, CFC12O2 and CCl3O2 radicals suggest that the major reaction pathway is

$$\text{CX}_3\text{O}^\cdot + \text{NO} \rightarrow \text{CX}_3\text{O}^+ + \text{NO}_2 \quad (X = \text{F and/or Cl})$$

However, no direct measurements are available concerning whether or not the haloalkyl nitrates are formed in similar yield from the reactions of the haloalkyl peroxy radicals with NO as they are from the alkyl peroxy radical reactions.

B. Reaction with NO2. The rate constant data obtained by absolute methods for the reactions of alkyl peroxy and haloalkyl peroxy radicals with NO2 are given in Table 4. The studies of Sander and Watson (1980) and Ravishankara et al. (1980) for CH3O2 and of Lesclaux and Caralp (1984), Lesclaux et al. (1986) and Caralp et al. (1988) for the CX3O2 radicals (X = F and/or Cl) show that at room temperature

Table 4. Low- and high-pressure rate constants $k_0$ and $k_\infty$ and the broadening coefficient $F$ (at 298 K), together with bimolecular rate constants $k$ at 300 K, 760 Torr total pressure and 220 K, 100 Torr total pressure, for the gas-phase reactions of alkyl and haloalkyl peroxy (RO2⋅) radicals with NO2

<table>
<thead>
<tr>
<th>R2O</th>
<th>$k_0$ (cm³ molecule⁻¹ s⁻¹)</th>
<th>$k_\infty$ (cm³ molecule⁻¹ s⁻¹)</th>
<th>F (298 K)</th>
<th>10¹² × k (cm³ molecule⁻¹ s⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>300 K</td>
<td>760 Torr</td>
<td>220 K</td>
</tr>
<tr>
<td>CH3O2</td>
<td>$2.3\times10^{-28}$ (T/300)=($4.0±2$)</td>
<td>$8\times10^{-12}$</td>
<td>(1.25±0.07)x10⁻¹⁰b (room temperature)</td>
<td>0.4</td>
<td>4.1</td>
</tr>
<tr>
<td>C2H5O2</td>
<td>$(1.25±0.07)x10^{-13}$</td>
<td>(T/300)=($4.0±2$)</td>
<td>(1.25±0.07)x10⁻¹⁰b (room temperature)</td>
<td>0.4</td>
<td>4.1</td>
</tr>
<tr>
<td>(CH3)2CHO2</td>
<td>$5.6\times10^{-12}$</td>
<td>(T/300)=($4.0±2$)</td>
<td>(1.25±0.07)x10⁻¹⁰b (room temperature)</td>
<td>0.4</td>
<td>4.1</td>
</tr>
<tr>
<td>(CH3)2CO2</td>
<td>$5.6\times10^{-12}$</td>
<td>(T/300)=($4.0±2$)</td>
<td>(1.25±0.07)x10⁻¹⁰b (room temperature)</td>
<td>0.4</td>
<td>4.1</td>
</tr>
<tr>
<td>CF3O2</td>
<td>$2.7\times10^{-29}$ (T/300)=($5±2$)</td>
<td>$9\times10^{-12}$ (T/300)=($0.7±1$)</td>
<td>0.49</td>
<td>7.6</td>
<td>9.6</td>
</tr>
<tr>
<td>CF2ClO2</td>
<td>$4.0\times10^{-29}$ (T/300)=($5±2$)</td>
<td>$1.0\times10^{-11}$ (T/300)=($0.7±1$)</td>
<td>0.45</td>
<td>8.4</td>
<td>11</td>
</tr>
<tr>
<td>CFC12O2</td>
<td>$5.5\times10^{-29}$ (T/300)=($5±1$)</td>
<td>$8.3\times10^{-12}$ (T/300)=($0.7±1$)</td>
<td>0.42</td>
<td>7.1</td>
<td>9.0</td>
</tr>
<tr>
<td>CCl3O2</td>
<td>$9.2\times10^{-29}$ (T/300)=($6±2$)</td>
<td>$1.5\times10^{-11}$ (T/300)=($0.3±1$)</td>
<td>0.32</td>
<td>12</td>
<td>14</td>
</tr>
</tbody>
</table>

a Calculated from fall-off expressions.

b Assumed to be erroneously low due to neglect of absorption of RO2NO2 products.
DEGRADATION MECHANISMS

these reactions are in the fall-off regime between second- and third-order kinetics below atmospheric pressure, and this is in agreement with the thermal decomposition data for the peroxynitrates (IUPAC, 1989; see below). The available limiting low- and high-pressure rate constants $k_0$ and $k_{oo}$ and the broadening factor $F$ (at 298 K) are given in Table 4, together with the calculated rate constants at 300 K and 760 Torr total pressure and at 220 K and 100 Torr total pressure. Under tropospheric conditions the bimolecular rate constants for the reactions of the C$_1$ alkyl peroxy and haloalkyl peroxy radicals with NO$_2$ are within a factor of ~2 of the high pressure rate constant $k_{oo}$, and the rate constants for the C$_2$ haloalkyl peroxy radicals will be still closer to the high-pressure limit. From the data given in Table 4, the rate constants $k_{oo}$ for the reactions of RO$_2$ radicals with NO$_2$ are,

$$k_{oo}(RO_2 + NO_2) \approx 1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

approximately independent of temperature over the range 200-300 K.

