VI. DEGRADATION MECHANISMS

Combined Summary and Conclusions

Fluorine-Containing Products in Atmospheric Degradation Table

Tropospheric Reactions of the Haloalkyl Radicals Formed from Hydroxyl Radical Reaction with a Series of Alternative Fluorocarbons

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Degradation Mechanisms of Selected Hydrochlorofluorocarbons in the Atmosphere: An Assessment of Current Knowledge

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An Assessment of Potential Degradation Products in the Gas-Phase Reactions of Alternative Fluorocarbons in the Troposphere

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Atmospheric Degradation Mechanisms of Hydrogen Containing Chlorofluorocarbons (HCFC) and Fluorocarbons (HFC)

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COMBINED SUMMARY AND CONCLUSIONS

Tropospheric reaction with the OH radical is the major and rate determining loss process for the HFCs and HCFCs in the atmosphere.

There are virtually no experimental data available concerning the subsequent reactions occurring in the atmospheric degradation of these molecules. By consideration of data for degradation of alkanes and chloroalkanes it is possible to postulate the reaction mechanisms and products formed in the troposphere from HCFC and HFCs. However, the results are subject to large qualitative and quantitative uncertainty, and may even be incorrect.

The current level of support for laboratory work is inadequate to enable significant improvement in the state of knowledge in this area in the near future.

Using the above mentioned analysis, a large variety of chlorine and fluorine containing intermediate products such as hydroperoxides, peroxynitrates, carbonyl halides, aldehydes and acids can be expected from the degradation of the 8 proposed CFC substitutes. These are listed in the accompanying Table.

Based on the available knowledge of gas phase chemistry only four of these products appear to be potentially significant carriers of chlorine to the stratosphere. These are $CClFO$, CF_3CClO, $CClF_2CO_3NO_2$ and $CCl_2FCO_3NO_2$. However physical renewal processes may reduce this potential. In addition, the possibility of pathways and products not predicted by the arguments-by-analogy are a cause for concern.

A large part of the uncertainty of the mechanistic details of the HCFC oxidation arises from all insufficient knowledge of the thermal stability and reactivity of halogenated alkoxyradicals. In particular, the mechanism of oxidation of the CF_3O radical, which is assumed to produce CF_2O, is not known for atmospheric conditions and needs further study.

Particular attention should be paid to obtaining data on the photochemistry, gas phase reactivity and solubility of the carbonyl, acetyl and formyl halides, in order to assess their removal rates and mechanisms.

Based on current knowledge, the products identified are unlikely to cause significant changes to the effective greenhouse warming potential of the 8 proposed CFC substitutes. This conclusion would be modified if long-lived products such as CF_3H were formed by unidentified pathways.

Laboratory tests and atmospheric measurements are urgently needed to test the validity of the proposed degradation mechanisms for HCFCs and HCFs.

Fluorine-Containing Products in the Atmospheric Degradation of Selected Fluorocarbons

Compound	Formula	Atom & Radical	Carbonyl	Acid	Hydroxide	Nitrate
HCFC	$HCCl_2CF_3$	CF_3CCl_2OO			CF_3CCl_2OOH	$CF_3CCl_2OONO_2$
123		CF_3CCl_2O	CF_3CClO			
		CF_3OO			CF_3OOH	CF_3OONO_2
		CF_3O			CF_3OH	CF_3ONO_2
HCFC	CCl_2FCH_3	CCl_2FCH_2OO			CCl_2FCH_2OOH	$CCl_2FCH_2OONO_2$
141B		CCl_2FCH_2O	CCl_2FCHO			
		CCl_2FOO			CCl_2FOOH	CCl_2FOONO_2
		CCl_2FO	$CClFO$			
		$CCl_2FC(O)OO$		$CCl_2FC(O)OOH$		$CCl_2FC(O)OONO_2$
				$CCl_2FC(O)OH$		
HCFC	$CClF_2CH_3$	$CClF_2CH_2OO$			$CClF_2CH_2OOH$	$CClF_2CH_2OONO_2$
142b		$CClF_2CH_2O$	$CClF_2CHO$			
		$CClF_2OO$			$CClF_2OOH$	$CClF_2OONO_2$
		$CClF_2O$	CF_2O			
		$CClF_2C(O)OO$		$CClF_2(O)OOH$		$CClF_2C(O)OONO_2$
				$CClF_2C(O)OH$		
HCFC	$CHClF_2$	$CClF_2OO$			$CClF_2OOH$	$CClF_2OONO_2$
22		$CClF_2O$	CF_2O			
HCFC	$CHClFCF_3$	$CF_3CClFOO$			$CF_3CClFOOH$	$CF_3CClFOONO_2$
124		CF_3CClFO	CF_3CFO			
		CF_3OO			CF_3OOH	CF_3OONO_2
		CF_3O			CF_3OH	CF_3ONO_2
HCF	CH_2FCF_3	CF_3CHFOO			$CF_3CHFOOH$	$CF_3CHFOONO_2$
134a		CF_3CHFO	$CHFO$			
			CF_3CHFO			
		CF_3OO			CF_3OOH	CF_3OONO_2
		CF_3O			CF_3OH	CF_3ONO_2
		CFO			$CF(O)OOH$	$CF(O)OONO_2$
HFC	CHF_2CH_3	CH_3CF_2Oo			CH_3CF_2OOH	$CH_3CF_2OONO_2$
52a		CH_3CF_2O	CF_2O			
		CHF_2CH_2OO			CHF_2CH_2OOH	$CHF_2CH_2OONO_2$
		CHF_2CH_2O	CHF_2CHO			
		CHF_2OO			CHF_2OOH	CHF_2OONO_2
		CHF_2O	$CHFO$			
		$CHF_2C(O)OO$		$CHF_2C(O)OOH$		$CHF_2C(O)OONO_2$
				$CHF_2C(O)OH$		
		CFO		$CF(O)OOH$		$CF(O)OONO_2$
HCF	CHF_2CF_3	CF_3CF_2OO			CF_3CF_2OOH	$CF_3CF_2OONO_2$
125		CF_3CF_2O	CF_2O			
			CF_3CFO			
		CF_3OO			CF_3OOH	CF_3OONO_2
		CF_3O			CF_3OH	CF_3ONO_2

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

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1. INTRODUCTION

The majority of the chlorofluorocarbons (CFCs) currently in use, such as CFC-11 ($CFCl_3$), 12 (CF_2Cl_2) and 113 ($CF_2ClCFCl_2$), 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 (CF_3CHCl_2), 141b ($CFCl_2CH_3$), 142b (CF_2ClCH_3), 22 (CHF_2Cl) and 124 (CF_3CHFCl) and the hydrofluorocarbons (HFCs) 134a (CF_3CH_2F), 152a (CHF_2CH_3) and 125 (CF_3CHF_2). All of these HCFCs and HFCs will react with the hydroxyl (OH) radical in the troposphere, giving rise to haloalkyl ($R^\cdot$) 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 ($R^\cdot$) radicals formed from the OH radical reactions with the HCFCs and HFCs listed above are as follows:

HCFC or HFC	Haloalkyl Radical, R
CF_3CHCl_2	$CF_3\dot{C}Cl_2$
$CFCl_2CH_3$	$CFCl_2\dot{C}H_2$
CF_2ClCH_3	$CF_2Cl\dot{C}H_2$
CHF_2Cl	$\dot{C}F_2Cl$
CF_3CHFCl	$CF_3\dot{C}FCl$
CF_3CH_2F	$CF_3\dot{C}HF$
CHF_2CH_3	$CHF_2\dot{C}H_2$ and $CH_3\dot{C}F_2$
CF_3CHF_2	$CF_3\dot{C}F_2$

Of these radicals, only for the $\dot{C}F_2Cl$ radical formed from CHF_2Cl (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 ($RO_2^\cdot$) and alkoxy ($RO^\cdot$) 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 C_1-C_5 alkyl and C_1 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 $R^\cdot$, $RO_2^\cdot$ and $RO^\cdot$ 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 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,

$$k = \left(\frac{k_0[M]}{1 + \frac{k_0[M]}{k_\infty}} \right) F^{\left\{1 + [\log(k_0[M]/k_\infty)]^2\right\}^{-1}}$$

where k_0 is the limiting low-pressure rate constant, k_∞ 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_0 and k_∞ 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, $CH_3\dot{O}_2$ and other $R\dot{O}_2$ radicals, NO, NO_2, 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 1.5×10^6 molecule cm^{-3} [equivalent to a diurnally-averaged concentration of 7.5×10^5 molecule cm^{-3}] (Prinn et al., 1987) and an approximate consideration of tropospheric CH_4 and CO chemistry, the HO_2 and $CH_3\dot{O}_2$ 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 $CF_3\dot{C}Cl_2$ 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

Species	Concentration (molecule cm^{-3}) Lower Troposphere	Concentration (molecule cm^{-3}) Upper Troposphere
M ($N_2 + O_2$)	2.5×10^{19}	4.5×10^{18}
O_2	5×10^{18}	9×10^{17}
O_3	7×10^{11}	4×10^{11}
NO	2.5×10^{8}	2.5×10^{8}
NO_2	2.5×10^{8}	2.5×10^{8}
OH	1.5×10^{6}	1.5×10^{6}
HO_2	10^{9}	10^{8}
$CH_3O_2^{\cdot}$	2.5×10^{8}	6×10^{6}

2.1. The $CF_3\dot{C}Cl_2$ Radical formed from HCFC-123 (CF_3CHCl_2)

A. $CF_3\dot{C}Cl_2$. The $CF_3\dot{C}Cl_2$ radical will react solely with O_2 to form the peroxy radical $CF_3CCl_2O_2^{\cdot}$,

$$CF_3\dot{C}Cl_2 + O_2 \xrightarrow{M} CF_3CCl_2\dot{O}_2$$

with a rate constant $k \geq 5 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}. This results in a tropospheric lifetime of the $CF_3\dot{C}Cl_2$ radical of $<2 \times 10^{-6}$ s.

B. $CF_3CCl_2O_2^{\cdot}$. The expected reactions of this peroxy radical are,

$$CF_3CCl_2O_2^{\cdot} + NO \rightarrow CF_3CCl_2O^{\cdot} + NO_2 \qquad (a)$$

$$CF_3CCl_2O_2^{\cdot} + NO_2 \xrightarrow{M} CF_3CCl_2OONO_2 \qquad (b)$$

$$CF_3CCl_2O_2^{\cdot} + HO_2 \rightarrow CF_3CCl_2OOH + O_2 \qquad (c)$$

$$CF_3CCl_2O_2^{\cdot} + CH_3O_2^{\cdot} \rightarrow CF_3CCl_2O^{\cdot} + CH_3O^{\cdot} + O_2 \qquad (d1)$$

$$CF_3CCl_2O_2^{\cdot} + CH_3O_2^{\cdot} \rightarrow CF_3CCl_2OH + HCHO + O_2 \qquad (d2)$$

with rate constants (cm^3 $molecule^{-1}$ s^{-1} units) of $k_a \sim 1.5 \times 10^{-11} (T/300)^{-1.2}$, $k_b \sim 1.0 \times 10^{-11}$, $k_c = 3.4 \times 10^{-13} e^{800/T}$, and $k_{d1} + k_{d2} \sim 2 \times 10^{-13}$. Based on the approximate concentrations of NO, NO_2, HO_2

and $CH_3O_2^{\cdot}$ given in Table 1, the decay rates (s^{-1}) of the $CF_3CCl_2O_2^{\cdot}$ 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 $CF_3CCl_2O_2^{\cdot}$ radical suggest that reaction with $RO_2^{\cdot}$ 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 $CF_3CCl_2O_2^{\cdot}$ radical is expected to be $\sim 10^2$ s. The products of reactions (a), (b) and (c) are the $CF_3CCl_2O^{\cdot}$ radical, the peroxynitrate $CF_3CCl_2OONO_2$ and the hydroperoxide CF_3CCl_2OOH, respectively. Formation of the nitrate, $CF_3CCl_2ONO_2$, from the NO reaction (a) is expected to account for <2% of the $CF_3CCl_2O^{\cdot}$ radical yield.

C. $\underline{CF_3CCl_2OONO_2^{\cdot}}$ Under tropospheric conditions, this haloalkyl peroxynitrate will undergo thermal decomposition and photolysis. The thermal decomposition reaction

$$CF_3CCl_2OONO_2 \xrightarrow{M} CF_3CCl_2O_2^{\cdot} + NO_2$$

is expected to have a rate constant of $\sim 1 \times 10^{15} e^{-11000/T} s^{-1}$ 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 peroxynitrate may be longer than calculated from the thermal decomposition rate constant due to reformation from the reverse reaction.

Photolysis of $CF_3CCl_2OONO_2$ can occur by two channels

$$CF_3CCl_2OONO_2 + h\nu \rightarrow CF_3CCl_2O_2^{\cdot} + NO_2$$

$$CF_3CCl_2OONO_2 + h\nu \rightarrow CF_3CCl_2O^{\cdot} + NO_3$$

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 $HOONO_2$, CH_3OONO_2, $CFCl_2OONO_2$ and CCl_3OONO_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 $CF_3CCl_2OONO_2$ 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 $CF_3CCl_2O_2^{\cdot}$ radical and, possibly, the $CF_3CCl_2O^{\cdot}$ radical (from photolysis). The reactions of the peroxy radical have been dealt with above, and the haloalkoxy radical reactions are dealt with below.

D. $\underline{CF_3CCl_2OOH}$. As for methyl hydroperoxide (CH_3OOH), the gas-phase tropospheric reactions of CF_3CCl_2OOH are expected to be photolysis and reaction with the OH radical. Photolysis is expected to proceed by

$$CF_3CCl_2OOH + h\nu \rightarrow CF_3CCl_2O^{\cdot} + OH$$

Assuming an absorption cross-section similar to that for CH_3OOH and a photodissociation quantum yield of unity (Baulch et al., 1982; NASA, 1987), then the lifetime of CF_3CCl_2OOH with respect to photolysis is calculated to be ∼6 days in the lower troposphere.

Reaction of CF_3CCl_2OOH with the OH radical will lead to formation of the $CF_3CCl_2\dot{O}_2$ radical

$$OH + CF_3CCl_2OOH \rightarrow H_2O + CF_3CCl_2\dot{O}_2$$

The rate constant for this process can be estimated from the data for the corresponding OH radical reactions with $(CH_3)_3COOH$ (Anastasi et al., 1978) and CH_3OOH (Vaghjiani and Ravishankara, 1989) [noting that the OH radical reaction with CH_3OOH 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 $H_2O + R\dot{O}_2$ have rate constants of (3-4) x 10^{-12} cm^3 $molecule^{-1}$ s^{-1} (Atkinson, 1989b). With the temperature dependence determined by Vaghjiani and Ravishankara (1989) for this reaction channel, this yields

$$k(OH + ROOH \rightarrow H_2O + R\dot{O}_2) = 1.7 \times 10^{-12}\, e^{220/T}\ cm^3\ molecule^{-1}\ s^{-1}$$

The calculated OH radical reaction rates during daylight hours of (5-7) x 10^{-6} 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_3CCl_2OOH 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_3CCl_2OOH in cloud, rain and fog water.

E. $CF_3CCl_2O^{\cdot}$. Based upon the discussion in Section 4.3, the reactions of the $CF_3CCl_2O^{\cdot}$ radical which need to be considered are

$$CF_2CCl_2O^{\cdot} \rightarrow CF_3C(O)Cl + Cl \qquad (a)$$

$$CF_3CCl_2O^{\cdot} \rightarrow \dot{C}F_3 + COCl_2 \qquad (b)$$

The value of $\Delta H_f(CF_3C(O)Cl)$, 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 $\Delta H_f(CXYZC(O)B)$ 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 $CH_3C(O)Cl$ (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_3CHO (IUPAC, 1989), $CH_3C(O)Cl$ (Wagman et al., 1982) and $CH_3C(O)F$ (Wagman et al., 1982) as -29.5, -48.1 and -94.8 kcal mol^{-1}, respectively.

The sum of the heats of formation of the products of pathways (a) and (b) are then: $CF_3C(O)Cl$ + Cl, -177 kcal mol^{-1} [$\Delta H_f(CF_3C(O)Cl)$ = -206 kcal mol^{-1} by both the above methods]; and $\dot{C}F_3$ + $COCl_2$, -166.5 kcal mol^{-1}. Cl atom elimination [channel (a)] is then expected to dominate, with the concurrent formation of $CF_3C(O)Cl$. 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,

$$Cl + CH_2 \rightarrow HCl + \dot{C}H_3$$

which has a rate constant (IUPAC, 1989) of $k = 9.6 \times 10^{-12} e^{-1350/T}$ cm^3 $molecule^{-1}$ s^{-1} (1.0×10^{-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 CH_4 in polluted urban areas.

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

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. $CF_3C(O)Cl$. 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

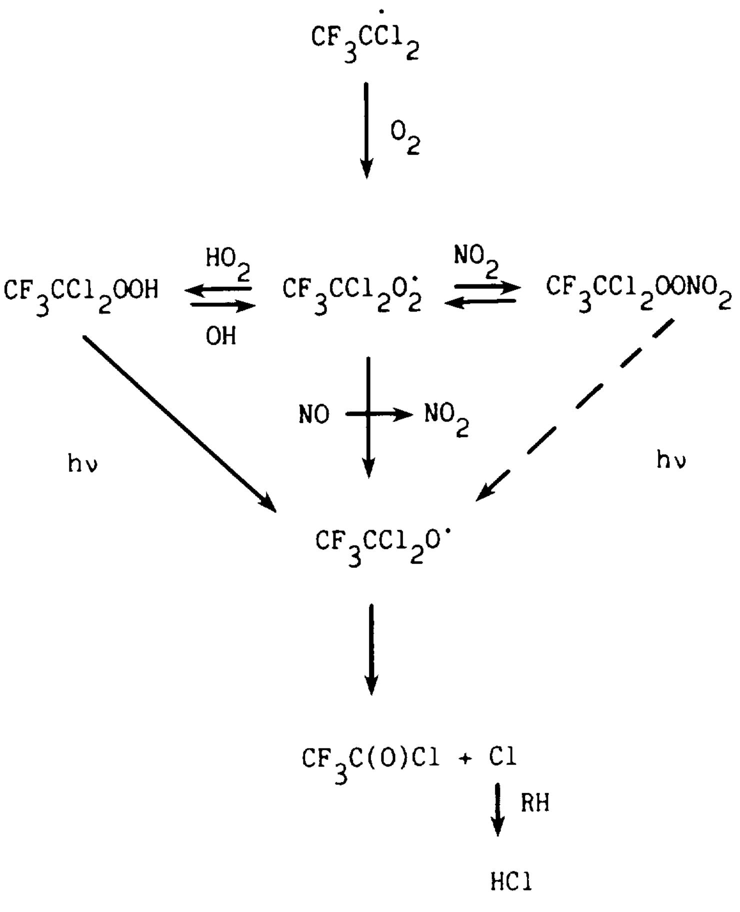
$$OH + HCl \rightarrow H_2O + Cl$$

has a rate constant (IUPAC, 1989) of $k = 2.4 \times 10^{-12} e^{-330/T}$ cm^3 $molecule^{-1}$ s^{-1} (8.1×10^{-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.