These reactions of the alkyl peroxy and haloperoxy radicals with NO$_2$ proceed solely by addition to form the alkyl and haloalkyl peroxynitrates (Niki et al., 1978, 1979; Edney et al., 1979; Morel et al., 1980; Reimer and Zabel, 1986).

\[ \text{M} \]

\[ RO_2 + NO_2 \rightarrow ROONO_2 \]

C. Reaction with HO$_2$ Radicals. Absolute rate constants for the reactions of alkyl peroxy and haloalkyl peroxy radicals with the HO$_2$ radical are available only for CH$_3$O$_2$ and C$_2$H$_5$O$_2$, and these data are given in Table 5. The IUPAC (1989) recommended rate constant expressions for these reactions are $k(\text{CH}_3\text{O}_2 + \text{HO}_2) = 1.7 \times 10^{-13} e^{1000/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (4.9 x 10$^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K) and $k(\text{C}_2\text{H}_5\text{O}_2 + \text{HO}_2) = 6.5 \times 10^{-13} e^{650/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (5.8 x 10$^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K). The measured rate constants for these reactions are independent of pressure (IUPAC, 1989). Assuming that the rate constants for all RO$_2$ + HO$_2$ reactions are similar to those for these two reactions, a room temperature rate constant of

$$k(\text{RO}_2 + \text{HO}_2) \approx 5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K}$$

and

$$k(\text{RO}_2 + \text{HO}_2) \approx 3.4 \times 10^{-13} e^{800/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

has been recommended by Atkinson (1989a) for all alkyl peroxy radicals. Clearly, a much wider data base is necessary to test this assumption since, for example, Niki et al. (1980) have obtained evidence from a product study of the Cl atom reactions with CH$_3$Cl and CH$_2$Cl$_2$ that the room temperature rate constant for the reaction of the HO$_2$ radical with CH$_2$Cl$_2$ is significantly slower than the corresponding HO$_2$ radical reaction rate constant for the CHCl$_3$O$_2$ radical.

These reactions have been assumed to proceed by the pathway.

$$\text{RO}_2 + \text{HO}_2 \rightarrow \text{ROOH} + \text{O}_2$$
### DEGRADATION MECHANISMS

#### Table 5. Absolute rate constants for the reactions of alkyl peroxy (RO$_2^\cdot$) radicals with the HO$_2$ radical

<table>
<thead>
<tr>
<th>RO$_2^\cdot$</th>
<th>10$^{12}$ x k (cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
<th>at T (K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$O$_2^\cdot$</td>
<td>8.5 ± 1.2</td>
<td>274</td>
<td>Cox and Tyndall (1980)</td>
</tr>
<tr>
<td></td>
<td>6.5 ± 1.0</td>
<td>298</td>
<td>McAdam et al. (1987)</td>
</tr>
<tr>
<td></td>
<td>3.5 ± 0.5</td>
<td>338</td>
<td>Kurylo et al. (1987)</td>
</tr>
<tr>
<td></td>
<td>3.5$^a$</td>
<td>298</td>
<td>Dagaut et al. (1988a)</td>
</tr>
<tr>
<td></td>
<td>2.9 ± 0.4</td>
<td>298</td>
<td>Dagaut et al. (1988b)</td>
</tr>
<tr>
<td></td>
<td>6.8 ± 0.5</td>
<td>228</td>
<td>Cattell et al. (1986)</td>
</tr>
<tr>
<td></td>
<td>5.5 ± 0.3</td>
<td>248</td>
<td>Dagaut et al. (1988a)</td>
</tr>
<tr>
<td></td>
<td>4.1 ± 0.3</td>
<td>273</td>
<td>Dagaut et al. (1988b)</td>
</tr>
<tr>
<td></td>
<td>2.4 ± 0.5</td>
<td>340</td>
<td>Jenkin et al. (1988)</td>
</tr>
<tr>
<td></td>
<td>2.1 ± 0.3</td>
<td>380</td>
<td>Jenkin et al. (1988)</td>
</tr>
<tr>
<td></td>
<td>5.4 ± 1.1</td>
<td>300</td>
<td>Jenkin et al. (1988)</td>
</tr>
<tr>
<td></td>
<td>6.8 ± 0.9</td>
<td>303</td>
<td>Jenkin et al. (1988)</td>
</tr>
<tr>
<td>C$_2$H$_5$O$_2^\cdot$</td>
<td>6.3 ± 0.9</td>
<td>295</td>
<td>Cattell et al. (1986)</td>
</tr>
<tr>
<td></td>
<td>7.3 ± 1.0</td>
<td>248</td>
<td>Dagaut et al. (1988b)</td>
</tr>
<tr>
<td></td>
<td>6.0 ± 0.5</td>
<td>273</td>
<td>Dagaut et al. (1988b)</td>
</tr>
<tr>
<td></td>
<td>5.3 ± 1.0</td>
<td>298</td>
<td>Dagaut et al. (1988b)</td>
</tr>
<tr>
<td></td>
<td>3.4 ± 1.0</td>
<td>340</td>
<td>Dagaut et al. (1988b)</td>
</tr>
<tr>
<td></td>
<td>3.1 ± 0.5</td>
<td>380</td>
<td>Dagaut et al. (1988b)</td>
</tr>
</tbody>
</table>

$^a$ Revised value as cited by Kurylo et al. (1987), Dagaut et al. (1988a) and Jenkin et al. (1988).

However, Jenkin et al. (1988) observed the formation of HDO from the reaction of CD$_2$O$_2^\cdot$ with the HO$_2$ radical, and postulated the additional reaction pathway,

$$\text{CD}_2\text{O}_2^\cdot + \text{HO}_2 \rightarrow \text{DCDO} + \text{HDO} + \text{O}_2$$

with this channel contributing $\sim$40% of the overall reaction at room temperature.

#### D. Reaction with Alkyl and Haloalkyl Peroxy (RO$_2^\cdot$) and Acyl Peroxy (RCO$_\cdot$) Radicals.

The available absolute rate constant data for the self-reactions of alkyl and haloalkyl peroxy (RO$_2^\cdot$) radicals and for their reactions with other alkyl peroxy and acyl peroxy radicals are given in Table 6. Clearly, the majority of the data concern the self-reactions of the alkyl peroxy radicals, with the only data for cross-combination reactions being for the reactions of the CH$_3$O$_2^\cdot$ radical with tert-butyl peroxy and acetyl peroxy radicals. Since the tropospheric formation rates of the haloalkyl peroxy radicals being dealt with in this assessment will be low (because of the low rate constants for the reactions of the OH radical with the HCFCs and
HFCs in question), self-reactions of these haloalkyl peroxy radicals will be of minimal importance. It is expected that the dominant RO₂ or RCO₃ radical with which these haloalkyl peroxy radicals will react with will be the CH₃O₂ radical, and the limited data available (Table 6) suggest a rate constant for the reaction of the CH₃O₂ radical with other RO₂ radicals of

\[ k(\text{RO}_2 + \text{CH}_3\text{O}_2) \approx 2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K} \]

with an uncertainty of \( \sim \pm \) a factor of 5.

Table 6. Rate constants, \( k = \text{Ae}^{B/T} \), for the gas-phase combination reactions of alkyl and haloalkyl peroxy (RO₂) radicals with RO₂ and RCO₃ radicals

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( 10^{13} \times A ) (cm³ molecule⁻¹ s⁻¹)</th>
<th>B (K)</th>
<th>( 10^{11} \times k ) (298 K) (cm³ molecule⁻¹ s⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃O₂ + CH₃O₂</td>
<td>1.7</td>
<td>-220 ± 220</td>
<td>3.6</td>
<td>IUPAC (1989)</td>
</tr>
<tr>
<td>C₂H₅O₂ + C₂H₅O₂</td>
<td>1.2</td>
<td>110 ± 100</td>
<td>0.86</td>
<td>IUPAC (1989)</td>
</tr>
<tr>
<td>CH₃CH₂CH₂O₂ + CH₃CH₂CH₂O₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(CH₃)₂CHO₂ + (CH₃)₂CHO₂</td>
<td>16</td>
<td>2200 ± 300</td>
<td>0.01</td>
<td>IUPAC (1989)</td>
</tr>
<tr>
<td>(CH₃)₃CO₂ + (CH₃)₃CO₂</td>
<td>1700</td>
<td>4775</td>
<td>0.00019</td>
<td>Kirsch et al. (1978)</td>
</tr>
<tr>
<td>CH₃O₂ + (CH₃)₂CO₂</td>
<td></td>
<td></td>
<td>1.0 ± 0.5</td>
<td>Parkes (1975)</td>
</tr>
<tr>
<td>CH₂ClCH₂O₂ + CH₂ClCH₂O₂</td>
<td>1.1</td>
<td>-1020 ± 170</td>
<td>35.7 ± 5.7</td>
<td>Dagaut et al. (1988c)</td>
</tr>
<tr>
<td>CH₂ClO₂ + CH₂ClO₂</td>
<td>3.1</td>
<td>-735 ± 95</td>
<td>37.8 ± 4.5</td>
<td>Dagaut et al. (1988d)</td>
</tr>
<tr>
<td>CH₃FO₂ + CH₃FO₂</td>
<td>3.3</td>
<td>-700 ± 100</td>
<td>30.7 ± 6.5</td>
<td>Dagaut et al. (1988d)</td>
</tr>
<tr>
<td>CH₃O₂ + CH₃CO₂</td>
<td></td>
<td></td>
<td>110</td>
<td>IUPAC (1989)</td>
</tr>
</tbody>
</table>

These combination reactions of RO₂ radicals can proceed by the reaction channels

\[ R_3R_4CHO₂ + R_3R_4CHO₂ \rightarrow R_1R_2CHO₂ + R_3R_4CHO₂ + O₂ \]  
(a)

\[ R_3R_2CHO₂ + R_3R_4CHO₂ \rightarrow R_1R_2CHOH + R_3R_4CO + O₂ \]  
(b)

\[ R_3R_2CHO₂ + R_3R_4CHO₂ \rightarrow R_1R_2CHOCHR_3R_4 + O₂ \]  
(c)

with channel (b) not being accessible for tertiary RO₂ radicals. Product data are available for the self-reactions of CH₃O₂, C₂H₅O₂, (CH₃)₂CHO₂ and (CH₃)₃CO₂ radicals (Kirsch and Parkes, 1981; Niki et al., 1981, 1982; Anastasi et al., 1983; IUPAC, 1989). For the primary and secondary RO₂ radicals, the room temperature rate constant ratios \( k_a/k \) and \( k_b/k \) (where \( k = k_a + k_b + k_c \)) are both \( \sim 0.5 \), with \( k_c < 0.1 \). For the reaction of the (CH₃)₃CO₂ radical with the CH₃O₂ radical, Parkes (1975) and Kirsch and Parkes (1981) also proposed that the operative reaction pathways were (a) and (b) above, with \( k_a = k_b \) at around room temperature. However, Niki et al. (1980) concluded that reaction pathway (b) was of minor significance for the self-reaction of the CHCl₂O₂ radical, and further product data are required for these RO₂ radical reactions.
DEGRADATION MECHANISMS

For the self-reaction of the tert-butyl peroxy radical, Kirsch and Parkes (1981) determined that \( k_c/k = 0.12 \) at 298 K, with this ratio decreasing rapidly with increasing temperature.