I. $COCl_2$. Although $COCl_2$ 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, $COCl_2$ 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. $\dot{C}F_3$. The tropospheric reactions of this radical are dealt with in Section 2.9 below.

The tropospheric degradation scheme for the $CF_3\dot{C}Cl_2$ radical is then as follows



2.2. The $CFCl_2\dot{C}H_2$ Radical formed from HCFC-141b ($CFCl_2CH_3$).

A. $CFCl_2\dot{C}H_2$. The $CFCl_2\dot{C}H_2$ radical will react solely with O_2,

$$CFCl_2\dot{C}H_2 + O_2 \xrightarrow{M} CFCl_2CH_2O_2^{\cdot}$$

with a rate constant of k $\geq 5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. The tropospheric lifetime of the $CFCl_2\dot{C}H_2$ radical will thus be $<2 \times 10^{-6}$ s.

B. $CFCl_2CH_2O_2^{\cdot}$. As discussed in Section 2.1, the $CFCl_2CH_2O_2^{\cdot}$ radical will react with NO, NO_2 and the HO_2 radical,

$$CFCl_2CH_2O_2^{\cdot} + NO \rightarrow CFCl_2CH_2O^{\cdot} + NO_2$$

$$CFCl_2CH_2O_2^{\cdot} + NO_2 \xrightarrow{M} CFCl_2CH_2OONO_2$$

$$CFCl_2CH_2O_2^{\cdot} + HO_2 \rightarrow CFCl_2CH_2OOH + O_2$$

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): $\sim 1.5 \times 10^{-11}\ (T/300)^{-1.2}$, $\sim 1.0 \times 10^{-11}$, and $3.4 \times 10^{-13}\ e^{800/T}$, respectively. With the concentrations of the reactive species given in Table 1, the lifetime of the $CFCl_2CH_2O_2^{\cdot}$ radical is $\sim 10^2$ 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. $CFCl_2CH_2OONO_2$. The reactions to be considered are thermal decomposition

$$CFCl_2CH_2OONO_2 \xrightarrow{M} CFCl_2CH_2O_2^{\cdot} + NO_2$$

with a rate constant at the high-pressure limit of $\sim 1 \times 10^{15}\ e^{-11000/T}$ s^{-1}, and photolysis

$$CFCl_2CH_2OONO_2 + h\nu \rightarrow CFCl_2CH_2O_2^{\cdot} + NO_2$$

$$CFCl_2CH_2OONO_2 + h\nu \rightarrow CFCl_2CH_2O^{\cdot} + NO_3$$

which is calculated to have a rate of $\sim 2 \times 10^{-6}$ 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

$$CFCl_2CH_2OOH + h\nu \rightarrow CFCl_2CH_2O^{\cdot} + OH$$

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

$$OH + CFCl_2CH_2OOH \rightarrow H_2O + CFCl_2CH_2O_2^{\cdot}$$

The rate constant for this reaction pathway is expected to be k $\sim 1.7 \times 10^{-12}\ e^{220/T}$ cm^3 molecule^{-1} s^{-1}. Abstraction of an H atom from the $-CH_2-$ group to form the $CFCl_2\dot{C}HOOH$ 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 $CFCl_2\dot{C}HOOH$ radical is expected to be followed by rapid decomposition to yield an OH radical and $CFCl_2CHO$

$$CFCl_2\dot{C}HOOH \rightarrow CFCl_2CHO + OH$$

Reaction with the OH radical and photolysis of $CFCl_2CH_2OOH$ are calculated to occur at comparable rates in the troposphere, with a lifetime of $CFCl_2CH_2OOH$ of ∿2 to 3 days. Physical removal processes leading to incorporation of $CFCl_2CH_2OOH$ into rain, cloud and fog water may also be important.

E. $\underline{CFCl_2CH_2O^{\cdot}}$. Based on the discussion in Section 4.3, the reactions of this radical which need to be considered are

$$CFCl_2CH_2O^{\cdot} + O_2 \rightarrow CFCl_2CHO + HO_2 \qquad \text{(a)}$$

$$CFCl_2CH_2O^{\cdot} \rightarrow \dot{C}FCl_2 + HCHO \qquad \text{(b)}$$

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 O_2 concentrations). Again, this expectation is in agreement with the conclusions of Sanhueza et al. (1976). The decomposition to HCHO and the $\dot{C}FCl_2$ radical cannot be ruled out at the present time, however. The reactions of the $\dot{C}FCl_2$ radical will be totally analogous to those of the $\dot{C}F_2Cl$ radical discussed in Section 2.4 below, except that the $CFCl_2O^{\cdot}$ radical will eliminate a Cl atom to yield COFCl (instead of the COF_2 formed from the $CF_2ClO^{\cdot}$ radical).

Assuming that the rate constant for the reaction (a) is identical to that for the ethoxy radical of k_a = $3.7 \times 10^{-14} e^{-460/T}$ cm^3 $molecule^{-1}$ s^{-1}, the lifetime of the $CFCl_2CH_2O^{\cdot}$ radical will be ∿2×10^{-4} to 2×10^{-5} s in the troposphere.

F. $\underline{CFCl_2CHO}$. The possible tropospheric reactions of dichlorofluoroacetaldehyde are reaction with OH and NO_3 radicals and O_3, and photolysis. By analogy with CH_3CHO, for which the O_3 reaction rate constant at room temperature is $< 10^{-20}$ cm^3 $molecule^{-1}$ s^{-1} (Atkinson and Carter, 1984), reaction with O_3 is expected to be of totally negligible importance as a loss process. Reaction with the NO_3 radical is expected to be no faster than the corresponding reaction with CH_3CHO [k = $1.4 \times 10^{-12} e^{-1860/T}$ cm^3 $molecule^{-1}$ s^{-1}, = 2.7×10^{-15} cm^3 $molecule^{-1}$ s^{-1} at 298 K (IUPAC, 1989)], and in the clean troposphere this NO_3 radical reaction will be of no importance (Winer et al., 1984), although it should be noted that this reaction yields the same $CFCl_2\dot{C}O$ radical as does the OH radical reaction.

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

$$OH + CFCl_2CHO \rightarrow H_2O + CFCl_2\dot{C}O$$

Assuming that the substituent group factor for the $-CFCl_2$ group is similar to those for the $-CCl_3$, $-CF_3$ and $-CF_2Cl$ groups (Atkinson, 1987), the estimation technique of Atkinson (1987) allows an approximate room temperature rate constant of ∿$(0.5\text{-}2) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} to be calculated. A rate constant of this magnitude leads to a lifetime of $CFCl_2CHO$ 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 CH_3CHO, which leads to a lifetime with respect to photolysis of $\geq$5-10 days. In the absence of data for the absorption cross-sections, photodissociation quantum yields and photodissociation products of $CFCl_2CHO$, it is assumed that the OH radical reaction, while relatively slow, is the dominant tropospheric loss process, leading to the formation of the $CFCl_2\dot{C}O$ radical.

G. <u>$CFCl_2\dot{C}O$</u>. This acyl radical will rapidly add O_2, with a rate constant of $\sim 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} (Atkinson, 1989a).

$$CFCl_2\dot{C}O + O_2 \xrightarrow{M} CFCl_2C(O)\dot{O}_2$$

This will be the sole reaction of the $CFCl_2\dot{C}O$ radical, which will have a lifetime of $< 10^{-6}$ s^{-1} in the troposphere.

H. <u>$CFCl_2C(O)\dot{O}_2$</u> . Analogous to the alkyl and haloalkyl peroxy ($R\dot{O}_2$) radicals and the acetyl peroxy ($CH_3C(O)\dot{O}_2$) radical, this acyl peroxy radical will react with NO and NO_2.

$$CFCl_2C(O)\dot{O}_2 + NO \rightarrow CFCl_2C\dot{O}_2 + NO_2$$

$$\dot{C}FCl_2 + CO_2$$

$$CFCl_2C(O)\dot{O}_2 + NO_2 \xrightarrow{M} CFCl_2C(O)OONO_2$$

Assuming identical rate constants for these NO and NO_2 reactions to those for the analogous reactions with the acetyl peroxy radical, rate constants of $5.1 \times 10^{-12} e^{200/T}$ cm^3 $molecule^{-1}$ s^{-1} for the NO reaction and 8×10^{-12} cm^3 $molecule^{-1}$ s^{-1} for the NO_2 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 $\dot{C}FCl_2$ radical, while the NO_2 reaction forms an analog to peroxyacetyl nitrate (PAN).

In addition, reaction with the HO_2 radical and, at least in the lower troposphere, with $CH_3\dot{O}_2$ radicals cannot be ruled out as being of importance. The reaction of the $CH_3C(O)\dot{O}_2$ radical with HO_2 has been reported to lead to the formation of $CH_3C(O)OOH + O_2$ and $CH_3COOH + O_3$ in an approximately 3:1 ratio at room temperature (Niki et al., 1985) [see also Moortgat et al., 1987]. The reaction of the $CH_3C(O)\dot{O}_2$ radical with the $CH_3\dot{O}_2$ radical is rapid, with a rate constant of 1.1×10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 298 K, forming $CH_3O^{\cdot} + CH_3C\dot{O}_2 + O_2$ and $CH_3COOH + HCHO + O_2$ in equal yield at room temperature (IUPAC, 1989; Moortgat et al., 1989).

The analogous products would then be $CFCl_2C\dot{O}_2$, which should rapidly decompose to $\dot{C}FCl_2 + CO_2$, $CFCl_2COOH$ and $CFCl_2C(O)OOH$. The reactions of the $\dot{C}FCl_2$ radical are dealt with below in Section 2.4. By analogy with CH_3COOH, the acid $CFCl_2COOH$ 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 $CFCl_2COOH$ and $CFCl_2C(O)OOH$ will be by wet deposition and rain-out.

I. $CFCl_2C(O)OONO_2$. 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

$$CFCl_2C(O)OONO_2 \xrightarrow{M} CFCl_2C(O)\dot{O}_2 + NO_2$$

is expected to be similar to that for PAN, with $k = 2.2 \times 10^{16} e^{-13435/T} s^{-1}$ 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 $CFCl_2C(O)OONO_2$ should be close to the high pressure limit throughout the troposphere. The lifetime of $CFCl_2C(O)OONO_2$ 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 at 300 nm of 1×10^{-21} cm^2 (IUPAC, 1989). Photolysis of $CFCl_2C(O)OONO_2$, 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 $CFCl_2C(O)OONO_2$ 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 $CF_2Cl\dot{C}H_2$ Radical formed from HCFC-142b (CF_2ClCH_3).

The reactions undergone by the $CF_2Cl\dot{C}H_2$ radical in the troposphere are expected to be totally analogous to the reactions of the $CFCl_2\dot{C}H_2$ radical discussed above in Section 2.2. However, the possible reactions of the $CF_2ClCH_2O^{\cdot}$ radical which is formed during the overall reaction scheme need to be evaluated, as follows.

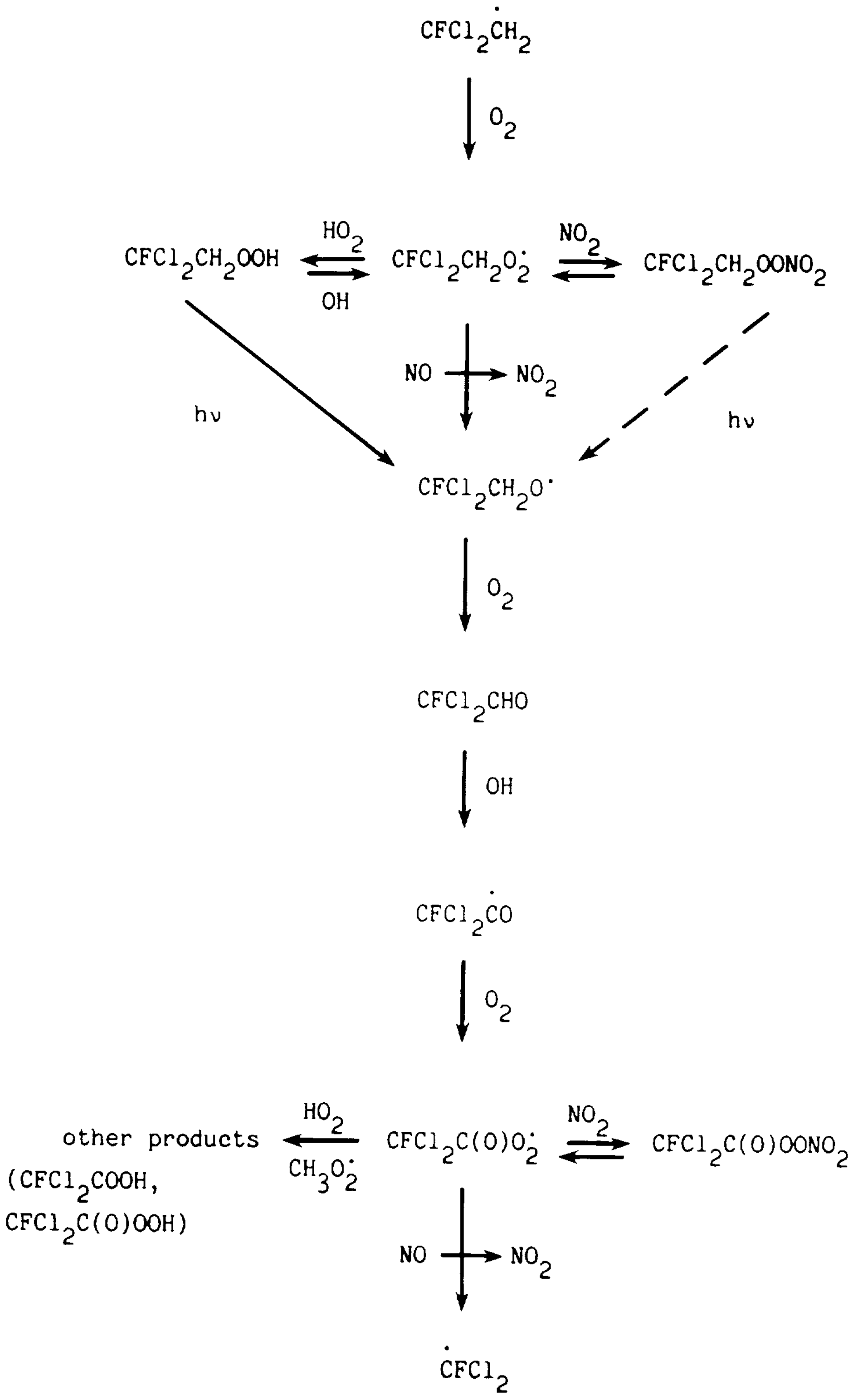
A. $CF_2ClCH_2O^{\cdot}$. The likely reaction pathways are (see Section 2.2.E above)

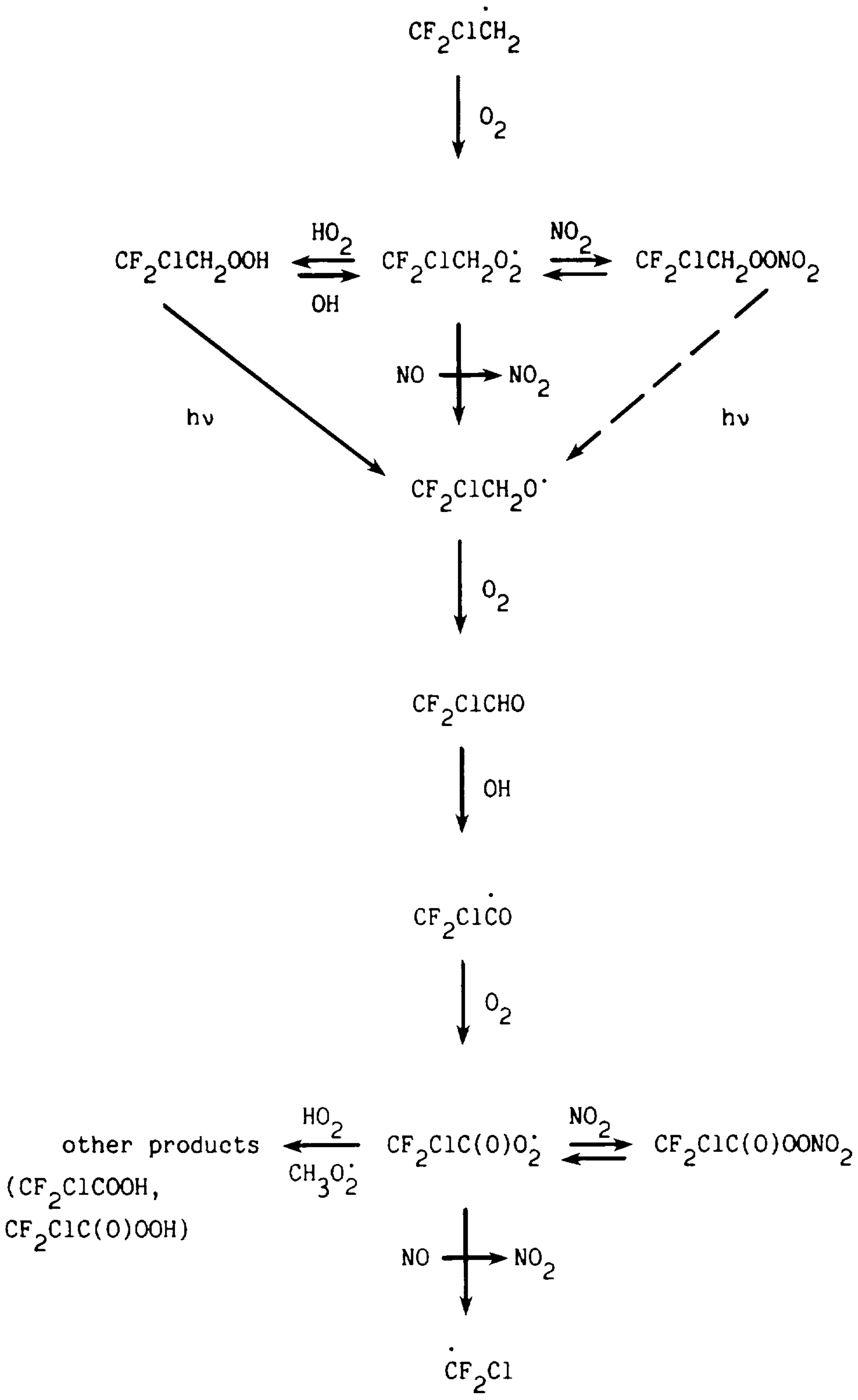
$$CF_2ClCH_2O^{\cdot} + O_2 \rightarrow CF_2ClCHO + HO_2 \qquad (a)$$

$$CF_2ClCH_2O^{\cdot} \rightarrow \dot{C}F_2Cl + HCHO \qquad (b)$$

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 $CFCl_2CH_2O^{\cdot}$ radical in Section 2.2.E., that pathway (a) will dominate, leading to the formation of CF_2ClCHO.

A portion of the tropospheric degradation scheme of the $CF_2Cl\dot{C}H_2$ radical, leading to the formation of the $\dot{C}F_2Cl$ radical, is shown below.


CFCl2ĊH2
O2
CFCl2CH2OOH
HO2
OH
CFCl2CH2O2·
NO2
CFCl2CH2OONO2
NO
NO2
hν
hν
CFCl2CH2O·
O2
CFCl2CHO
OH
CFCl2ĊO
O2
other products
(CFCl2COOH,
CFCl2C(O)OOH)
HO2
CH3O2·
CFCl2C(O)O2·
NO2
CFCl2C(O)OONO2
NO
NO2
ĊFCl2


CF2ClCH2
O2
CF2ClCH2OOH
HO2
OH
CF2ClCH2O2
NO2
CF2ClCH2OONO2
NO
NO2
hν
hν
CF2ClCH2O
O2
CF2ClCHO
OH
CF2ClCO
O2
other products
(CF2ClCOOH,
CF2ClC(O)OOH)
HO2
CH3O2
CF2ClC(O)O2
NO2
CF2ClC(O)OONO2
NO
NO2
CF2Cl

As noted above, the tropospheric reactions of the $CFCl_2\dot{C}H_2$ and $CF_2Cl\dot{C}H_2$ radicals formed from HCFC-141b and HCFC-142b, respectively, are expected to be totally analogous, except that the $\dot{C}FCl_2$ radical is formed subsequent to the reactions of the $CFCl_2\dot{C}H_2$ radical, while the $\dot{C}F_2Cl$ radical is the subsequent product from the $CF_2Cl\dot{C}H_2$ radical.

2.4. The $\dot{C}F_2Cl$ Radical formed from HCFC-22 (CHF_2Cl)

In addition to being the primary product of the OH radical reaction with CHF_2Cl, the $\dot{C}F_2Cl$ radical is also expected to be formed from the reactions subsequent to the OH radical reaction with HCFC-142b. The analogous radical $\dot{C}FCl_2$ is expected to be formed subsequent to the OH radical reaction with HCFC-141b, and the reaction sequence discussed in this section for the $\dot{C}F_2Cl$ radical is also applicable for the $\dot{C}FCl_2$ radical, with the differences being noted at the appropriate points.

A. $\dot{C}F_2Cl$. No experimental data are available for this particular radical. Experimental data are available for the analogous $\dot{C}FCl_2$ radical reaction (Caralp and Lesclaux, 1983), and the IUPAC (1989) recommended values of k_0, k_∞ and F for the reaction of the $\dot{C}FCl_2$ radical with O_2 are given in Table 2 (see Section 4). Both the $\dot{C}F_2Cl$ and $\dot{C}FCl_2$ radicals rapidly add O_2 to form the $CF_2ClO_2^{\cdot}$ and $CFCl_2O_2^{\cdot}$ peroxy radicals, respectively,

$$\dot{C}F_2Cl + O_2 \xrightarrow{M} CF_2ClO_2^{\cdot}$$

$$\dot{C}FCl_2 + O_2 \rightarrow CFCl_2O_2^{\cdot}$$

with rate constants of $\geq 5 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} under the temperature and pressure conditions in the troposphere. The lifetimes of the $\dot{C}F_2Cl$ and $\dot{C}FCl_2$ radicals will then be $< 2 \times 10^{-6}$ s in the troposphere.

B. $CF_2ClO_2^{\cdot}$. This peroxy radical can, as described above in Section 2.1, react with NO, NO_2 and the HO_2 radical under tropospheric conditions.

$$CF_2ClO_2^{\cdot} + NO \rightarrow CF_2ClO^{\cdot} + NO_2 \qquad (a)$$

$$CF_2ClO_2^{\cdot} + NO_2 \xrightarrow{M} CF_2ClOONO_2 \qquad (b)$$

$$CF_2ClO_2^{\cdot} + HO_2 \rightarrow CF_2ClOOH + O_2 \qquad (c)$$

The reactions of the $CFCl_2O_2^{\cdot}$ radical are totally analogous. Experimental rate constant data are available for the reactions of the $CF_2ClO_2^{\cdot}$ radical with NO (Dognon et al., 1985), and for the reactions of the $CFCl_2O_2^{\cdot}$ 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 cm^3 $molecule^{-1}$ 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 $k_c \sim 3.4 \times 10^{-13} e^{800/T}$. 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 $CF_2ClO^{\cdot}$ radical, $CF_2ClOONO_2$ and CF_2ClOOH.

Formation of the nitrate, CF_2ClONO_2, from the reaction of the $CF_2ClO_2^{\cdot}$ radical with NO is expected to be of negligible importance. Analogous products will be formed from the $CFCl_2O_2^{\cdot}$ radical reactions.

C. CF₂ClOONO₂. As in Sections 2.1 and 2.2 above, this peroxynitrate can undergo thermal decomposition or photolyze. The thermal decomposition

$$CF_2ClOONO_2 \overset{M}{\rightarrow} CF_2ClO_2^{\cdot} + NO_2$$

rate data have been evaluated by IUPAC (1989), and the recommended rate expressions for this reaction and the analogous thermal decomposition of $CFCl_2OONO_2$ are given in Table 10 (Section 4). The lifetimes of these two peroxynitrates with respect to thermal decomposition increase from ~15 s in the lower troposphere to ~(2-3) x 10^7 s (~290 days) in the upper troposphere.

No absorption cross-section data are available for $CF_2ClOONO_2$. However, data are available for $CFCl_2OONO_2$ (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

$$CF_2ClOONO_2 + h\nu \rightarrow CF_2ClO_2^{\cdot} + NO_2$$

$$CF_2ClOONO_2 + h\nu \rightarrow CF_2ClO^{\cdot} + NO_3$$

will dominate in the upper troposphere, with a lifetime with respect to this process of ~5 days. The photolysis products are not known, but are expected to be mainly the peroxy radical plus NO_2.

D. CF₂ClOOH. The homogeneous gas-phase tropospheric loss processes for CF_2ClOOH and $CFCl_2OOH$ are photolysis and reaction with the OH radical. As discussed in Section 2.1 above, photolysis

$$CF_2ClOOH + h\nu \rightarrow CF_2ClO^{\cdot} + OH$$

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

$$OH + CF_2ClOOH \rightarrow H_2O + CF_2ClO_2^{\cdot}$$

and the rate constant for this reaction is estimated to be $k = 1.7 \times 10^{-12} e^{220/T}$ cm^3 molecule^{-1} s^{-1}. Reaction with the OH radical and photolysis are expected to occur at comparable rates in the troposphere, leading to a lifetime of CF_2ClOOH with respect to these reactions of 2 to 3 days. Incorporation into aqueous systems may also be important. The reactions of $CFCl_2OOH$ are expected to be totally analogous.

E. CF₂ClO˙. As discussed in Section 4.3.B., the $CF_2ClO^{\cdot}$ radical will undergo decomposition to yield COF_2 and a Cl atom (Table 8).

$$CF_2ClO^{\cdot} \rightarrow COF_2 + Cl$$

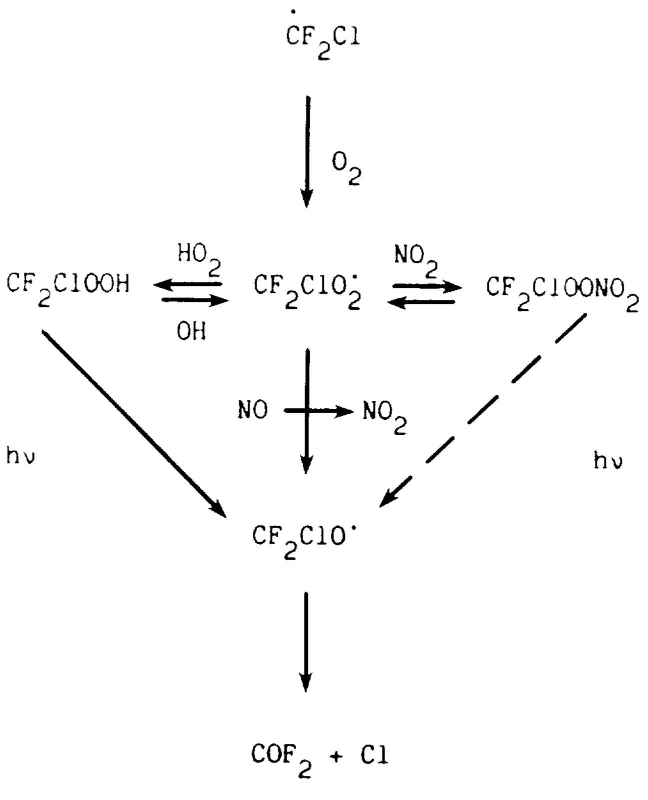
The $CFCl_2O^{\cdot}$ radical decomposes in an analogous manner

$$CFCl_2O^{\cdot} \rightarrow COFCl + Cl$$

The lifetimes of these halomethoxy radicals are calculated (Table 8) to be <0.1 s throughout the troposphere, and reactions with NO and NO_2 will be unimportant.

F. COF_2 and COFCl. 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 COFCl) HCl, are then expected to be the major tropospheric loss processes for these carbonyl halides.

The reaction scheme for the $\dot{C}F_2Cl$ radical is shown below



The reaction scheme for the $\dot{C}FCl_2$ radical is totally analogous, except that the final products are COFCl and a Cl atom.

2.5. The $CF_3\dot{C}FCl$ Radical formed from HCFC-124 (CF_3CHFCl)

The tropospheric reactions of this radical will be totally analogous to those of the $CF_3\dot{C}Cl_2$ radical formed from HCFC-123, discussed in Section 2.1. The reactions of the $CF_3CFClO^{\cdot}$ radical which is formed during the degradation need to be evaluated.

A. $CF_3CFClO^{\cdot}$. The likely reactions of this radical are

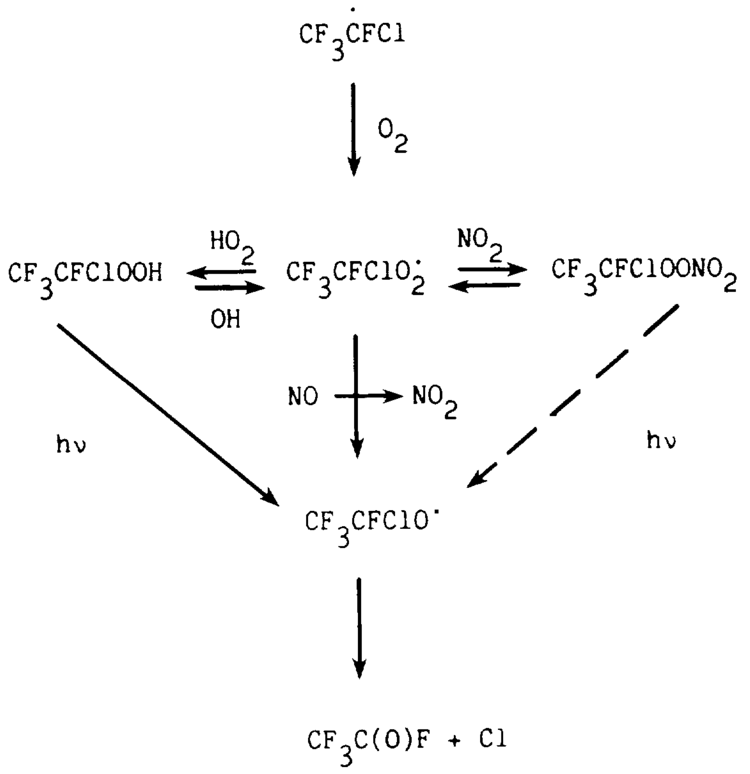
$$CF_3CFClO^{\cdot} \rightarrow CF_3C(O)F + Cl \tag{a}$$

$$CF_3CFClO^{\cdot} \rightarrow \dot{C}F_3 + COFCl \tag{b}$$

The heats of formation of the products of reaction pathways (a) and (b) are: $CF_3C(O)F$ + Cl from pathway (a), -222.1 kcal mol^{-1} ($\Delta H_f(CF_3C(O)F)$ = -251.1 kcal mol^{-1} with an uncertainty of at least 2 kcal mol^{-1}); and $\dot{C}F_3$ + 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 $CF_3C(O)F$ and a Cl atom.

B. $CF_3C(O)F$. 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 $CF_3C(O)F$ to $\dot{C}F3$ + FCO or to CF_4 + CO, photodissociation to $\dot{C}F_3$ + 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 CF_3COOH + HF) being expected to dominate.

The expected reaction scheme for the $CF_3\dot{C}FCl$ radical is shown below



2.6. The $CF_3\dot{C}HF$ Radical formed from HFC-134a (CF_3CH_2F).

The tropospheric reactions of the $CF_3\dot{C}HF$ radical are expected to be generally similar to those of the

$CF_2Cl\dot{C}H_2$ and $CFCl_2\dot{C}H_2$ radicals discussed above in Sections 2.2 and 2.3.

A. $CF_3\dot{C}HF$. Reaction with O_2 to form the peroxy radical will be the sole reaction of this radical in the troposphere.

$$CF_3\dot{C}HF + O_2 \xrightarrow{M} CF_3CHFO_2^{\cdot}$$

The rate constant is expected to be $>5 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} at the temperatures and pressures encountered in the troposphere, leading to a lifetime of the $CF_3\dot{C}HF$ radical of $<2 \times 10^{-6}$ s.

B. $CF_3CHFO_2^{\cdot}$. The tropospherically important reactions of the $CF_3CHFO_2^{\cdot}$ radical are expected to be with NO, NO_2 and the HO_2 radical

$$CF_3CHFO_2^{\cdot} + NO \rightarrow CF_3CHFO^{\cdot} + NO_2 \tag{a}$$

$$CF_3CHFO_2^{\cdot} + NO_2 \xrightarrow{M} CF_3CHFOONO_2 \tag{b}$$

$$CF_3CHFO_2^{\cdot} + HO_2 \rightarrow CF_3CHFOOH + O_2 \tag{c}$$

The rate constants for these reactions are estimated (in cm^3 $molecule^{-1}$ 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 $k_c \sim 3.4 \times 10^{-13}$ $e^{800/T}$, respectively. With the tropospheric concentrations of NO, NO_2 and the HO_2 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 $CF_3CHFO_2^{\cdot}$ radical is calculated to be $\sim 10^2$ s.

C. $CF_3CHFOONO_2$. This species is expected to undergo thermal decomposition and photolysis. Thermal decomposition

$$CF_3CHFOONO_2 \xrightarrow{M} CF_3CHFO_2^{\cdot} + NO_2$$

is expected to have a rate constant at the high-pressure limit of $\sim 1 \times 10^{15}$ $e^{-11000/T}$ s^{-1}, leading to lifetimes of this peroxynitrate, with respect to thermal decomposition, of ~ 10 s in the lower troposphere (298 K) and $\sim 10^7$ s in the upper troposphere (220 K). The peroxy radical $CF_3CHFO_2^{\cdot}$ is reformed. Photolysis

$$CF_3CHFOONO_2 + h\nu \rightarrow CF_3CHFO_2^{\cdot} + NO_2$$

$$CF_3CHFOONO_2 + h\nu \rightarrow CF_3CHFO^{\cdot} + NO_3$$

is expected to be slow, with a lifetime of the peroxynitrate due to photolysis of ~ 5 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 $CF_3CHFOONO_2$.

D. $CF_3CHFOOH$. 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

$$CF_3CHFOOH + h\nu \rightarrow CF_3CHFO^{\cdot} + OH$$

forms the haloalkoxy radical $CF_3CHFO^{\cdot}$. Based upon the absorption cross-section for CH_3OOH (NASA, 1987), the lifetime of $CF_3CHFOOH$ with respect to photolysis is estimated to be ~6 days in the lower troposphere.

The OH radical reaction will proceed mainly by

$$OH + CF_3CHFOOH \rightarrow H_2O + CF_3CHFO_2^{\cdot}$$

with an estimated rate constant of $\sim 1.7 \times 10^{-12} e^{220/T}$ cm^3 $molecule^{-1}$ s^{-1}. The reaction to form the $CF_3\dot{C}FOOH$ radical

$$OH + CF_3CHFOOH \rightarrow H_2O + CF_3\dot{C}FOOH$$

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 $CF_3CHFOOH$, with a lifetime due to these processes of 2-3 days. Physical removal of $CF_3CHFOOH$ from the gas phase into rain, cloud and fog water and aerosols may also be important.

E. $CF_3CHFO^{\cdot}$. The possible reactions of this haloalkoxy radical are

$$CF_3CHFO^{\cdot} + O_2 \rightarrow CF_3C(O)F + HO_2 \tag{a}$$

$$CF_3CHFO^{\cdot} \rightarrow CF_3C(O)F + H \tag{b}$$

$$CF_3CHFO^{\cdot} \rightarrow \dot{C}F_3 + HC(O)F \tag{c}$$

$$CF_3CHFO^{\cdot} \rightarrow CF_3CHO + F \tag{d}$$

The sum of the heats of formation of the products from these reactions are (with $\Delta H_f(CF_3C(O)F) = -251.1$ kcal mol^{-1} being calculated, with an uncertainty of at least ± 2 kcal mol^{-1}): $CF_3C(O)F + HO_2$ from reaction (a), -247.6 kcal mol^{-1}; $CF_3C(O)F + H$ from reaction (b), -199.0 kcal mol^{-1}; $\dot{C}F_3 + HC(O)F$ from reaction (c), -205.3 kcal mol^{-1} (with $\Delta H_f(HC(O)F) = -90.9$ 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 $CF_3CHO + F$ 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 O_2 and C-C bond cleavage as the likely reaction routes of the $CF_3CHF\dot{O}$ 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 ± 2-3 kcal mol^{-1} uncertainty, indicates that both reactions may be of comparable importance at room temperature (with the reaction with O_2 presumably 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 $CF_3C(O)F$ and of $\dot{C}F_3$ + HC(O)F must be considered.