4.3. Reactions of Alkoxy and Haloalkoxy (RO·) Radicals

For the C₁ and C₂ haloalkoxy radicals involved in the tropospheric degradation reactions of the HCFCs and HFCs considered in this article, the reactions of concern are with O₂,

\[
R_1R_2CHO^· + O_2 \rightarrow R_1R_2CO + HO_2
\]

unimolecular decomposition,

\[
R_1R_2CHO \rightarrow R_1^· + R_2CHO
\]

and reaction with NO and NO₂.

\[
R_1R_2CHONO \\
\rightarrow R_1R_2CO + HNO
\]

\[
R_1R_2CHONO_2 \\
\rightarrow R_1R_2CO + HONO
\]

A. Reaction with O₂. Absolute rate constants for the reactions of alkoxy radicals with O₂ are available only for the CH₃O·, C₂H₅O· and (CH₃)₂CHO· radicals, and the rate constant data obtained are given in Table 7. For the methoxy radical the rate constants of Gutman et al. (1982), Lorenz et al. (1985) and Wantuck et al. (1987) are in good agreement, and Atkinson (1989a) recommended that for temperatures \( \leq 300 \) K (the Arrhenius plot exhibits marked curvature at temperatures \( > 500 \) K).

\[
k(CH₃O· + O₂) = 5.5 \times 10^{-14} \ e^{-1000/T} \ \text{cm}^3 \ \text{molecule}^{-1} \ \text{s}^{-1}
\]

This recommended temperature expression is that of Lorenz et al. (1985), and is similar to the NASA (1987) and IUPAC (1989) recommendations of k(CH₃O· + O₂) = \( 3.9 \times 10^{-14} \ e^{-900/T} \ \text{cm}^3 \ \text{molecule}^{-1} \ \text{s}^{-1} \) and \( 7.2 \times 10^{-14} \ e^{-1080/T} \ \text{cm}^3 \ \text{molecule}^{-1} \ \text{s}^{-1} \), respectively. Combining the rate constants of Gutman et al. (1982) at 296 and 353 K for the C₂H₅O· radical with a preexponential factor of \( 3.7 \times 10^{-14} \ \text{cm}^3 \ \text{molecule}^{-1} \ \text{s}^{-1} \) leads to

\[
k(RCH₂O· + O₂) = 3.7 \times 10^{-14} \ e^{-460/T} \ \text{cm}^3 \ \text{molecule}^{-1} \ \text{s}^{-1}
\]

(Atkinson, 1989a). Similarly, the data of Balla et al. (1985) for the (CH₃)₂CHO· radical can be combined with a preexponential factor of \( 1.8 \times 10^{-14} \ \text{cm}^3 \ \text{molecule}^{-1} \ \text{s}^{-1} \) to yield (Atkinson, 1989a)
Table 7. Absolute rate constants, k, for the gas-phase reactions of alkoxy (RO') radicals with O₂

<table>
<thead>
<tr>
<th>RO'</th>
<th>10¹⁵ x k (cm³ molecule⁻¹ s⁻¹)</th>
<th>T (K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃O'</td>
<td>&lt;2</td>
<td>295</td>
<td>Sanders et al. (1980)</td>
</tr>
<tr>
<td></td>
<td>4.7</td>
<td>413</td>
<td>Gutman et al. (1982)</td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>475</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.7</td>
<td>563</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12.7</td>
<td>608</td>
<td></td>
</tr>
<tr>
<td></td>
<td>55 e⁻¹⁰⁰⁰/T</td>
<td>298-450</td>
<td>Lorenz et al. (1985)</td>
</tr>
<tr>
<td></td>
<td>1.9ᵃ</td>
<td>298</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[1.5 x 10⁴ e⁻⁶⁰²⁸/T + 36 e⁻⁸⁸⁰/T]ᵇ</td>
<td>298-973</td>
<td>Wantuck et al. (1987)</td>
</tr>
<tr>
<td></td>
<td>2.1</td>
<td>298</td>
<td></td>
</tr>
<tr>
<td>C₂H₅O'</td>
<td>8.0</td>
<td>296</td>
<td>Gutman et al. (1982)</td>
</tr>
<tr>
<td></td>
<td>9.8</td>
<td>353</td>
<td></td>
</tr>
<tr>
<td>(CH₃)₂CHO'</td>
<td>15.1 e⁻¹⁹⁶/T</td>
<td>294-384</td>
<td>Balla et al. (1985)</td>
</tr>
<tr>
<td></td>
<td>7.8ᵃ</td>
<td>298</td>
<td></td>
</tr>
</tbody>
</table>

ᵃ Calculated from cited Arrhenius expressions.
b Stated fit to data of Gutman et al. (1982), Lorenz et al. (1985) and Wantuck et al. (1987).

k(R₁R₂CHO' + O₂) = 1.8 x 10⁻¹⁴ e⁻²⁸⁰/T cm³ molecule⁻¹ s⁻¹

These rate constant expressions for the RCH₂O' and R₁R₂CHO' alkoxy radicals are assumed to be applicable to haloalkoxy radicals. The reaction rate of primary and secondary RO' radicals with O₂ at 298 K and 760 Torr total pressure of air are then essentially identical at 4.0 x 10⁴ s⁻¹.