F. $CF_3C(O)F$. As discussed in Section 2.5 above, the reaction of OH radical with $CF_3C(O)F$ will be unimportant as a tropospheric loss process, and photolysis is also expected to be slow or negligible. The removal of $CF_3C(O)F$ 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 + CF_3COOH.

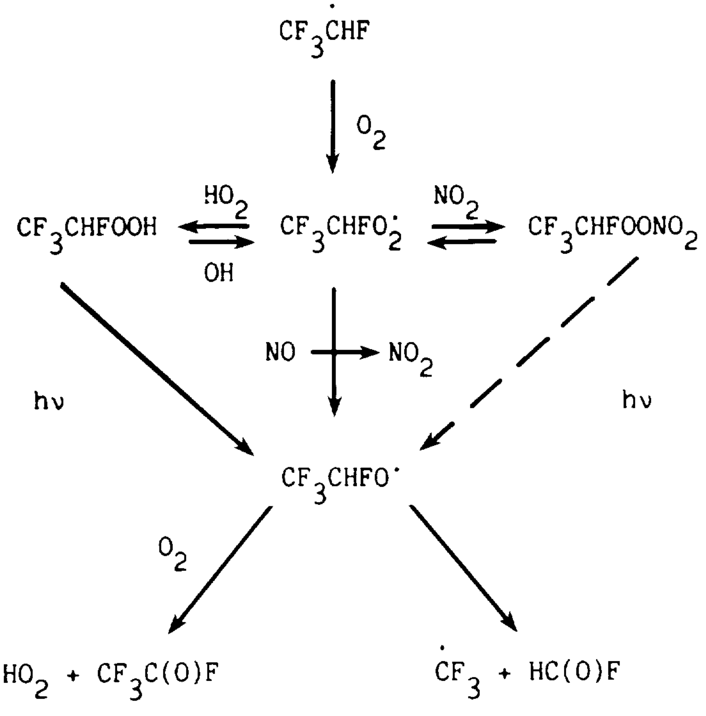
G. HC(O)F. The expected tropospheric removal routes for formyl fluoride are photolysis, reaction with the OH radical and wet deposition. Reaction with the OH radical

$$OH + HC(O)F \rightarrow H_2O + FCO$$

is calculated (Atkinson, 1987) to have a rate constant at room temperature of $\sim 1.6 \times 10^{-12}$ cm^3 molecule^{-1} 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 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. $\dot{C}F_3$. The reactions of this radical are dealt with in Section 2.9 below.

The expected reaction scheme in the troposphere for the $CF_3\dot{C}HF$ radical is shown below



2.7. The $CHF_2\dot{C}H_2$ Radical formed from HFC-152a (CHF_2CH_3).

The expected reactions of the $CHF_2\dot{C}H_2$ radical are essentially identical to those of the $CF_2Cl\dot{C}H2$ and $CFCl_2\dot{C}H_2$ radicals discussed above in Sections 2.2. and 2.3. The fate of the resulting haloalkoxy radical $CHF_2CH_2O^{\cdot}$ needs to be considered, as follows.

A. $CHF_2CH_2O^{\cdot}$. The reactions of this radical which need to be considered are,

$$CHF_2CH_2O^{\cdot} + O_2 \rightarrow CHF_2CHO + HO_2 \qquad \text{(a)}$$

$$CHF_2CH_2O^{\cdot} \rightarrow \dot{C}HF_2 + HCHO \qquad \text{(b)}$$

with H atom elimination to yield CHF_2CHO + H being of no importance. The sum of the heats of formation of the products from reactions (a) and (b) are: $CHF_2CHO + HO_2$ from reaction (a), -134.1 kcal mol^{-1} [using the bond additivity method of Benson (1976) to calculate $\Delta H_f(CHF_2CHO)$]; and $\dot{C}HF_2$ + HCHO from reaction (b), -84.2 kcal mol^{-1} [$\Delta H_f(\dot{C}HF_2)$ being obtained from McMillen and Golden (1982) and Pickard and Rodgers (1983)]. The difference in the these heats of formation of the products of 50 kcal mol^{-1} indicates that reaction (a) to form $CHF_2CHO + HO_2$ will be the totally dominant reaction pathway for the $CHF_2CH_2\dot{O}$ radical throughout the troposphere, as expected from the discussion in Section 4.3.

B. CHF_2CHO. Difluoroacetaldehyde will react in a similar manner to CF_2ClCHO and $CFCl_2CHO$ discussed above in Sections 2.2 and 2.3. The OH radical reaction

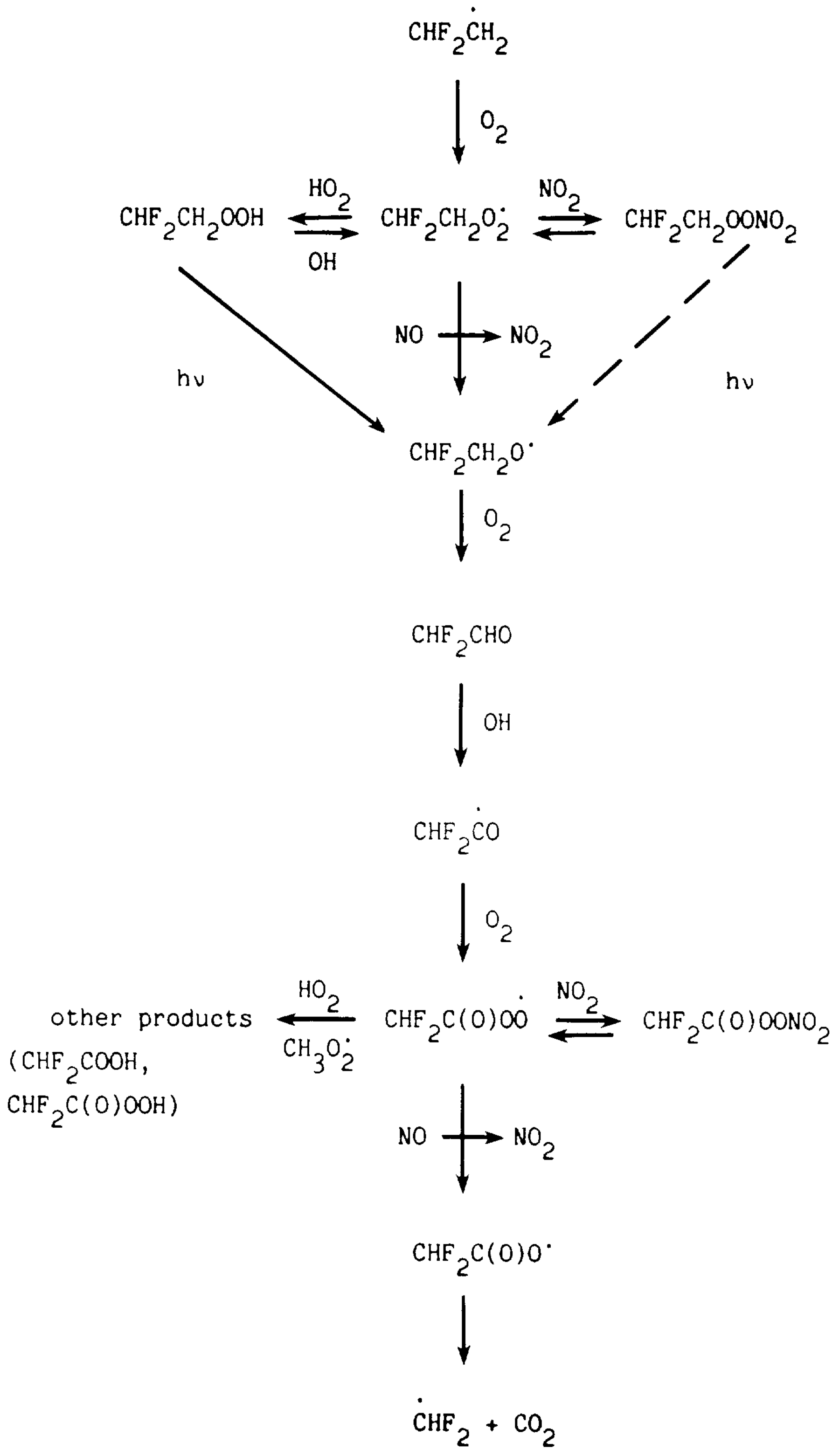
$$OH + CHF_2CHO \rightarrow H_2O + CHF_2\dot{C}O$$

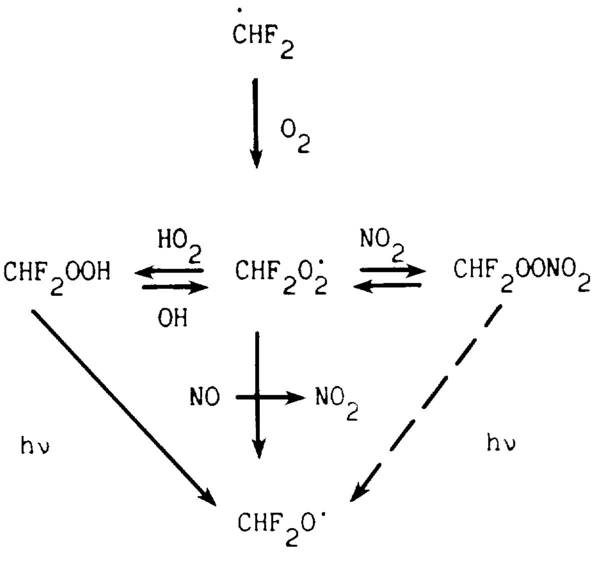
will proceed as shown, with an estimated rate constant of $\sim 1.6 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at room temperature (Atkinson, 1987). The reaction pathway involving H atom abstraction from the $-CHF_2$ group to form the $\dot{C}F_2CHO$ radical has an estimated room temperature rate constant of $\sim 1.4 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} (Atkinson, 1987), and is hence of negligible importance. It should be noted that no data are available concerning the photolysis of CHF_2CHO under tropospheric conditions.

The subsequent reactions of the $CHF_2\dot{C}O$ radical will be as discussed in Section 2.2 above [H atom abstraction by the OH radical from the $-CHF_2$ group will be of no importance during the subsequent reactions of this $CHF_2\dot{C}O$ radical]. The reaction scheme for the $CHF_2\dot{C}H_2$ radical is thus as shown below.

The $CHF_2C(O)O^{\cdot}$ radical formed in the final stages of this reaction sequence is expected to rapidly unimolecularly decompose to CO_2 plus the $\dot{C}HF_2$ radical. Under tropospheric conditions, this $\dot{C}HF_2$ radical will undergo the sequence of reactions generally similar to those discussed above in Section 2.4 for the $\dot{C}F_2Cl$ radical, to yield the $CHF_2O^{\cdot}$ radical. The reactions of this radical are as follows.

DEGRADATION MECHANISMS





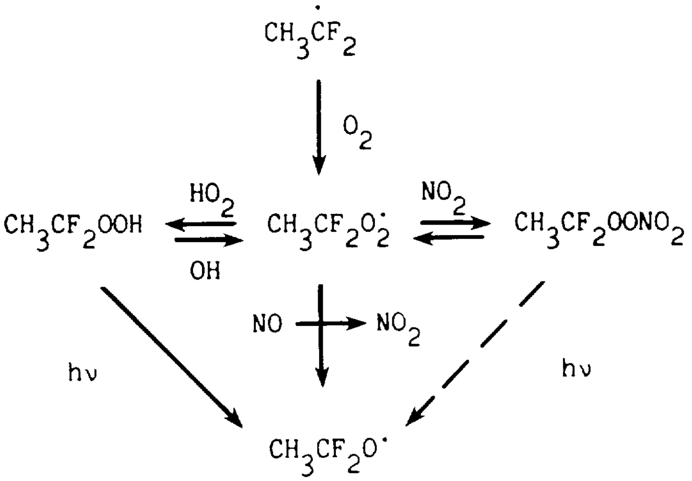
C. CHF$_2$O$^{\cdot}$. Reaction with O_2 will be the only important reaction pathway

$$CHF_2O^{\cdot} + O_2 \rightarrow COF_2 + HO_2$$

under tropospheric conditions (Table 8). The tropospheric loss processes for COF_2 have been dealt with in Section 2.4 above.

2.8. The $CH_3\dot{C}F_2$ Radical formed from HFC-152a (CHF_2CH_3).

The reactions of the $CH_3\dot{C}F_2$ radical in the troposphere will be generally similar to those of the $CF_3\dot{C}Cl_2$ and $CF_3\dot{C}FCl$ radicals dealt with in Sections 2.1 and 2.5 above. The reactions of the $CH_3\dot{C}F_2$ radical leading to the formation of the $CH_3CF_2O^{\cdot}$ radical are then as shown below



The reactions of $CH_3CF_2OONO_2$ and CH_3CF_2OOH with the OH radical by H atom abstraction from the $-CH_3$ group are calculated to be of negligible importance, with a room temperature rate constant for this

H atom abstraction process of $< 1 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} being expected (Atkinson, 1987). The subsequent reactions of the haloalkoxy radical $CH_3CF_2\dot{O}$ need to be considered, as discussed below.

A. CH₃CF₂O˙. The reactions of this radical which can occur are

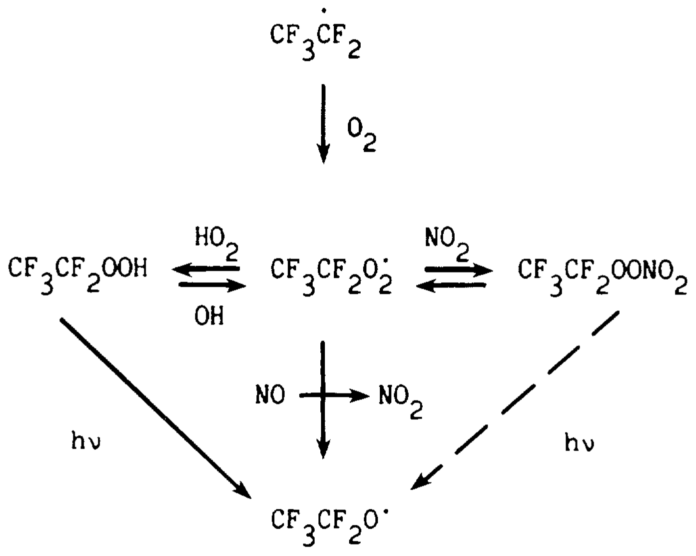
$$CH_3CF_2\dot{O} \rightarrow \dot{C}H_3 + COF_2 \qquad (a)$$

$$CH_3CF_2\dot{O} \rightarrow CH_3C(O)F + F \qquad (b)$$

Reaction pathway (a) is calculated to be 32 kcal mol^{-1} more exothermic than pathway (b), and hence the unimolecular decomposition of the $CH_3CF_2\dot{O}$ radical to $\dot{C}H_3$ + 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 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 CH_3OOH, CH_3OONO_2 and HCHO, which react further to ultimately form CO, CO_2 and H_2O.

2.9. The $CF_3\dot{C}F_2$ Radical formed from HFC-125 (CF_3CHF_2).

The tropospheric reactions of this radical are analogous to those of the $CF_3\dot{C}Cl_2$, $CF_3\dot{C}FCl$ and $CH_3\dot{C}F_2$ radicals dealt with in Sections 2.1, 2.5 and 2.8, respectively. The reaction sequence leading to the formation of the $CF_3CF_2\dot{O}$ haloalkoxy radical will be as shown below.



A. CF₃CF₂Ȯ. The reactions of the $CF_3CF_2\dot{O}$ 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):

$$CF_3CF_2\dot{O} \rightarrow \dot{C}F_3 + COF_2 \qquad (a)$$

$$CF_3CF_2\dot{O} \rightarrow CF_3C(O)F + F \qquad (b)$$

Reaction pathway (a) is calculated to be 33.5 kcal mol^{-1} more exothermic than pathway (b), and hence unimolecular decomposition of the $CF_3CF_2O^{\cdot}$ radical to yield $\dot{C}F_3$ + 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. $\dot{C}F_3$. As discussed in Section 4, reaction with O_2 will be the sole tropospheric reaction of the $\dot{C}F_3$ radical

$$\dot{C}F_3 + O_2 \xrightarrow{M} CF_3O_2^{\cdot}$$

and the rate constant data for this reaction are given in Table 2. The reactions of the $CF_3O_2^{\cdot}$ radical with NO, NO_2 and the HO_2 radical, and the reactions of the CF_3OONO_2 and CF_3OOH species formed, are expected to be totally analogous to those of the $\dot{C}F_2Cl$ and $\dot{C}FCl_2$ radicals dealt with in Section 2.4 above. The rate constants for the reactions of the $CF_3O_2^{\cdot}$ 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_3OONO_2 are expected to be similar to those for $CF_2ClOONO_2$, $CFCl_2OONO_2$ and CCl_3OONO_2 given in Table 10 (Caralp et al., 1988).

C. Reaction of $CF_3O_2^{\cdot}$ 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

$$CF_3O_2^{\cdot} + NO \rightarrow CF_3O^{\cdot} + NO_2$$

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 $\dot{C}F_3$ 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 $CF_3O_2^{\cdot}$ radicals with NO proceeded, presumably through the expected intermediate CF_3OONO, to yield COF_2 and FNO_2

$$CF_3O_2^{\cdot} + NO \rightarrow COF_2 + FNO_2$$

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

If, as expected, $CF_3O^{\cdot}$ is formed from the reaction of the $CF_3O_2^{\cdot}$ radical with NO, as well as from the photolysis of CF_3OOH, 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 $CF_3O^{\cdot}$ radical would then be with NO

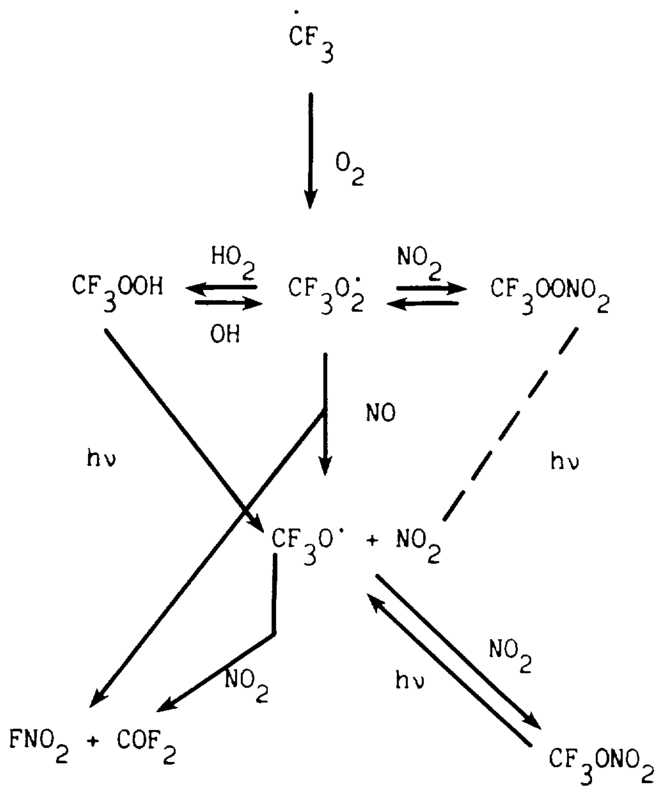
$$CF_3OO^{\cdot} + NO \xrightarrow{M} CF_3ONO$$

to form the nitrite, which is expected to rapidly photolyze back to the $CF_3O^{\cdot}$ radical and NO, and with NO_2

$$CF_3O^{\cdot} + NO_2 \xrightarrow{M} CF_3ONO_2$$

to form the nitrate. The tropospheric chemistry of this nitrate is not known, but unimolecular decomposition to COF_2 + FNO_2, photolysis and wet and/or dry deposition are the likely tropospheric removal pathways.

However, photolysis of CF_3Br in the presence of O_2 gave rise to the formation of COF_2 with a unit formation yield (Withnall and Sodeau, 1986), showing that under the conditions employed the $\dot{C}F_3$ radicals ultimately formed only COF_2. These data then suggest that the $CF_3O_2^{\cdot}$ radicals formed from the $\dot{C}F_3$ radical reaction with O_2 do yield COF_2. Possible tropospheric reactions of the $\dot{C}F_3$ radical are shown schematically below



Clearly, the reactions of the $CF_3O^{\cdot}$ radical under tropospheric conditions need to be investigated, and the formation of $CF_3O^{\cdot}$ from the reaction of $CF_3O_2^{\cdot}$ with NO confirmed. While it may be anticipated that the final product of the tropospheric degradation of the $\dot{C}F_3$ radical is 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 $\dot{C}F_2Cl$ radical formed from HCFC-22 are experimental data concerning its tropospheric reactions available. 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 ($R\dot{O}$) 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 ($CX_3C(O)Y$) and halogenated acetaldehydes (CX_3CHO) need to be determined. A quantitative understanding of physical removal processes for several of the product species, including the hydroperoxides, peroxynitrates, 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 ($\dot{R}$) Radicals

Under tropospheric conditions, alkyl and haloalkyl ($\dot{R}$) radicals react rapidly with O_2 to form the corresponding peroxy alkyl ($R\dot{O}_2$) radicals.

$$\dot{R} + O_2 \xrightarrow{M} R\dot{O}_2$$

For the methyl and ethyl radicals and the C_1 haloalkyl radicals, the rate constants at room temperature for these reactions with O_2 are in the fall-off region between second and third-order kinetics below atmospheric pressure. The low and high pressure rate constants k_0 and k_∞ 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 C_4 and C_5 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 C_1 alkyl and haloalkyl radicals are within a factor of $\sim$2-3 of the limiting high-pressure rate constant k_∞ at the temperatures and pressures applicable to the troposphere. The rate constants for the $\geq C_2$ 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 O_2 of $>5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} throughout the troposphere. Since the O_2 concentration in the troposphere is $\geq 10^{18}$ molecule cm^{-3}, the lifetime of the alkyl and haloalkyl radicals are $<2 \times 10^{-6}$ s and reaction with O_2 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.

Table 2. Low- and high-pressure rate constants k_0 and k_{∞} 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 ($R^{\cdot}$) radicals with O_2

				10^{12} x k (cm^3 $molecule^{-1}$ s^{-1})[a]		
$R^{\cdot}$	k_0(cm^6 $molecule^{-2}$ s^{-1})	k_{∞}(cm^3 $molecule^{-1}$ s^{-1})	F (298 K)	300 K 760 Torr	220 K 100 Torr	Reference
$\dot{C}H_3$	$8\text{x}10^{-31}$ $(T/300)^{-(3.3 \pm 1)}$	$2.2 \text{ x } 10^{-12}$ $(T/300)^{1 \pm 1}$	0.27	1.0	0.76	IUPAC (1989)
$C_2H_5^{\cdot}$	$2.0\text{x}10^{-28}$ $(T/300)^{-(3.8 \pm 1)}$	$5\text{x}10^{-12}$	0.7	4.8	4.8	IUPAC (1989)
$CH_3CH_2\dot{C}H_2$		$6\text{x}10^{-12}$		6		IUPAC (1989)
$(CH_3)_2\dot{C}H$		$1.5\text{x}10^{-11}$		15		IUPAC (1989)
$CH_3CH_2CH_2\dot{C}H_2$		$(7.5 \pm 1.4)\text{x}10^{-12}$[b] (room temperature)				Lenhardt et al. (1980)
$CH_3CH_2\dot{C}HCH_3$		$(1.66 \pm 0.22) \text{ x } 10^{-11}$[b] (room temperature)				Lenhardt et al. (1980)
$(CH_3)_3\dot{C}$		$(2.34 \pm 0.39)\text{x}10^{-11}$[b] (room temperature)				Lenhardt et al. (1980)
$(CH_3)_2CH\dot{C}H_2$		$(2.9 \pm 0.7)\text{x}10^{-12}$[b] (298 ± 2 K)				Wu and Bayes (1986)
$(CH_3)_3C\dot{C}H_2$		$(1.6 \pm 0.3)\text{x}10^{-12}$[b] (298 ± 2 K)				Wu and Bayes (1986)
		$2.1\text{x}10^{-12}$ $(T/300)^{-2.1}$[b] (266-374 K)				Xi et al. (1988)
$\dot{C}F_3$	$1.9\text{x}10^{-29}$ $(T/300)^{-(4.7 \pm 1)}$	$1\text{x}10^{-11}$	0.4-0.5	7.9	8.2	IUPAC (1989)
$\dot{C}FCl_2$	$5\text{x}10^{-30}$ $(T/300)^{-(4 \pm 2)}$	$6\text{x}10^{-12}$	0.6	4.7	4.7	IUPAC (1989)
$\dot{C}Cl_3$	$1.5\text{x}10^{-30}$ $(T/300)^{-(4 \pm 2)}$	$5\text{x}10^{-12}$	0.25	2.0	2.0	IUPAC (1989)

a Calculated from fall-off expression.

b Rate constants obtained at 1-4 Torr total pressure; expected to be close to the high pressure limit.

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 radical

$$\begin{tikzcd} R^{\cdot} + O_2 = & {[RO_2^{\cdot}]^*} \arrow[r] \arrow[d, "M"] & HO_2 + \text{alkene} \\ & RO_2^{\cdot} & \end{tikzcd}$$

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 ($RO_2^{\cdot}$) Radicals

Under tropospheric conditions, $RO_2^{\cdot}$ radicals are expected to react with NO, NO_2, HO_2 radicals, $RO_2^{\cdot}$ radicals and acyl peroxy ($RCO_3^{\cdot}$) radicals, with the reaction with $RO_2^{\cdot}$ 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 $RO_2^{\cdot}$ radicals depends on the rate constants for the individual reactions and the concentrations of NO, NO_2, HO_2 radicals and the various $RO_2^{\cdot}$ and $RCO_3^{\cdot}$ 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 ($RO_2^{\cdot}$) 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 $C_2H_5O_2^{\cdot}$ is similar to that recommended by NASA (1987) and IUPAC (1989) for $CH_3O_2^{\cdot}$, 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 $CH_3O_2^{\cdot}$:

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

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 $CH_3O_2^{\cdot}$ with NO proceeds by

$$CH_3O_2^{\cdot} + NO \rightarrow CH_3O^{\cdot} + NO_2$$

(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 $C_2H_5O_2^{\cdot}$ radicals with NO yields NO_2 with a yield of ≥ 0.80. However, for the larger alkyl peroxy radicals, the reaction pathway

$$RO_2^{\cdot} + NO \rightarrow [ROONO] \rightarrow RONO_2$$

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

$RO_2^{\cdot}$	k(cm^3 molecule^{-1} s^{-1})	10^{12} x k (cm^3 molecule^{-1} s^{-1})	at T (K)	Reference
$CH_3O_2^{\cdot}$	$4.2 \times 10^{-12}\, e^{(180 \pm 180)/T}$	7.6	298	NASA (1987), IUPAC (1989)
$C_2H_5O_2^{\cdot}$		2.66 ± 0.17	Room Temperature	Adachi and Basco (1979a)
		8.9 ± 3.0	298	Plumb et al. (1982)
$(CH_3)_2CHO_2^{\cdot}$		3.5 ± 0.4	Room Temperature	Adachi and Basco (1982)
$(CH_3)_2CO_2^{\cdot}$		>1	298	Anastasi et al. (1978)
$CF_3O_2^{\cdot}$	$1.6 \times 10^{-11}\ (T/300)^{-1.2}$	16	298	IUPAC (1989)
$CF_2ClO_2^{\cdot}$	$1.6 \times 10^{-11}\ (T/300)^{-1.5}$	16	298	IUPAC (1989)
$CFCl_2O_2^{\cdot}$	$1.5 \times 10^{-11} (T/300)^{-1.3}$	15	298	IUPAC (1989)
$CCl_3O_2^{\cdot}$	$1.8 \times 10^{-11}\ (T/300)^{-1.0}$	18	298	IUPAC (1989)

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 $C_2H_5O_2^\bullet$ + 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 $CF_3O_2^\bullet$, $CF_2ClO_2^\bullet$, $CFCl_2O_2^\bullet$ and $CCl_3O_2^\bullet$ radicals suggest that the major reaction pathway is

$$CX_3O_2^\bullet + NO \rightarrow CX_3O^\bullet + NO_2 \quad (X = F \text{ and/or } Cl)$$

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 NO_2. The rate constant data obtained by absolute methods for the reactions of alkyl peroxy and haloalkyl peroxy radicals with NO_2 are given in Table 4. The studies of Sander and Watson (1980) and Ravishankara et al. (1980) for $CH_3O_2^\bullet$ and of Lesclaux and Caralp (1984), Lesclaux et al. (1986) and Caralp et al. (1988) for the $CX_3O_2^\bullet$ radicals (X = F and/or Cl) show that at room temperature

Table 4. Low- and high-pressure rate constants k_0 and k_∞ 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 ($RO_2^\bullet$) radicals with NO_2

				10^{12} x k (cm^3 molecule^{-1} s^{-1})[a]		
$R^\bullet$	k_0(cm^6 molecule^{-2} s^{-1})	k_∞(cm^3 molecule^{-1} s^{-1})	F (298 K)	300 K 760 Torr	220 K 100 Torr	Reference
$CH_3O_2^\bullet$	2.3×10^{-30} $(T/300)^{-(4.0\pm2)}$	8×10^{-12}	0.4	4.1	4.0	IUPAC (1989)
$C_2H_5O_2^\bullet$		$(1.25\pm0.07)\times10^{-12}$[b] (room temperature)				Adachi and Basco (1979b)
$(CH_3)_2CHO_2^\bullet$		$(5.65\pm0.17)\times10^{-12}$[b] (room temperature)				Adachi and Basco (1982)
$(CH_3)_3CO_2^\bullet$		$\geq5\times10^{-13}$ (298 K)				Anastasi et al. (1978)
$CF_3O_2^\bullet$	2.7×10^{-29} $(T/300)^{-(5\pm2)}$	9×10^{-12} $(T/300)^{-(0.7\pm1)}$	0.49	7.6	9.6	IUPAC (1989)
$CF_2ClO_2^\bullet$	4.0×10^{-29} $(T/300)^{-(5\pm2)}$	1.0×10^{-11} $(T/300)^{-(0.7\pm1)}$	0.45	8.4	11	IUPAC (1989)
$CFCl_2O_2^\bullet$	5.5×10^{-29} $(T/300)^{-(5\pm1)}$	8.3×10^{-12} $(T/300)^{-(0.7\pm1)}$	0.42	7.1	9.0	IUPAC (1989)
$CCl_3O_2^\bullet$	9.2×10^{-29} $(T/300)^{-(6\pm2)}$	1.5×10^{-11} $(T/300)^{-(0.3\pm1)}$	0.32	12	14	IUPAC (1989)

a Calculated from fall-off expressions.

b Assumed to be erroneously low due to neglect of absorption of RO_2NO_2 products.

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_∞ 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_∞, 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_∞ for the reactions of $RO_2^{\cdot}$ radicals with NO_2 are,

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

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).

$$RO_2^{\cdot} + NO_2 \overset{M}{\rightleftarrows} ROONO_2$$

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 $CH_3O_2^{\cdot}$ and $C_2H_5O_2^{\cdot}$, and these data are given in Table 5. The IUPAC (1989) recommended rate constant expressions for these reactions are $k(CH_3O_2^{\cdot} + HO_2) = 1.7 \times 10^{-13} e^{1000/T}$ cm^3 molecule^{-1} s^{-1} (4.9×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K) and $k(C_2H_5O_2^{\cdot} + HO_2) = 6.5 \times 10^{-13} e^{650/T}$ cm^3 molecule^{-1} s^{-1} (5.8×10^{-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 $RO_2^{\cdot} + HO_2$ reactions are similar to those for these two reactions, a room temperature rate constant of

$$k(RO_2^{\cdot} + HO_2) \cong 5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K}$$

and

$$k(RO_2^{\cdot} + HO_2) \cong 3.4 \times 10^{-13} e^{800/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

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_3Cl and CH_2Cl_2 that the room temperature rate constant for the reaction of the HO_2 radical with $CH_2ClO_2^{\cdot}$ is significantly slower than the corresponding HO_2 radical reaction rate constant for the $CHCl_2O_2^{\cdot}$ radical.

These reactions have been assumed to proceed by the pathway.

$$RO_2^{\cdot} + HO_2 \rightarrow ROOH + O_2$$

Table 5. Absolute rate constants for the reactions of alkyl peroxy ($RO_2^{\cdot}$) radicals with the HO_2 radical

$RO_2^{\cdot}$	10^{12} x k (cm^3 $molecule^{-1}$ s^{-1})	at T (K)	Reference
$CH_3O_2^{\cdot}$	8.5 ± 1.2	274	Cox and Tyndall (1980)
	6.5 ± 1.0	298	
	3.5 ± 0.5	338	
	3.5[a]	298	McAdam et al. (1987)
	2.9 ± 0.4	298	Kurylo et al. (1987)
	6.8 ± 0.5	228	Dagaut et al. (1988a)
	5.5 ± 0.3	248	
	4.1 ± 0.3	273	
	2.4 ± 0.5	340	
	2.1 ± 0.3	380	
	5.4 ± 1.1	300	Jenkin et al. (1988)
	6.8 ± 0.9	303	
$C_2H_5O_2^{\cdot}$	6.3 ± 0.9	295	Cattell et al. (1986)
	7.3 ± 1.0	248	Dagaut et al. (1988b)
	6.0 ± 0.5	273	
	5.3 ± 1.0	298	
	3.4 ± 1.0	340	
	3.1 ± 0.5	380	

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 $CD_2O_2^{\cdot}$ with the HO_2 radical, and postulated the additional reaction pathway,

$$CD_2O_2^{\cdot} + HO_2 \rightarrow DCDO + HDO + O_2$$

with this channel contributing ∿40% of the overall reaction at room temperature.

D. Reaction with Alkyl and Haloalkyl Peroxy ($RO_2^{\cdot}$) and Acyl Peroxy ($RCO_3^{\cdot}$) 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 $CH_3O_2^{\cdot}$ 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 $RO_2^{\cdot}$ or $RCO_3^{\cdot}$ radical with which these haloalkyl peroxy radicals will react with will be the $CH_3O_2^{\cdot}$ radical, and the limited data available (Table 6) suggest a rate constant for the reaction of the $CH_3O_2^{\cdot}$ radical with other $RO_2^{\cdot}$ radicals of

$$k(RO_2^{\cdot} + CH_3O_2^{\cdot}) \cong 2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}$$

with an uncertainty of ~ ± a factor of 5.

Table 6. Rate constants, $k = Ae^{-B/T}$, for the gas-phase combination reactions of alkyl and haloalkyl peroxy ($RO_2^{\cdot}$) radicals with $RO_2^{\cdot}$ and $RCO_3^{\cdot}$ radicals

Reaction	10^{13} x A (cm^3 molecule^{-1} s^{-1})	B (K)	10^{13} x k (298 K) (cm^3 molecule^{-1} s^{-1})	Reference
$CH_3O_2^{\cdot} + CH_3O_2^{\cdot}$	1.7	-220 ± 220	3.6	IUPAC (1989)
$C_2H_5O_2^{\cdot} + C_2H_5O_2^{\cdot}$	1.2	110^{+300}_{-100}	0.86	IUPAC (1989)
$CH_3CH_2CH_2O_2^{\cdot} + CH_3CH_2CH_2O_2^{\cdot}$			3	IUPAC (1989)
$(CH_3)_2CHO_2^{\cdot} + (CH_3)_2CHO_2^{\cdot}$	16	2200 ± 300	0.01	IUPAC (1989)
$(CH_3)_3CO_2^{\cdot} + (CH_3)_3CO_2^{\cdot}$	1700	4775	0.00019	Kirsch et al. (1978)
$CH_3O_2^{\cdot} + (CH_3)_3CO_2^{\cdot}$			1.0 ± 0.5	Parkes (1975)
$CH_2ClCH_2O_2^{\cdot} + CH_2ClCH_2O_2^{\cdot}$	1.1	-1020 ± 170	35.7 ± 5.7	Dagaut et al. (1988c)
$CH_2ClO_2^{\cdot} + CH_2ClO_2^{\cdot}$	3.1	-735 ± 95	37.8 ± 4.5	Dagaut et al. (1988d)
$CH_2FO_2^{\cdot} + CH_2FO_2^{\cdot}$	3.3	-700 ± 100	30.7 ± 6.5	Dagaut et al. (1988d)
$CH_3O_2^{\cdot} + CH_3CO_3^{\cdot}$			110	IUPAC (1989)

These combination reactions of $RO_2^{\cdot}$ radicals can proceed by the reaction channels

$$R_2R_2CHO_2^{\cdot} + R_3R_4CHO_2^{\cdot} \rightarrow R_1R_2CHO^{\cdot} + R_3R_4CHO^{\cdot} + O_2 \tag{a}$$

$$R_1R_2CHO_2^{\cdot} + R_3R_4CHO_2^{\cdot} \rightarrow R_1R_2CHOH + R_3R_4CO + O_2 \tag{b}$$

$$R_1R_2CHO_2^{\cdot} + R_3R_4CHO_2^{\cdot} \rightarrow R_1R_2CHOOCHR_3R_4 + O_2 \tag{c}$$

with channel (b) not being accessible for tertiary $RO_2^{\cdot}$ radicals. Product data are available for the self-reactions of $CH_3O_2^{\cdot}$, $C_2H_5O_2^{\cdot}$, $(CH_3)_2CHO_2^{\cdot}$ and $(CH_3)_3CO_2^{\cdot}$ radicals (Kirsch and Parkes, 1981; Niki et al., 1981, 1982; Anastasi et al., 1983; IUPAC, 1989). For the primary and secondary $RO_2^{\cdot}$ radicals, the room temperature rate constant ratios k_a/k and k_b/k (where $k = k_a + k_b + k_c$) are both ~0.5, with $k_c < 0.1$. For the reaction of the $(CH_3)_3CO_2^{\cdot}$ radical with the $CH_3O_2^{\cdot}$ 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 $CHCl_2O_2^{\cdot}$ radical, and further product data are required for these $RO_2^{\cdot}$ radical reactions.