B. Alkoxy Radical Decomposition. Rate data for the decompositions of the methoxy, ethoxy and the C₁ haloalkoxy radicals are summarized in Table 8, together with the experimentally measured lower limits to the rate constants for several haloalkoxy radicals. The rate expressions for the chloroalkoxy radicals and the CHF₂O' radical are those calculated by Rayez et al. (1987). The experimentally determined lower limits to the decomposition rate constants for the CF₂ClO', CFCl₂O' and CHCl₃O' radicals are in good agreement with the calculated rates. The data in Table 8 show that:

(a) H atom elimination from the C₁ alkoxy radicals is extremely slow (< 10⁻⁵ s⁻¹ at 298 K). When compared to the reaction rate of these species with O₂ of 4 x 10⁴ s⁻¹ at 298 K and atmospheric pressure, the H atom elimination reactions can be totally neglected. Based upon the rate data for the ethoxy radical, decomposition by H atom elimination can also be totally neglected for the C₂ alkoxy radicals.

(b) For the CF₂ClO', CFCl₂O' and CCl₃O' radicals, decomposition by Cl atom elimination is rapid, and this process will be the dominant loss process for these haloalkoxy radicals in the troposphere. This conclusion is in agreement with the reaction schemes proposed for these radicals by Jayanty et al. (1975),
### Table 8. Unimolecular decomposition rate constants, $k = A e^{-B/T}$, for $C_1$ and $C_2$ alkoxy and haloalkoxy (RO') radicals

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$A \ (s^{-1})$</th>
<th>$B \ (K)$</th>
<th>$k \ (s^{-1})$ at $T \ (K)$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_3\text{O} \rightarrow \text{HCHO} + \text{H}$</td>
<td>$2.4 \times 10^{13}$</td>
<td>14450</td>
<td>$2 \times 10^{41}$</td>
<td>298</td>
</tr>
<tr>
<td>$\text{CH}_2\text{CH}_2\text{O} \rightarrow \text{HCHO} + \text{CH}_3$</td>
<td>$8 \times 10^{13}$</td>
<td>10800</td>
<td>$0.015$</td>
<td>298</td>
</tr>
<tr>
<td>$\text{CF}_2\text{O} \rightarrow \text{COF}_2 + \text{F}$</td>
<td>$5 \times 10^{13}$</td>
<td>14300</td>
<td>$7 \times 10^{4}$</td>
<td>298</td>
</tr>
<tr>
<td>$\text{CF}_2\text{ClO} \rightarrow \text{COF}_2 + \text{Cl}$</td>
<td>$\sim 1 \times 10^{14}$</td>
<td>6240$^c$</td>
<td>$8 \times 10^{4}$</td>
<td>298</td>
</tr>
<tr>
<td>$\text{CFC}_3\text{O} \rightarrow \text{COFCI} + \text{Cl}$</td>
<td>$\sim 1 \times 10^{14}$</td>
<td>5335$^c$</td>
<td>$7 \times 10^{4}$</td>
<td>Room temperature</td>
</tr>
<tr>
<td>$\text{CCl}_3\text{O} \rightarrow \text{COCl}_2 + \text{Cl}$</td>
<td>$\sim 1 \times 10^{14}$</td>
<td>4880$^c$</td>
<td>$8 \times 10^{4}$</td>
<td>233</td>
</tr>
<tr>
<td>$\text{CHCl}_2\text{O} \rightarrow \text{HC(O)Cl} + \text{Cl}$</td>
<td>$\sim 1 \times 10^{14}$</td>
<td>5940$^c$</td>
<td>$2 \times 10^{4}$</td>
<td>298</td>
</tr>
<tr>
<td>$\text{CH}_2\text{Cl}_2\text{O} \rightarrow \text{HC(O)Cl} + \text{Cl}$</td>
<td>$\sim 1 \times 10^{14}$</td>
<td>10320$^c$</td>
<td>$0.1$</td>
<td>298</td>
</tr>
<tr>
<td>$\text{CHFClO} \rightarrow \text{HC(O)F} + \text{Cl}$</td>
<td>$\sim 1 \times 10^{14}$</td>
<td>5230$^c$</td>
<td>$2 \times 10^{4}$</td>
<td>298</td>
</tr>
<tr>
<td>$\text{CHF}_2\text{O} \rightarrow \text{COF}_2 + \text{H}$</td>
<td>$\sim 1 \times 10^{14}$</td>
<td>17770$^c$</td>
<td>$1 \times 10^{12}$</td>
<td>298</td>
</tr>
<tr>
<td>$\text{CHFClO} \rightarrow \text{COFCI} + \text{H}$</td>
<td>$\sim 1 \times 10^{14}$</td>
<td>14800$^c$</td>
<td>$3 \times 10^{4}$</td>
<td>298</td>
</tr>
<tr>
<td>$\text{CH}_2\text{ClO} \rightarrow \text{COCl}_2 + \text{H}$</td>
<td>$\sim 1 \times 10^{14}$</td>
<td>14900$^c$</td>
<td>$2 \times 10^{4}$</td>
<td>298</td>
</tr>
<tr>
<td>$\text{CHCl}_2\text{O} \rightarrow \text{HC(O)Cl} + \text{H}$</td>
<td>$\sim 1 \times 10^{14}$</td>
<td>13340$^c$</td>
<td>$4 \times 10^{4}$</td>
<td>298</td>
</tr>
<tr>
<td>$\text{CH}_2\text{FO} \rightarrow \text{HC(O)F} + \text{H}$</td>
<td>$\sim 1 \times 10^{14}$</td>
<td>14540$^c$</td>
<td>$6 \times 10^{4}$</td>
<td>298</td>
</tr>
</tbody>
</table>

- **a** High-pressure limits.
- **b** Calculated from cited Arrhenius expression.
- **c** Calculated.

Gillespie et al. (1977), Suong and Carr (1982) and Withnall and Sodeau (1986).

(c) For the CHCl$_2$O$^-$ radical, decomposition by Cl atom elimination dominates over reaction with O$_2$ at room temperature and atmospheric pressure. However, this may not be the case at the lower temperatures and O$_2$ concentrations encountered in the middle and upper troposphere. In contrast, decomposition of the CH$_2$ClO$^-$ radical is slow and the reaction with O$_2$

\[
\text{CH}_2\text{ClO}^- + \text{O}_2 \rightarrow \text{HC(O)Cl} + \text{HO}_2
\]
DEGRADATION MECHANISMS

dominate at room temperature and atmospheric pressure of air (Sanhueza et al., 1976; Niki et al., 1980), and is expected to totally dominate for all tropospheric conditions.

For the C₂ haloalkoxy radicals, Sanhueza et al. (1976) concluded that:

(a) For CX₃CH₂O⁻ radicals (X = F, Cl and/or H), the decomposition pathways are sufficiently endothermic that decomposition does not occur, and hence it is expected that reaction with O₂ will dominate.

(b) For CX₃CF₂O⁻ radicals (X = F, Cl and/or (presumably) H), the C-F bond dissociation energy is sufficiently higher than the C-C bond dissociation energy that C-C bond cleavage occurs.

Thus, for example, as discussed by Sanhueza and Heicklen (1975) and Sanhueza et al. (1976), the dominant reactions for the following haloalkoxy radicals are

- \[ \text{CFCl}_2\text{CFClO}^- \rightarrow \text{CFCl}_2\text{C(O)F} + \text{Cl} \]
- \[ \text{CF}_2\text{ClCICl}_2\text{O}^- \rightarrow \text{CF}_2\text{ClCIC(O)Cl} + \text{Cl} \]
- \[ \text{CCl}_3\text{CF}_2\text{O}^- \rightarrow \text{COF}_2 + \cdot\text{Cl}_3 \]
- \[ \text{CF}_2\text{ClCF}_2\text{O}^- \rightarrow \text{COF}_2 + \cdot\text{CF}_2\text{Cl} \]

For tropospheric conditions, the important parameters are the rate constant ratios for the reactions of the alkoxy and haloalkoxy radicals with O₂ and their various decomposition pathways. It is anticipated that the rate constants for these processes will depend on their heats of reaction [since (Table 8) the preexponential factors for the various decomposition pathways appear to be reasonably similar at ~1 x 10¹⁴ s⁻¹]. Since in most cases the heats of formation of the reactant alkoxy and haloalkoxy radicals are not known with any certainty, it is possible that the differences between the summed heats of formation of the reaction products for the reactions of the various alkoxy and haloalkoxy radicals can be used as a tool in deciding the relative importance of these reaction pathways. Table 9 gives examples of the summed heats of formation of the products for the various reactions of the ethoxy, 2-butoxy, CH₂CIO⁻ and CH₂CICCl⁻ radicals. These data in Table 9 show that the H atom elimination pathway is the most endothermic decomposition route (being relatively close to the Cl atom elimination pathway for the CH₂ClO⁻ radical, consistent with Table 8).

The differences in the heats of reaction, \[ [(\Delta H)_{\text{reaction}} - (\Delta H)_{\text{decomposition}}] = (\Delta (\Delta H)), \] in kcal mol⁻¹ (rounded to the nearest kcal mol⁻¹) are then: C₂H₅O⁻, 45; 2-butoxy, 42; CH₂ClO⁻, 48; and CHCl₂O⁻, 30. At room temperature and atmospheric pressure of air, the removal processes of these RO⁻ radicals are: C₂H₅O⁻, reaction with O₂ (Carter and Atkinson, 1985); 2-butoxy, reaction with O₂ and decomposition by C-C bond cleavage in an approximately 60%/40% split (Carter and Atkinson, 1985; Atkinson, 1989a); CH₂ClO⁻, reaction with O₂ (Niki et al., 1980); and CHCl₂O⁻, Cl atom elimination (Niki et al., 1980). Thus, as expected, there is a relation between the reaction pathway and the difference in the heats of reaction between the pathways. For \( (\Delta (\Delta H)) > 43 \) kcal mol⁻¹, reaction with O₂ dominates, while for \( (\Delta (\Delta H)) < 40 \) kcal mol⁻¹, decomposition by either Cl atom elimination or C-C bond cleavage will dominate. It should be noted that at 298 K, 1 kcal mol⁻¹ is equivalent to a factor of ~5 in the (reaction with O₂)/decomposition
DEGRADATION MECHANISMS

rate constant ratio. This approach of estimating the difference in heats of reaction for the various reaction pathways is used in Section 2 dealing with the specific haloalkoxy radicals to assess the importance of these reaction pathways.