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 ($RO^{\cdot}$) Radicals

For the C_1 and C_2 haloalkoxy radicals involved in the tropospheric degradation reactions of the HCFCs and HFCs considered in this article, the reactions of concern are with O_2,

$$R_1R_2CHO^{\cdot} + O_2 \rightarrow R_1R_2CO + HO_2$$

unimolecular decomposition,

$$R_1R_2CH\dot{O} \rightarrow R_1^{\cdot} + R_2CHO$$

and reaction with NO and NO_2.

$$R_1R_2CHO^{\cdot} + NO \rightarrow \begin{cases} R_1R_2CHONO \\ R_1R_2CO + HNO \end{cases}$$

$$R_1R_2CHO^{\cdot} + NO_2 \rightarrow \begin{cases} R_1R_2CHONO_2 \\ R_1R_2CO + HONO \end{cases}$$

A. Reaction with O_2. Absolute rate constants for the reactions of alkoxy radicals with O_2 are available only for the $CH_3O^{\cdot}$, $C_2H_5O^{\cdot}$ and $(CH_3)_2CHO^{\cdot}$ 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 ≤ 300 K (the Arrhenius plot exhibits marked curvature at temperatures >500 K).

$$k(CH_3O^{\cdot} + O_2) = 5.5 \times 10^{-14}\ e^{-1000/T}\ cm^3\ molecule^{-1}\ s^{-1}$$

This recommended temperature expression is that of Lorenz et al. (1985), and is similar to the NASA (1987) and IUPAC (1989) recommendations of $k(CH_3O^{\cdot} + O_2) = 3.9 \times 10^{-14}\ e^{-900/T}\ cm^3\ molecule^{-1}\ s^{-1}$ and $7.2 \times 10^{-14}\ e^{-1080/T}\ cm^3\ molecule^{-1}\ s^{-1}$, respectively. Combining the rate constants of Gutman et al. (1982) at 296 and 353 K for the $C_2H_5O^{\cdot}$ radical with a preexponential factor of $3.7 \times 10^{-14}\ cm^3\ molecule^{-1}\ s^{-1}$ leads to

$$k(RCH_2O^{\cdot} + O_2) = 3.7 \times 10^{-14}\ e^{-460/T}\ cm^3\ molecule^{-1}\ s^{-1}$$

(Atkinson, 1989a). Similarly, the data of Balla et al. (1985) for the $(CH_3)_2CHO^{\cdot}$ radical can be combined with a preexponential factor of $1.8 \times 10^{-14}\ cm^3\ molecule^{-1}\ s^{-1}$ to yield (Atkinson, 1989a)

Table 7. Absolute rate constants, k, for the gas-phase reactions of alkoxy ($RO^{\cdot}$) radicals with O_2

$RO^{\cdot}$	10^{15} x k (cm^3 molecule^{-1} s^{-1})	T (K)	Reference
$CH_3O^{\cdot}$	<2	295	Sanders et al. (1980)
	4.7	413	Gutman et al. (1982)
	6.0	475	
	10.7	563	
	12.7	608	
	$55\ e^{-1000/T}$	298-450	Lorenz et al. (1985)
	1.9^a	298	
	$[1.5 \times 10^5\ e^{-6028/T} + 36\ e^{-880/T}]^b$	298-973	Wantuck et al. (1987)
	2.1	298	
$C_2H_5O^{\cdot}$	8.0	296	Gutman et al. (1982)
	9.8	353	
$(CH_3)_2CHO^{\cdot}$	$15.1\ e^{-196/T}$	294-384	Balla et al. (1985)
	7.8^a	298	

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).

$$k(R_1R_2CHO^{\cdot} + O_2) = 1.8 \times 10^{-14}\ e^{-260/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

These rate constant expressions for the $RCH_2O^{\cdot}$ and $R_1R_2CHO^{\cdot}$ alkoxy radicals are assumed to be applicable to haloalkoxy radicals. The reaction rate of primary and secondary $RO^{\cdot}$ radicals with O_2 at 298 K and 760 Torr total pressure of air are then essentially identical at 4.0×10^4 s^{-1}.

B. Alkoxy Radical Decomposition. Rate data for the decompositions of the methoxy, ethoxy and the C_1 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 $CHF_2O^{\cdot}$ radical are those calculated by Rayez et al. (1987). The experimentally determined lower limits to the decomposition rate constants for the $CF_2ClO^{\cdot}$, $CFCl_2O^{\cdot}$ and $CHCl_2O^{\cdot}$ radicals are in good agreement with the calculated rates. The data in Table 8 show that:

(a) H atom elimination from the C_1 alkoxy radicals is extremely slow ($< 10^{-5}$ s^{-1} at 298 K). When compared to the reaction rate of these species with O_2 of 4×10^4 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 C_2 alkoxy radicals.

(b) For the $CF_2ClO^{\cdot}$, $CFCl_2O^{\cdot}$ and $CCl_3O^{\cdot}$ 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 = $Ae^{-B/T}$, for C_1 and C_2 alkoxy and haloalkoxy ($RO^{\cdot}$) radicals

Reaction	A (s^{-1})^a	B (K)^a	k (s^{-1}) at	T (K)	Reference
$CH_3O^{\cdot} \rightarrow HCHO + H$	2.4×10^{13}	14450	2×10^{-8b}	298	Batt et al. (1986)
$CH_3CH_2O^{\cdot} \rightarrow HCHO + \dot{C}H_3$	8×10^{13}	10800	0.015^b	298	Batt (1987)
$CF_3O^{\cdot} \rightarrow COF_2 + F$	5×10^{13}	14300	7×10^{-8b}	298	Batt et al. (1986)
$CF_2ClO^{\cdot} \rightarrow COF_2 + Cl$	$\sim 1 \times 10^{14}$	6240^c	8×10^{4b}	298	Rayez et al. (1987)
			$>7 \times 10^5$	Room temperature	Carr et al. (1986)
$CFCl_2O^{\cdot} \rightarrow COFCl + Cl$	$\sim 1 \times 10^{14}$	5335^c	7×10^{4b}	253	Rayez et al. (1987)
			$>3 \times 10^4$	253	Lesclaux et al. (1987)
$CCl_3O^{\cdot} \rightarrow COCl_2 + Cl$	$\sim 1 \times 10^{14}$	4880^c	8×10^{4b}	233	Rayez et al. (1987)
			$>1 \times 10^5$	233	Lesclaux et al. (1987)
$CHCl_2O^{\cdot} \rightarrow HC(O)Cl + Cl$	$\sim 1 \times 10^{14}$	5940^c	2×10^{5b}	298	Rayez et al. (1987)
			$>10^5$	298	Niki et al. (1980)
$CH_2ClO^{\cdot} \rightarrow HCHO + Cl$	$\sim 1 \times 10^{14}$	10320^c	0.1^b	298	Rayez et al. (1987)
$CHFClO^{\cdot} \rightarrow HC(O)F + Cl$	$\sim 1 \times 10^{14}$	5230^c	2×10^{-6b}	298	Rayez et al. (1987)
$CHF_2O^{\cdot} \rightarrow COF_2 + H$	$\sim 1 \times 10^{14}$	17770^c	1×10^{-12b}	298	Rayez et al. (1987)
$CHFClO^{\cdot} \rightarrow COFCl + H$	$\sim 1 \times 10^{14}$	14800^c	3×10^{-8b}	298	Rayez et al. (1987)
$CH_2ClO^{\cdot} \rightarrow HC(O)Cl + H$	$\sim 1 \times 10^{14}$	14900^c	2×10^{-8b}	298	Rayez et al. (1987)
$CHCl_2O^{\cdot} \rightarrow COCl_2 + H$	$\sim 1 \times 10^{14}$	13340^c	4×10^{6b}	298	Rayez et al. (1987)
$CH_2FO^{\cdot} \rightarrow HC(O)F + H$	$\sim 1 \times 10^{14}$	14540^c	6×10^{-8b}	298	Rayez et al. (1987)

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 $CHCl_2O^{\cdot}$ 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 $CH_2ClO^{\cdot}$ radical is slow and the reaction with O_2

$$CH_2ClO^{\cdot} + O_2 \rightarrow HC(O)Cl + HO_2$$

dominates 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 C_2 haloalkoxy radicals, Sanhueza et al. (1976) concluded that:

(a) For $CX_3CH_2O^{\cdot}$ 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 O_2 will dominate.

(b) For $CX_3CF_2O^{\cdot}$ 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

$$CFCl_2CFClO^{\cdot} \rightarrow CFCl_2C(O)F + Cl$$

$$CF_2ClCCl_2O^{\cdot} \rightarrow CF_2ClC(O)Cl + Cl$$

$$CCl_3CF_2O^{\cdot} \rightarrow COF_2 + \dot{C}Cl_3$$

$$CF_2ClCF_2O^{\cdot} \rightarrow COF_2 + \dot{C}F_2Cl$$

For tropospheric conditions, the important parameters are the rate constant ratios for the reactions of the alkoxy and haloalkoxy radicals with O_2 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 $\sim 1 \times 10^{14}$ 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, $CH_2ClO^{\cdot}$ and $CH_2ClO^{\cdot}$ 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 $CH_2ClO^{\cdot}$ radical, consistent with Table 8).

The differences in the heats of reaction, $\{[\Delta HO_{2\,\mathrm{reaction}} - \Delta H_{\mathrm{decomposition}}]\} = \Delta(\Delta H)$, in kcal mol^{-1} (rounded to the nearest kcal mol^{-1}) are then: $C_2H_5O^{\cdot}$, 45; 2-butoxy, 42; $CH_2ClO^{\cdot}$, 48; and $CHCl_2O^{\cdot}$, 30. At room temperature and atmospheric pressure of air, the removal processes of these $RO^{\cdot}$ radicals are: $C_2H_5O^{\cdot}$, reaction with O_2 (Carter and Atkinson, 1985); 2-butoxy, reaction with O_2 and decomposition by C-C bond cleavage in an approximately 60%/40% split (Carter and Atkinson, 1985; Atkinson, 1989a); $CH_2ClO^{\cdot}$, reaction with O_2 (Niki et al., 1980); and $CHCl_2O^{\cdot}$, 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 O_2 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 O_2)/decomposition 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 ($RO^{\cdot}$) radicals: thermochemistries of reactions with O_2, decomposition and H and Cl atom elimination

$RO^{\cdot}$	Reaction	$\Sigma\Delta H_f$ (Products) kcal mol^{-1a}
$CH_3CH_2O^{\cdot}$	$CH_3CH_2O^{\cdot} + O_2 \rightarrow CH_3CHO + HO_2$	-36.1
	$CH_3CH_2O^{\cdot} \rightarrow CH_3CHO + H$	12.5
	$CH_3CH_2O^{\cdot} \rightarrow \dot{C}H_3 + HCHO$	8.8
$CH_3CH_2CH(\dot{O})CH_3$	$CH_3CH_2CH(\dot{O})CH_3 + O_2 \rightarrow CH_3CH_2COCH_3 + HO_2$	-53.4
	$CH_3CH_2CH(\dot{O})CH_3 \rightarrow C_2H_5^{\cdot} + CH_3CHO$	-11.6
$CH_2ClO^{\cdot}$	$CH_2ClO^{\cdot} + O_2 \rightarrow HC(O)Cl + HO_2$	-44.7
	$CH_2Cl\dot{O} \rightarrow HC(O)Cl + H$	3.9
	$CH_2ClO^{\cdot} \rightarrow HCHO + Cl$	3.0
$CHCl_2O^{\cdot}$	$CHCl_2O^{\cdot} + O_2 \rightarrow COCl_2 + HO_2$	-49.1
	$CHCl_2O^{\cdot} \rightarrow COCl_2 + H$	-0.5
	$CHCl_2O^{\cdot} \rightarrow HC(O)Cl + Cl$	-19.2

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 $\Delta H_f(CH_3CH_2COCH_3) = 56.9$ kcal mol^{-1} calculated by the group additivity method of Benson (1976).

For the $CF_3O^{\cdot}$ radical, reaction with O_2 cannot occur and F atom elimination is endothermic by 24 kcal mol^{-1} (Batt and Walsh, 1983; IUPAC, 1989).

C. Reactions with NO and NO_2. Absolute rate constant data are available only for the reactions of NO and NO_2 with the $CH_3O^{\cdot}$ and $(CH_3)_2CHO^{\cdot}$ radicals (Sanders et al., 1980; Balla et al., 1985; McCaulley et al., 1985; Zellner, 1987). For the reaction of the $CH_3O^{\cdot}$ radical with NO, the data of Zellner (1987) yield a high pressure rate constant of $k_{\infty} = 1.4 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K [IUPAC (1989) recommend 2×10^{-11} cm^3 $molecule^{-1}$ s^{-1}, independent of temperature over the range 200-400 K, with an uncertainty of ± 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 $CH_3O^{\cdot}$ radical with NO_2, carried out at 0.6-4 Torr total pressure. The rate constants were in the fall-off regime, and the abstraction channel was concluded to have a rate constant of $9.6 \times 10^{-12} e^{-1150/T}$ cm^3 molecule^{-1} s^{-1} over the temperature range 220-473 K (2.0×10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K).

The rate data of Balla et al. (1985) for the reactions of the $(CH_3)_2CHO^{\cdot}$ radical with NO and NO_2 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 [$k = 1.22 \times 10^{-11} e^{312/T}$ cm^3 molecule^{-1} s^{-1} for the reaction with NO and $1.5 \times 10^{-11} e^{252/T}$ cm^3 molecule^{-1} s^{-1} for reaction with NO_2].

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 NO_2 that,

$$k(RO^{\cdot} + NO) = k(RO^{\cdot} + NO_2) = 1.3 \times 10^{-11} e^{300/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with these reactions proceeding essentially entirely by addition,

$$RO^{\cdot} + NO \xrightarrow{M} RONO$$

$$RO^{\cdot} + NO_2 \xrightarrow{M} RONO_2$$

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).

$$RONO + h\nu \rightarrow RO^{\cdot} + NO$$

Hence, the $RO^{\cdot}$ radical reaction with NO is of no actual importance for tropospheric purposes.

4.4. Reactions of the Alkyl and Haloalkyl Peroxynitrates ($ROONO_2$)

Under tropospheric conditions, the loss processes of the alkyl and haloalkyl peroxynitrates ($ROONO_2$) 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 ($ROONO_2$),

$$ROONO_2 \overset{M}{\rightleftarrows} RO_2^{\cdot} + NO_2$$

with the $RO_2^{\cdot}$ radical and NO_2 being in thermal equilibrium with the peroxynitrate. For the C_1 peroxynitrates, these thermal decomposition reactions are in the fall-off regime between first- and second-order kinetics under the temperature and pressure conditions applicable to the troposphere. The low- and high-pressure rate constants k_0 and k_∞, 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 peroxynitrate [a mixture of $CH_3CH_2CH_2OONO_2$ and $(CH_3)_2CHOONO_2$] (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_∞.

For the C_1 haloalkyl peroxynitrates studied, the decomposition rates under tropospheric conditions are within 10-20% of the high-pressure rate constant k_∞, with the lifetimes of these haloalkyl peroxynitrates with respect to thermal decomposition increasing from ~10 s at 298 K to ~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 peroxynitrate, the $R\dot{O}_2$ radical and NO_2). The corresponding lifetimes of the alkyl peroxynitrates, with respect to thermal decomposition, are shorter by approximately one order of magnitude at room temperature and two orders of magnitude at 220 K. The thermal decomposition rate constants are approximately given by

Table 10. Low- and high-pressure rate constants k_0 and k_∞ and the broadening factor F at 298 K for the thermal decomposition of alkyl and haloalkyl peroxynitrates, $ROONO_2$, together with calculated rate constants at 298 K and 760 Torr total pressure and 220 K and 100 Torr total pressure

				k (s^{-1})		
$ROONO_2$	**k_0 (cm^3 $molecule^{-1}$ s^{-1})**	**k_∞ (s^{-1})**	**F (298 K)**	**298 K 760 Torr**	**220 K 100 Torr**	**Reference**
CH_3OONO_2	$9 \times 10^{-5} e^{-9690/T}$	$1.1 \times 10^{16} e^{-10560/T}$	0.4	1.8	5.4×10^{-6}	IUPAC (1989)
$C_3H_7OONO_2$		$3.3 \times 10^{14} e^{-9965/T}$[a]		1.0[a]	7×10^{-6}[a]	Edney et al. (1979)
$CF_2ClOONO_2$	$5.6 \times 10^{-4} e^{-9310/T}$	$1.0 \times 10^{16} e^{-11880/T}$	0.4	0.046	3.4×10^{-8}	IUPAC (1989)
$CFCl_2OONO_2$	$3 \times 10^{-3} e^{-10570/T}$	$2.1 \times 10^{16} e^{-11980/T}$	0.4	0.065	4.3×10^{-8}	IUPAC (1989)
CCl_3OONO_2	$5.6 \times 10^{-4} e^{-9310/T}$	$9.1 \times 10^{14} e^{-10820/T}$	0.2	0.14	3.6×10^{-7}	IUPAC (1989)

a At 700 Torr total pressure of air; uncertain by at least a factor of 2 because of uncertainties in the rate constant ratio $k(R\dot{O}_2 + NO)/k(R\dot{O}_2 + NO_2)$.

$$k_\infty(\text{haloalkyl peroxynitrate}) \cong 1 \times 10^{15} e^{-11000/T} s^{-1}$$

$$k_\infty(\text{alkyl peroxynitrate}) \cong 2 \times 10^{15} e^{-10300/T} s^{-1}$$

B. Photolysis. The absorption cross-sections of CH_3OONO_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 $CFCl_2OONO_2$ and CCl_3OONO_2 over the wavelength range 210-280 nm by Morel et al. (1980). The absorption cross-sections decrease with increasing wavelength above ~240 nm, with cross-sections ≤ 1 x 10^{-19} cm^2 at 280 nm for all three of these peroxynitrates (Morel et al., 1980; Baulch et al., 1982).

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DEGRADATION MECHANISMS OF SELECTED HYDROCHLOROFLUOROCARBONS IN THE ATMOSPHERE:
AN ASSESSMENT OF THE CURRENT KNOWLEDGE

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1. INTRODUCTION

Volatile organic compounds are mainly degraded in the troposphere by attack of OH with abstraction of H atoms or addition to unsaturated linkages. The CFC's (chlorofluorocarbons) do not contain these reactive sites and consequently cannot be degraded in this way in the lower atmosphere. This results in pollution of the stratosphere by these molecules and attendant problems for ozone. The proposed replacements for CFC's, the HCFC's (hydrochlorofluorocarbons) and HFC's (hydrofluorocarbons), contain at least one hydrogen atom in the molecule, which confers on these compounds a much greater sensitivity toward oxidation by OH in the troposphere and in the lower stratosphere, resulting in much shorter atmospheric lifetimes than the CFC's. Consequently the Ozone Depletion Potential and the Atmospheric Warming Potential are reduced substantially compared to the CFC's. We shall examine in this paper all the possible degradation processes of the HCFC's and HFC's proposed to replace the CFC's, with the principal aim of identifying chlorine- and fluorine-containing products which are stable under tropospheric conditions.

2. THE ATMOSPHERIC DEGRADATION PROCESS

The general processes involved in the degradation of organic compounds in the atmosphere are outlined in detail in Appendix I. We summarise here the relevant reactions for halogen substituted alkanes of which the HCFC's and HFC's are typical examples. The atmospheric degradation generally begins in the troposphere by the H-abstraction reaction by OH radicals. In addition, haloalkanes may be degraded by H-abstraction by O^1D atoms in the lower stratosphere and this minor process is included for completeness. The hydrogen abstraction results in the formation of a water molecule and a haloalkyl radical which rapidly combines with oxygen, yielding a haloalkyl peroxy radical.

$$RH + OH \rightarrow R + H \tag{1}$$

$$RH + O(^1D) \rightarrow R + OH \tag{2}$$

$$R + O_2 + M \rightarrow RO_2 + M \tag{3}$$

In addition, $O(^1D)$ atoms can abstract a Cl atom from HCFC's, thereby generating a different peroxy radical

$$R'Cl + O(^1D) \rightarrow R' + ClO \tag{4}$$

$$R' + O_2 + M \rightarrow R'O_2 + M \tag{5}$$

All the studies published to date in the literature show that the oxidation of alkanes or haloalkanes always starts by the formation of a peroxy radical, according to the above mechanisms. It is therefore important to identify in the first place all the potentially important reaction pathways of peroxy radicals, under atmospheric conditions. Current knowledge shows that alkoxy radicals are the principal products formed eventually through these reactions. Alkoxy radicals can react in several ways and a major concern of this review is to examine the details of the possible reactions of these radicals, in order to identify all the stable products formed in this first oxidation sequence. In a further section, the subsequent degradation of these stable products will be discussed and an attempt made to identify their final fate.

DEGRADATION MECHANISMS

Very few studies have been reported in the literature on the oxidation mechanism of HCFC's and HFC's. However, we have now a fairly good understanding of oxidation processes of hydrocarbons, chlorofluoromethanes and some C_2 halocarbons, which allows an extrapolation to HCFC's and CFC's with a fairly good degree of confidence. Nevertheless, because of our lack of knowledge of the thermodynamics or the kinetics of the elementary reactions in HCFC and HFC degradation, there are considerable uncertainties on the reaction rates. Appendix II gives a discussion of the current state of knowledge of the kinetics of the important reactions in the atmospheric degradation of halocarbons.

I - CHEMISTRY OF PEROXY RADICALS DERIVED FROM HCFC's AND HFC's

I-1 - Structure of the peroxy radicals

As a result of a reduced number of hydrogen atoms in the HCFC and HFC molecules which have been considered as alternative compounds for replacement of CFC's, the hydrogen abstraction by OH or $O(^1D)$ leads to a single peroxy radical for each molecule, except for HFC 152a, which may yield two different radicals. Similarly, the chlorine atom abstraction by $O(^1D)$ in HCFC's lead to the formation of a single radical.

The compounds which are considered in this review and the corresponding peroxy radicals are listed in Table I.

Table I : List of compounds and corresponding peroxy radicals

Abstraction of:				H (by OH and O^1D)	Cl (by O^1D)
HCFC	22	$CHClF_2$	→	$CClF_2O_2$	CHF_2O_2
HCFC	123	$CHCl_2CF_3$	→	$CF_3CCl_2O_2$	CF_3CHClO_2
HCFC	124	$CHClFCF_3$	→	CF_3CClFO_2	CF_3CHFO_2
HCFC	141b	CCl_2FCH_3	→	$CCl_2FCH_2O_2$	CH_3CClFO_2
HCFC	142b	$CClF_2CH_3$	→	$CClF_2CH_2O_2$	$CH_3CF_2O_2$
HFC	125	CHF_2CF_3	→	$F_3CF_2O_2$	
HFC	134	CH_2FCF_3	→	CF_3CFHO_2	
HFC	152a	CHF_2CH_3	→	$CHF_2CH_2O_2$	
			→	$CH_3CF_2O_2$	

In the case of HFC 152a, two radicals may be formed, according to the site of the OH attack. No data are available to date for predicting which site of the molecule will preferentially react. However, in both cases, the subsequent reactions lead to formation of CF_2O, as shown in the next section.

I-2 - Reactions of peroxy radicals

Under atmospheric conditions, peroxy radicals principally react with NO, NO_2 and HO_2. Reactions with other peroxy radicals are also possible but, considering the low concentrations of these radicals, they can be neglected.

Reactions with NO

Most small alkylperoxy or halogen substitued alkylperoxy radicals react with NO by a single reaction channel, yielding an alkoxy radical and NO_2:

$$RO_2 + NO \rightarrow RO + NO_2 \qquad (6)$$

It can therefore be anticipated with confidence that all peroxy radicals listed in Table I react according to reaction (6) with the formation of an RO radical.

Reactions with NO_2

All peroxy radicals are known to react with NO_2, in a combination reaction forming a peroxynitrate

$$RO_2 + NO_2 + M \rightarrow RO_2NO_2 + M \qquad (7, -7)$$

This reaction is generally fast in the troposphere as its rate constant is close to the high pressure limit.

The principal fate of peroxynitrates is the thermal decomposition (-7) into the initial reactants. Photolysis may also occur in the stratosphere and the products are likely to be either $RO_2 + NO_2$ or $RO + NO_3$. Therefore, the only possible product resulting from reaction (7) is again an RO radical.

Reactions with HO_2

In the background troposphere, under conditions of low NO_x concentrations, peroxy radicals react with HO_2 according to reaction (8), forming an hydroperoxide:

$$RO_2 + HO_2 \rightarrow ROOH + O_2 \qquad (8)$$

The hydroperoxide is removed from the atmosphere either by physical removal (which is probably rather slow), or by photodissociation into RO + OH. The extent of the alternative pathway for reaction with HO_2,

$$CX_3CH_2O + HO_2 \rightarrow CX_3CHO + H_2O + O_2 \qquad (9)$$

is unknown for halogen substituted RO_2 radicals. The aldehyde produced is the same as that resulting from the RO radical formed via the hydroperoxide, so the nature of the overall degradation products is unaffected.

It can be concluded from this section that the reactions of peroxy radicals in the atmosphere essentially generate RO radicals, other products being of minor importance.

II - ALKOXY RADICALS DERIVED FROM HCFC's AND HFC's

II-1 - General reactions of alkoxy radicals

The RO radicals that we have to consider are those corresponding to peroxy radicals listed in Table I.

Only limited information can be found in the literature on the reactions of these radicals and it is therefore necessary to extrapolate our present knowledge concerning other radicals of this type. RO radicals may undergo three kinds of reactions under atmospheric conditions:

- Reaction with oxygen, for those radicals having at least one H atom on the carbon on the α position from the oxygen atom. These reactions yield a carbonyl compound and HO_2

$$RCXHO + O_2 \rightarrow RCXO + HO_2 \qquad (10)$$

(X = H,Cl or F)

- Chlorine atom detachment, yielding a carbonyl compound

$$RCXClO \rightarrow RCXO + Cl \qquad (11)$$

This reaction always occur in the case of radicals produced from the oxidation of chlorofluoromethanes.

- Thermal dissociation into a carbonyl compound and a radical.

$$RCX_2O \rightarrow R + CX_2O \qquad (12)$$

More details are given in Appendix II concerning these and other reactions of alkoxy radicals. Since most HCFC's and HFC's listed in Table I are C_2 compounds, particular attention is given in Appendix II to the reactions of CX_3CX_2O radicals and the information is used below for establishing the ways radicals relevant to this review react.

II-2 - Reactions of RO radicals produced from HCFC's and HFC's

The fate of the RO radicals corresponding to the peroxy radicals listed in Table I, are now considered in order to predict the carbonyl compounds which are formed under atmospheric conditions. Account is taken of the general properties of the halogenated RO radicals that are reviewed in Appendix II. These properties can be summarised as follows (X = H, Cl or F):

- CX_3CH_2O radicals react with oxygen by hydrogen abstraction;

- CX_3CCl_2O and CX_3CClFO undergo Cl atom detachment;

- CX_3CF_2O, CX_3CHClO and CX_3CHFO undergo a C-C bond cleavage. A small fraction of CX_3CHClO and CX_3CHFO may react with oxygen.

- CF_3O is assumed to yield CF_2O, although the reaction mechanism occuring in the atmosphere is unknown.

HCFC 22 $CHClF_2$

The RO radicals formed are $CClF_2O$ and CHF_2O which can only react by Cl atom detachment and with oxygen, respectively:

$$CClF_2O \rightarrow CF_2O + Cl$$

$$CHF_2O + O_2 \rightarrow CF_2O + HO_2$$

This last reaction is probably fairly slow and reactions of CHF_2O similar to those of CF_3O (see Appendix II) are possible.

Principal product from HCFC 22 : CF_2O

HCFC 123 $CHCl_2CF_3$

The RO radicals formed are CF_3CCl_2O and CF_3CHClO for which Cl atom detachment and C-C bond cleavage, respectively, are the most likely reactions :

$$CF_3CCl_2O \rightarrow CF_3CClO + Cl$$

$$CF_3CHClO \rightarrow CF_3 + CHClO$$

A small fraction of CF_3CHClO may react with oxygen, yielding again CF_3CClO.

Principal products from HCFC 123 : CF_3CClO, CF_2O (from CF_3) and $CHClO$.

HCFC 124 CF_3CHClF

The RO radicals formed are CF_3CClFO and CF_3CHFO, which undergo the same reactions as in the preceding case :

$$CF_3CClFO \rightarrow CF_3CFO + Cl$$

$$CF_3CHFO \rightarrow CF_3 + CHFO$$

The reaction of CF_3CHFO with oxygen would yield again CF_3CFO.

Principal products from HCFC 124 : CF_3CFO, CF_2O (from CF_3) and $CHFO$.

HCFC 141b CH_3CCl_2F

The RO radicals formed are CCl_2FCH_2O and CH_3CClFO, reacting with oxygen and by Cl atom detachment, respectively:

$$CCl_2FCH_2O + O_2 \rightarrow CCl_2FCHO + HO_2$$

$$CH_3CClFO \rightarrow CH_3CFO + Cl$$

It can be expected that CCl_2FCHO will react quite rapidly in the troposphere (Appendix II), releasing the CCl_2F radical. However, the $CCl_2FC(O)O_2$ radical formed in the oxidation sequence may react with NO_2 with the formation of the peroxynitrate $CCl_2FC(O)O_2NO_2$, similar to the well known peroxyacetylnitrate (PAN). Like PAN, this molecule is probably thermally stable, particularly in the upper troposphere and no reaction with OH is expected. In addition, photolysis of these peroxynitrates is expected to be very slow and therefore, the residence time is probably long in the troposphere. Thus, the formation of such a molecule may result in enhanced transport of chlorine to the stratosphere.

According to the well established oxidation mechanism of CFC's, the radical CCl_2F will end up as CClFO. It should be pointed out that a C-C bond cleavage in the CCl_2FCH_2O radical would result in the same product. Also, the hydrogen abstraction should be predominent over the Cl abstraction, in the reaction of CH_3CCl_2F with $O(^1D)$ atoms, resulting in minor contribution of the CH_3CFO product.

Principal products from HCFC 141b: CClFO and to a lesser extend CH_3CFO. The peroxynitrate $CCl_2FC(O)O_2NO_2$ should also be considered as a stable product.

HCFC 142b CH_3CClF_2

The RO radicals formed are $CClF_2CH_2O$ and CH_3CF_2O, which undergo reaction with oxygen and C-C bond cleavage, respectively.

$$CClF_2CH_2O + O_2 \rightarrow CClF_2CHO + HO_2$$

$$CH_3CF_2O \rightarrow CH_3 + CF_2O$$

For the same reasons as in the preceding case, the oxidation of $CClF_2CHO$ will yield CF_2O and the stable peroxynitrate $CClF_2C(O)O_2NO_2$.

Principal products from HCFC 142b : CF_2O and $CClF_2C(O)O_2NO_2$.

HFC 125 CF_3CHF_2

The RO radical formed is CF_3CF_2O, which can only undergo a C-C bond cleavage.

$$CF_3CF_2O \rightarrow CF_3 + CF_2O$$

Principal product from HFC 125 : CF_2O.

HFC 134a CF_3CH_2F

The RO radical formed is CF_3CHFO, which is expected mainly to undergo a C-C bond cleavage, with a possible minor contribution from the reaction with oxygen.

$$CF_3CHFO \rightarrow CF_3 + CHFO$$

$$CF_3CHFO + O_2 \rightarrow CF_3CFO + HO_2$$

Principal products from HFC 134a : CF_2O (from CF_3) and CHFO.

HFC 152a CH_3CHF_2

The RO radicals formed are CHF_2CH_2O and CH_3CF_2O. These radicals react with oxygen and by C-C bond cleavage, respectively.

$$CHF_2CH_2O + O_2 \rightarrow CHF_2CHO + HO_2$$

$$CH_3CF_2O \rightarrow CH_3 + CF_2O$$

For the same reasons as those given above for other aldehydes, CHF_2CHO will end up as CF_2O.

Principal product from HFC 152a : CF_2O.

III - INVENTORY AND FATE OF THE PRINCIPAL CARBONYL COMPOUNDS PRODUCED IN THE OXIDATION OF THE LISTED HCFC's AND HFC's

The principal carbonyl products obtained as a result of hydrogen and chlorine abstraction from the different HCFC's and HFC's by OH and $O(^1D)$ are summarised in Table II.

Table II : Principal carbonyl products obtained from the degradation of the HCFC's and HFC's in the troposphere and the lower stratosphere.

Product obtained from abstraction of :				(by OH and O^1D)	Cl (by O^1D)
HCFC	22	$CHClF_2$	→	CF_2O	CF_2O
HCFC	123	$CHCl_2CF_3$	→	CF_3CClO	CF_2O, CHClO
HCFC	124	$CHClFCF_3$	→	CF_3CFO	CF_2O, CHFO
HCFC	141b	CCl_2FCH_3	→	CClFO	(CH_3CFO)[a]
HCFC	142b	$CClF_2CH_3$	→	CF_2O	CF_2O
HFC	125	CHF_2CF_3	→	CF_2O	
HFC	134	CH_2FCF_3	→	CF_2O, CHFO	
HFC	152a	CHF_2CH_3	→	CF_2O	
Inventory of products :				CF_2O	CF_2O
				CHFO	CHClO
				CClFO	CHFO
				CF_3CClO	(CH_3CFO)[a]
				CF_3CFO	
Should also be included in stable products : the peroxynitrates				$CCl_2FC(O)O_2NO_2$	
				$CClF_2C(O)O_2NO_2$	

)[a] : Probably a minor product

The most striking feature is the limited number of the principal carbonyl products obtained, of which CF_2O is obviously the most abundant one. In contrast CH_3CFO is probably a minor product which in addition should be efficiently degraded in the troposphere, due to the presence of the methyl group. The reaction CH_3CFO with OH will form HCOCOF which will further be photolysed into HCO + FCO, FCO ending up as HF + CO. The direct photolysis of CH_3CFO would give CH_3 + CFO.

The other compounds still containing a hydrogen atom are : CHClO and CHFO. In the troposphere, these compounds may undergo photolysis, reaction with OH or hydrolysis. The photolysis should be negligible as the presence of the halogen atom on the carbonyl group shifts the $n \rightarrow \Pi^*$ band to the UV ($\lambda <$ 270 nm), compared to formaldehyde. To our knowledge, no data are available on the kinetics of the reactions with OH and measurements of the rates constants should be performed. Nevertheless, these reactions should be an efficient ^{S}ink for these compounds. Hydrolysis in clouds and rain droplets, yielding HCl or HF + CO, could also be an efficient sink for carbonyl hydrohalides but, as far as we know, the Henry's Law coefficients for these molecules have not been measured and so it is difficult to estimate their propensity for incorporation into the precipitation elements.

The carbonyl products containing chlorine are CClFO, CHClO, CF_3CClO and possibly some small amounts of phosgene, CCl_2O, formed as a side product in the HCFC 123 oxidation (by C-C bond cleavage in CF_3CCl_2O radical). For the same reason given above, the photolysis of such compounds is likely to be negligible in the troposphere but could become significant in the lower stratosphere, particularly for compounds such as CHClO or CF_3CClO. The photolysis rate of this class of compounds, i.e. RCClO, should be carefully investigated in the conditions of upper troposphere/lower stratosphere. In particular, it should be verified that the photolysis of CF_3CClO do not produce CF_3Cl which would be a long lived chlorine carrier in the atmosphere. These compounds are not expected to react with OH, with the exception of CHClO which will be converted to CO and HCl in the troposphere. Reaction with $O(^1D)$ atoms in the lower stratosphere may be significant and an evaluation of this sink could be obtained from models, assuming rate constants for $O(^1D)$ reactions of about 2×10^{-11} $cm_3molecule^{-1}s^{-1}$ (value for CFClO).