Table 9. Reactions of representative alkoxy and haloalkoxy (RO') radicals: thermochemistries of reactions with O₂, decomposition and H and Cl atom elimination

<table>
<thead>
<tr>
<th>RO'</th>
<th>Reaction</th>
<th>( \Sigma \Delta H_f ) (Products) kcal mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃CH₂O'</td>
<td>CH₃CH₂O' + O₂ \rightarrow CH₃CHO + HO₂</td>
<td>-36.1</td>
</tr>
<tr>
<td></td>
<td>CH₃CH₂O' \rightarrow CH₃CHO + H</td>
<td>12.5</td>
</tr>
<tr>
<td></td>
<td>CH₃CH₂O' \rightarrow CH₃ + HCHO</td>
<td>8.8</td>
</tr>
<tr>
<td>CH₃CH₂CH(Ö)CH₃</td>
<td>CH₃CH₂CH(Ö)CH₃ + O₂ \rightarrow CH₃CH₂COCH₃ + HO₂</td>
<td>-53.4</td>
</tr>
<tr>
<td></td>
<td>CH₃CH₂CH(Ö)CH₃ \rightarrow C₂H₆ + CH₃CHO</td>
<td>-11.6</td>
</tr>
<tr>
<td>CH₂ClO'</td>
<td>CH₂ClO' + O₂ \rightarrow HC(O)Cl + HO₂</td>
<td>-44.7</td>
</tr>
<tr>
<td></td>
<td>CH₂ClO' \rightarrow HC(O)Cl + H</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td>CH₂ClO' \rightarrow HCHO + Cl</td>
<td>3.0</td>
</tr>
<tr>
<td>CHCl₂O'</td>
<td>CHCl₂O' + O₂ \rightarrow COCl₂ + HO₂</td>
<td>-49.1</td>
</tr>
<tr>
<td></td>
<td>CHCl₂O' \rightarrow COCl₂ + H</td>
<td>-0.5</td>
</tr>
<tr>
<td></td>
<td>CHCl₂O' \rightarrow HC(O)Cl + Cl</td>
<td>-19.2</td>
</tr>
</tbody>
</table>

a Heats of formation from IUPAC (1989), except for \( \Delta H_f(HC(O)Cl) = -48.2 \) kcal mol\(^{-1}\) from Dewar and Rzepa (1983) and \( \Delta H_f(CH₃CH₂COCH₃) = 56.9 \) kcal mol\(^{-1}\) calculated by the group additivity method of Benson (1976).

For the CF₃O' radical, reaction with O₂ cannot occur and F atom elimination is endothermic by 24 kcal mol\(^{-1}\) (Batt and Walsh, 1983; IUPAC, 1989).

C. Reactions with NO and NO₂. Absolute rate constant data are available only for the reactions of NO and NO₂ with the CH₃O' and (CH₃)₂CHO' radicals (Sanders et al., 1980; Balla et al., 1985; McCaulley et al., 1985; Zellner, 1987). For the reaction of the CH₃O' radical with NO, the data of Zellner (1987) yield a high pressure rate constant of \( k_{oo} = 1.4 \times 10^{-11} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) at 298 K [IUPAC (1989) recommend 2 \( \times 10^{-11} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), independent of temperature over the range 200-400 K, with an uncertainty of \( \pm \) a factor of 2], with a rate constant for the H atom abstraction route of \( \leq 6 \times 10^{-13} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) at 298 K.

Similar data arise from the study of McCaulley et al. (1985) for the reaction of the CH₃O' radical with NO₂, carried out at 0.6-4 Torr total pressure. The rate constants were in the fall-off regime,

202
and the abstraction channel was concluded to have a rate constant of $9.6 \times 10^{-12} \ e^{-11.50/T} \ cm^3 \ molecule^{-1} \ s^{-1}$ over the temperature range 220-473 K (2.0 x 10^{-13} \ cm^3 \ molecule^{-1} \ s^{-1} \ at \ 298 \ K)$. 

The rate data of Balla et al. (1985) for the reactions of the (CH₃)₂CHO radical with NO and NO₂ were at the high-pressure limit, with room temperature rate constants of (3-4) x 10^{-11} \ cm^3 \ molecule^{-1} \ s^{-1} and small negative temperature dependencies [k = 1.22 x 10^{-11} \ e^{112/T} \ cm^3 \ molecule^{-1} \ s^{-1} for the reaction with NO and 1.5 x 10^{-11} \ e^{252/T} \ cm^3 \ molecule^{-1} \ s^{-1} for reaction with NO₂].

These absolute rate constant data are in reasonable agreement with the large body of relative rate data (see Atkinson and Lloyd, 1984). Atkinson (1989a) has recently recommended for the reactions of the alkoxy radicals with NO and NO₂ that,

$$k(RO' + NO) = k(RO' + NO₂) = 1.3 \times 10^{-11} \ e^{100/T} \ cm^3 \ molecule^{-1} \ s^{-1}$$

with these reactions proceeding essentially entirely by addition,

$$M$$

$$RO' + NO \rightarrow RONO$$

$$M$$

$$RO' + NO₂ \rightarrow RONO₂$$

and the H atom abstraction routes being of minor or negligible importance for temperatures ≤ 298 K. In the absence of experimental data, these rate expressions are assumed to be applicable for the corresponding reactions of the haloalkoxy radicals.

The formation of alkyl nitrites, RONO, is balanced by the rapid photolysis of these compounds (see, for example, Taylor et al., 1980).

$$RONO + hν \rightarrow RO' + NO$$

Hence, the RO' radical reaction with NO is of no actual importance for tropospheric purposes.

4.4. Reactions of the Alkyl and Haloalkyl Peroxynitrates (ROONO₂)

Under tropospheric conditions, the loss processes of the alkyl and haloalkyl peroxynitrates (ROONO₂) which need to be considered are thermal decomposition and photolysis.

A. Thermal Decomposition. Thermal decomposition is expected to be the dominant tropospheric loss process of the alkyl and haloalkyl peroxynitrates (ROONO₂),

$$M$$

$$ROONO₂ \rightarrow RO' + NO₂$$

with the RO₂ radical and NO₂ being in thermal equilibrium with the peroxynitrate. For the C₁ peroxynitrates, these thermal decomposition reactions are in the fall-off regime between first- and second-order
DEGRADATION MECHANISMS

kinetics under the temperature and pressure conditions applicable to the troposphere. The low- and high-pressure rate constants $k_0$ and $k_{oo}$, respectively, and the broadening factor $F$ (at 298 K) are given in Table 10, together with the calculated unimolecular thermal decomposition rates, $k$, at 298 K and 760 Torr total pressure and 220 K and 100 Torr total pressure. Data obtained at 700 Torr total pressure for propyl peroxy nitrate [a mixture of CH$_3$CH$_2$CH$_2$OOONO$_2$ and (CH$_3$)$_2$CHOONO$_2$] (Edney et al., 1979) are also included in Table 10, and these rate constants are expected to be close (within a factor of 2) to the high-pressure rate constant $k_{oo}$.

For the C$_1$ haloalkyl peroxy nitrates studied, the decomposition rates under tropospheric conditions are within 10-20% of the high-pressure rate constant $k_{oo}$, with the lifetimes of these haloalkyl peroxy nitrates with respect to thermal decomposition increasing from $\sim$10 s at 298 K to $\sim$10$^7$ s at 220 K (note that the actual lifetimes of these ROONO$_2$ species depend on the NO$_2$/NO concentration ratio, and increase as this [NO$_2$]/[NO] ratio increases, due to the equilibrium between the peroxy nitrate, the RO$_2$ radical and NO$_2$). The corresponding lifetimes of the alkyl peroxy nitrates, with respect to thermal decompos-

Table 10. Low- and high-pressure rate constants $k_0$ and $k_{oo}$ and the broadening factor $F$ at 298 K for the thermal decomposition of alkyl and haloalkyl peroxy nitrates, ROONO$_2$, together with calculated rate constants at 298 K and 760 Torr total pressure and 220 K and 100 Torr total pressure

<table>
<thead>
<tr>
<th>ROONO$_2$</th>
<th>$k_0$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
<th>$k_{oo}$ (s$^{-1}$)</th>
<th>$F$ (298 K)</th>
<th>k (s$^{-1}$) @ 760 Torr</th>
<th>k (s$^{-1}$) @ 220 K</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$OOONO$_2$</td>
<td>9 x 10$^{-3}$ e$^{-9969/T}$</td>
<td>1.1 x 10$^{16}$ e$^{-19569/T}$</td>
<td>0.4</td>
<td>1.8</td>
<td>5.4 x 10$^{6}$</td>
<td>IUPAC (1989)</td>
</tr>
<tr>
<td>C$_3$H$_7$OOONO$_2$</td>
<td>3.3 x 10$^{14}$ e$^{-9965/T}$</td>
<td>1.0 x 10$^{16}$ e$^{-19868/T}$</td>
<td>0.4</td>
<td>0.046</td>
<td>3.4 x 10$^{4}$</td>
<td>Edney et al. (1979)</td>
</tr>
<tr>
<td>CF$_2$CIOONO$_2$</td>
<td>5.6 x 10$^{-4}$ e$^{-9310/T}$</td>
<td>1.0 x 10$^{16}$ e$^{-11888/T}$</td>
<td>0.4</td>
<td>0.065</td>
<td>4.3 x 10$^{4}$</td>
<td>IUPAC (1989)</td>
</tr>
<tr>
<td>CFCl$_2$OOONO$_2$</td>
<td>3 x 10$^{-3}$ e$^{-10570/T}$</td>
<td>2.1 x 10$^{16}$ e$^{-11980/T}$</td>
<td>0.4</td>
<td>0.14</td>
<td>3.6 x 10$^{4}$</td>
<td>IUPAC (1989)</td>
</tr>
<tr>
<td>CCl$_3$OOONO$_2$</td>
<td>5.6 x 10$^{-4}$ e$^{-9310/T}$</td>
<td>9.1 x 10$^{14}$ e$^{-10420/T}$</td>
<td>0.2</td>
<td>0.14</td>
<td>3.6 x 10$^{4}$</td>
<td>IUPAC (1989)</td>
</tr>
</tbody>
</table>

a At 700 Torr total pressure of air; uncertain by at least a factor of 2 because of uncertainties in the rate constant ratio $k(RO_2 + NO)/k(ROI + NO_2)$.

For the C$_1$ haloalkyl peroxy nitrates studied, the decomposition rates under tropospheric conditions are within 10-20% of the high-pressure rate constant $k_{oo}$, with the lifetimes of these haloalkyl peroxy nitrates with respect to thermal decomposition increasing from $\sim$10 s at 298 K to $\sim$10$^7$ s at 220 K (note that the actual lifetimes of these ROONO$_2$ species depend on the NO$_2$/NO concentration ratio, and increase as this [NO$_2$]/[NO] ratio increases, due to the equilibrium between the peroxy nitrate, the RO$_2$ radical and NO$_2$). The corresponding lifetimes of the alkyl peroxy nitrates, with respect to thermal decompos-

B. Photolysis. The absorption cross-sections of CH$_3$OOONO$_2$ have been measured over the wavelength range 200-310 nm by Cox and Tyndall (1979), Morel et al. (1980) and Sander and Watson (1980), and for CFCl$_2$OOONO$_2$ and CCl$_3$OOONO$_2$ over the wavelength range 210-280 nm by Morel et al. (1980). The absorption cross-sections decrease with increasing wavelength above $\sim$240 nm, with cross-sections $\leq$ 1
x $10^{-19}$ cm$^2$ at 280 nm for all three of these peroxynitrates (Morel et al., 1980; Baulch et al., 1982).

Acknowledgments

The author gratefully thanks Ms. Christy J. LaClaire for assistance in the preparation of this manuscript and the reviewers for their helpful comments.