The other possible sink of these compounds in the troposphere is hydrolysis in the precipitation elements, but this cannot be quantified in the absence of solubility data.

The halogenated PAN's, $CCl_2FC(O)O_2NO_2$ and $CClF_2C(O)O_2NO_2$ may be stable enough result in a transport of chlorine to the stratosphere. Their principal sink in the troposphere is certainly hydrolysis and the efficiency of this process should be investigated.

The other major product molecules are the perfluorocarbonyls : CF_2O and CF_3CFO. Based on laboratory studies, CF_2O has been assumed to be the principal oxidation product of the CF_3 radical. However, the mechanism is not fully established. The reactions of the CF_3 radical with O_2 to give CF_3O_2 and of CF_3O_2 with NO to give CF_3O :

$$CF_3 + O_2\ (+M) \rightarrow CF_3O_2\ (+\ M)$$

$$CF_3O_2 + NO \rightarrow CF_3O + NO$$

appear to be well established. CF_3O is also likely to be formed following CF_3O_2 reaction with HO_2 to form CF_3OOH followed by photolysis.

The reaction pathways for CF_3O in the atmosphere are not obvious. This radical is stable with respect to thermal decomposition to CF_2 + F or formation of FO_2 via reaction with oxygen (see Appendix II). It can combine with nitrogen oxides, yielding a nitrite or a nitrate with NO and NO_2 respectively.

$$CF_3O + NO\ (+\ M) \rightarrow CF_3ONO\ (+\ M)$$

$$CF_3O + NO_2\ (+\ M) \rightarrow CF_3ONO_2\ (+\ M)$$

However, the nitrate CF_3ONO_2 is not known as a stable molecule and another pathway for this latter reaction could be :

$$CF_3O + NO_2 \rightarrow CF_2O + FNO_2$$

CF_3ONO can only be a temporary reservoir since, by analogy with the methyl derivative, it is expected to be photolysed into the initial reactants. Another possible path for CF_3O is the reaction with other radicals or molecules having weak C-H bonds, such as HO_2 or aldehydes :

$$\begin{aligned} CF_3O + HO_2 &\rightarrow CF_3OH + O_2 \\ &\rightarrow CF_2O + HF + O_2 \\ CF_3O + RCHO &\rightarrow CF_3OH + RCO \\ &\rightarrow CF_2O + HF + RCO \end{aligned}$$

However, the rate constants and products of such reactions are unknown and need to be investigated experimentally. If trifluoromethanol were formed to a significant extent, it could represent a significant sink for fluorine compounds, by precipitation scavenging.

In laboratory experiments, CF_3O is generally converted into CF_2O, probably by heterogeneous reactions. Similar reactions may occur in the atmosphere, particularly in the presence of aqueous droplets and aerosols, but the extent of such heterogeneous processes is difficult to assess. It can nevertheless be anticipated that the principal degradation products of CF_3 are CF_2O and possibly CF_3OH.

As was mentioned in the preceding section, the CHF_2O radical can react with oxygen,

$$CHF_2O + O_2 \rightarrow CF_2O + HO_2$$

but this reaction may be very slow and if so, similar alternative reactions to those of CF_3O should be envisaged.

The only way of degradation of CF_2O and CF_3CFO in the gas phase is photolysis at short wavelengths i.e. above the ozone layer. It is likely that the residence time of such compounds in the stratosphere is quite long but they will be removed in the troposphere by physical processes. Data on the hydrolysis rate should be obtained in order to evaluate the atmospheric lifetime of such compounds.

CONCLUSIONS

- The atmospheric photooxidation of hydrochlorofluorocarbons and hydrofluorocarbons is likely to occur by mechanisms similar to those which have been elucidated for alkanes and chloroalkanes, although virtually no experimenatal data is available to confirm this.

- The final chlorine containing products expected from the HCFC's are HCl, CFClO, CF_3CClO, $CCl_2FC(O)O_2NO_2$ and $CClF_2C(O)O_2NO_2$. These compounds are all stable and are expected to be removed only by photolysis in the stratosphere or through precipitation scavenging and hydrolysis. A slow thermal decomposition in the lower troposphere is also expected for the halogenated PAN's.

- The other major product molecules are expected to be HF and the perfluorocarbonyls CF_2O and CF_3CFO. The only loss processes for the carbonyls is photolysis in the upper stratosphere or precipitation scavenging in the troposphere.

- The mechanism of oxidation of CF_3O radicals, which is assumed to produce CF_2O, is not known for atmospheric conditions, and needs further study.

- The atmospheric lifetimes of CF_2O, CFClO, CCl_2O and other perhalogenocarbonyls need to be determined by acquisition of more data on their photochemistry and solubility.

- More information on the chemistry of the formylhalides HCClO and HCFO is required in order to determine their atmospheric lifetimes.

- Further laboratory tests and atmospheric measurements are needed to test the validity of the proposed mechanisms for HCFC and HFC degradation.

APPENDIX I (R.A. COX AND R. LESCLAUX)

Summary of degradation mechanisms of volatile organic compounds in the atmosphere

Volatile organic compounds are removed from the atmosphere predominantly by gas phase photochemically initiated oxidation. A pattern has emerged from the oxidation mechanisms of organics in the atmosphere, as a result of laboratory studies of oxidation of organic compounds under atmospheric conditions, together with knowledge of atmospheric trace gas composition (Atkinson, 1986; Atkinson and Lloyd, 1984; Cox, 1988). This pattern is best illustrated by considering the atmospheric oxidation of a simple hydrocarbon, RH, following attack by OH radicals. The first step involves formation of a peroxy radical by addition of molecular oxygen to the initially formed radical :

$$OH + RH \rightarrow H_2O + R \tag{1}$$

$$R + O_2 (+ M) \rightarrow RO_2 (+ M) \tag{2}$$

Peroxy radicals are formed quite generally in reaction (2), from organic radicals produced by radical attack or by photolysis.

The next stage involves conversion of the peroxy radical to a carbonyl compound. This may occur by one of several pathways, depending on local atmospheric composition. In the continental boundary layer and in the lower stratosphere/upper troposphere, sufficient nitrogen oxides are normally present for the peroxy radical chemistry to be dominated by their reactions with NO :

$$RO_2 + NO \rightarrow RO + NO_2 \tag{3}$$

Reaction (3) forms an alkoxy radical RO which typically can react with O_2 to give a carbonyl compound R_1R_2CO, and an HO_2 radical :

$$RO + O_2 \rightarrow R_1R_2CO + HO_2 \tag{4}$$

(R_1 and R_2 are H or organic fragment)

In the background middle troposphere where the concentration of nitrogen oxides is very low, the main alternative pathway to reaction (3) is reaction of RO_2 with HO_2 :

$$RO_2 + HO_2 \rightarrow ROOH + O_2 \tag{5a}$$

$$\rightarrow R_1R_2CO + H_2O + O_2 \tag{5b}$$

Reaction (5a) has generally been assumed to be the exclusive channel for the peroxy radical + HO_2 reaction but recent evidence (Jenkin et al. 1998) has shown that, at least in the case of simple hydrocarbon radicals, the alternate channel (5b), forming carbonyl compound and water directly, is significant under atmospheric conditions. It should be noted that this channel can occur only for organic peroxy radicals with an H-C-OO structure.

DEGRADATION MECHANISMS

Carbonyl compounds are producted by subsequent degradation of the hydroperoxide ROOH, either by OH attack or by photolysis, the reaction sequence being :

$$OH + ROOH \rightarrow H_2O + R_1R_2CO + OH \qquad (6)$$

or

$$ROOH + h\nu \rightarrow RO + OH \qquad (7)$$

with subsequent reaction of RO via reaction (4). Simple organic hydroperoxides are photolysed only slowly via the weak tail of their UV absorption bands, which extend into the near UV part of the solar spectrum.

The carbonyl compounds produced in the first stage of atmospheric degradation are further oxidized either by attack of OH (or another radical) or by photodissociation, resulting from absorption in the rather weak near UV bands of these compounds e.g.

$$OH + R_1HCO \rightarrow H_2O + R_1CO \qquad (8)$$

or

$$R_1R_2CO + h\nu \rightarrow R_2 + R_1CO \qquad (9)$$

The acyl radicals form peroxy radicals by addition of O_2 and the acyl peroxy radicals react either with NO or, in low NO_x situations, with HO_2. In the O-atom transfer reaction with NO, the initial product radical, R_1CO_2 rapidly loses CO_2 to form an organic radical of one less C atom than the original radical. This radical forms a new peroxy radical in reaction (2).

$$R_1CO + O_2 \rightarrow R_1CO_3 \qquad (10)$$

$$R_1CO_3 + NO \rightarrow NO_2 + R_1CO \qquad (11)$$

$$R_1CO_2 \rightarrow R_1 + CO_2 \qquad (12)$$

Two parallel reaction pathways occur in the reaction of the simplest acyl peroxy radical, CH_3CO_3, at room temperature (Niki et al. 198 5, Moortgat et al. 1989).

$$CH_3CO_3 + HO_2 \rightarrow CH_3C(O)OOH + O_2 \qquad (13)$$

$$CH_3CO_3 + HO_2 \rightarrow CH_3COOH + O_3 \qquad (14)$$

The first channel is analogous to reaction (5a) but the second channel, in which ozone is formed, has only been observed for acetylperoxy, but may well be general for acylperoxy and substituted acetylperoxy radicals. Degradation of peracid formed in reaction (13) is likely to be via photolysis or by rain out.

Another reaction pathway of general application to peroxy radicals also needs to be considered in conditions where NO_x is at significant concentrations i.e. the addition of NO_2 to form peroxynitrates :

$$RO_2 + NO_2\ (+ M) \longleftrightarrow RO_2NO_2\ (+ M) \qquad (15)$$

The pernitrates tend to be unstable at ambient temperatures and decompose back to the precursor, leading to no net chemical change via this reaction (Cox and Roffey, 1977). At the lower temperatures prevalent in the upper troposphere the thermal decomposition may become slow enough for the alternate removal process for the peroxynitrates, such as photolysis or reaction with OH, to become dominant (Crutzer, 1979). The rate of thermal decomposition is dependent on the nature of the organic radical, the acyl and the halogen substituted pernitrates, being much more stable than the alkyl derivates.

The above mechanisms have been formulated as a result of studies of the kinetics and products formed in reactions of simple organic radicals. Studies of the oxidation of higher alkanes and simple olefins seem to indicate a generality of behaviour, although the relative rates of some of the steps e.g. decomposition of alkoxy radicals compared to their reaction with O_2, show remarkable sensitivity to structure and lead to mechanistic differences (Batl, 1987). Information on substituted alkyl radicals is much more sparse and elucidation of the mechanisms is more difficult.

APPENDIX II (R.A. COX AND R. LESCLAUX)

Rate constants for selected reactions in the proposed degradation mechanism for hydrochlorofluorocarbons

In this section we examine the available knowledge of the kinetics of the elementary reactions in the general degradation mechanism for halogen substituted organic radicals.

1 - The reaction $CX_3 + O_2 (+ M) \rightarrow CX_3O_2 (+ M)$

The limiting third order rate constants for the association reaction increases with chlorine and fluorine substitution (see Table I)

Table I : Rate constants for combination of CX_3 radicals with oxygen (X = H, Cl or F)

CX_3	$k_0 \times 10^{30}$ $cm^6 molecule^{-2} s^{-1}$ at 298K
CH_3	0.8
CCl_3	1.5
CCl_2F	5.0
CF_3	19.0

Source : IUPAC evaluation, 1989

No experimental data are available for the reaction $CClF_2 + O_2$ or for the halogen substituted C_2 radical with O_2, but it seems likely that halogen substitution (particularly fluorine), enhances the rate of these association reactions, making this the exclusive pathway for the primary radical fragments from HCFC and CFC attack by OH.

2 - The reaction $CX_3O_2 + NO \rightarrow CX_3O + NO_2$

Data are available for the reactions of the halogen substituted methyl radicals with NO. The rate constants are of similar magnitude for X = Cl or F, but are a factor of two larger than the corresponding reactions of CH_3O_2 and $C_2H_5O_2$ (see Table II).

Table II : Rate coefficients for reaction of CX_3O_2 radicals with NO

CX_3O_2	$k \times 10^{11}$ $cm^3 molecule^{-1} s^{-1}$ at 298K
CH_3O_2	0.76
$C_2H_5O_2$	0.88
CF_3O_2	1.6
CF_2ClO_2	1.6
$CFCl_2O_2$	1.5
CCl_3O_2	1.8

Source : IUPAC evaluation, 1989

There are no experimental data for the halogen substituted C_2 radicals, but they are likely to react rapidly with NO, following the pattern of the CX_3O_2 radicals. A reasonable estimate for the C_2 radicals would be a value of 2.0 x 10^{-11} cm^{3}molecule^{-1}s^{-1}, at tropospheric temperature.

3 - The reaction $CX_3O_2 + NO_2 (+ M) \leftrightarrow CX_3O_2NO_2 (+ M)$

The addition reaction of halogen substituted methyl radicals with NO_2 has been measured at low pressure in the fall-off region and the limiting k_0 (termolecular) and k_{00} (high pressure) rate coefficients have been determined for CF_3O_2, CF_2ClO_2, $CFCl_2O_2$ and CCl_3O_2 reactions (Caralp et al. 1988). Experimental information has been obtained for the reverse decomposition of the peroxynitrates : $CF_2ClO_2NO_2$, $CFCl_2O_2NO_2$ and $CCl_3O_2NO_2$ (Reiner and Zabel, 1986). These peroxynitrates are all more stable than $CH_3O_2NO_2$ indicating that halogen substitution increases the bond energy of the central O-ONO_2 bond. By analogy fully halogenated C_2 peroxynitrates are expected to be more stable than alkylperoxynitrate (which are similar in stability to $CH_3O_2NO_2$).

Under tropospheric conditions it is likely that the C_2 radical addition reactions and corresponding decomposition are near the high pressure limits. The most appropriate parameters suggested for the fully halogenated C_2 radicals are those for CCl_3O_2 reaction with NO_2, which are given in Table III.

Table III : High pressure limit values for $CX_3O_2NO_2$ formation and decomposition

CX_3O_2	Formation k_{00}/cm^{3}molecule^{-1}s^{-1}	Decomposition k_{00}/s^{-1}
CF_2ClO_2	$1.0 \times 10^{-11}(T/300)^{-0.7}$	$1.0 \times 10^{16}\exp(-11880/T)$
$CFCl_2O_2$	$8.3 \times 10^{-12}(T/300)^{-0.7}$	$2.1 \times 10^{16}\exp(-11980/T)$
CCl_3O_2	$1.5 \times 10^{-11}(T/300)^{-0.7}$	$9.1 \times 10^{14}\exp(-10820/T)$

Source : IUPAC evaluation, 1989

The fall-off parameters to allow calculation of the rate cefficients for high altitudes, are given in the NASA evaluation (1987).

4 - The reaction of CX_3O_2 and $C_2X_5O_2$ with HO_2

No information is available on the kinetics and products of these reactions. By analogy with the most recent data for CH_3O_2 (Jenkin et al. 1988) we can expect a rate coefficient of the order of (0.5 - 1.0) x 10^{-11} cm^{3}molecule^{-1}s^{-1} with two channels of approximately equal rates :

$$CX_2HO_2 + HO_2 \rightarrow CX_2HOOH + O_2$$

$$\rightarrow CX_2O + H_2O + O_2$$

The second channel will not be possible for halogenated peroxy radical without an α H atom. For C_2 halogenated peroxy radicals a rate coefficient of the order of 1.0 x 10^{-11} cm^{3}molecule^{-1}s^{-1} is probably appropriate (c.f. $C_2H_5O_2 + HO_2$ (Cattel et al. 198 6; Dagant et al. 19886).

5 - Decomposition of halogen substituted alkoxy radicals.

There is now very strong evidence that the alkoxy radicals CX_2ClO (where X = Cl or F) are unstable and, under atmospheric conditions, they rapidly eliminate Cl and consequently have only a transitory existence :

$$CX_2ClO \rightarrow CX_2O + Cl$$

This reaction is responsible for the rapid chain reaction occuring in the laboratory photo-oxidation of certain chlorinated methanes CHX_2Cl (Sanhueza and Meicklen, 1975d; Sanhueza, 1977, Lescalux et al. 1987). When X = H, reaction with O_2 can become competitive, particularly in the case of CH_2ClO (e.g. in the oxidation of CH_3Cl) (Sanhueza and Meicklen, 1975d).

$$CH_2ClO + O_2 \rightarrow HO_2 + CHClO$$

For $CHCl_2O$, however, the favoured pathway appears to be dissociation into CHClO + Cl (Sanhueza and Meicklen, 1975d). Quantitative estimates of the rate coefficient for Cl atom elimination have been recently reported for CX_3 radicals (X = Cl or F). The values are given in Table IV.

Table IV - Decomposition of halogen substituted alkoxy radicals.

Radical decomposition	k/s^{-1} (temp)	Ref.
$CCl_3O \rightarrow CCl_2O + Cl$	$> 1 \times 10^5$ (233K)	Lesclaux et al. 1987
$CCl_2FO \rightarrow CFCLO + Cl$	$> 3 \times 10^4$ (253 K)	Lesclaux et al. 1987
$CClF_2O \rightarrow CF_2O + Cl$	$> 7 \times 10^5$ (298 K)	Carr et al. 1986

Reactions of hydrochlorofluoroethoxy radicals

Important information concerning the ways chloro- and chlorofluoro-ethoxy radicals react or decompose, can be obtained from studies of the chlorine atom-initiated oxidation of chloro- and chlorofluoroethylenes which proceeds by a long chain, free radical process. These reactions have been extensively studied, mainly by the groups of Shumacher, Huybrechts and Heicklen (see Muller and Schumacher, 1937a,b; Schumacher and Thurauf, 1941; Huybrechts and Meyers, 1966; Huybrechts et al. 1965; Sanhueza and Meicklen, 1975b,c,e) and the results have been collected by Sanhueza et al. in a review (1976). From these data, some general rules can be drawn on the reactions of such radicals.

i - Chlorine atom detachment

$$CX_3CYClO \rightarrow CX_3CYO + Cl$$

(X and Y = H, Cl or F)

This type of reaction always occurs preferentially if Y = Cl or F, independently of the nature of the CX_3 group. For example, CCl_3CCl_2O, $CHCl_2CCl_2O$, $CClF_2CCl_2O$, $CCl_2FCClFO$, $CClF_2CClFO$ radicals essentially undergo this type of reaction. By studying the photooxidation of methyl chloroform, Nelson et al. (1984), showed that the radical CH_3CCl_2O also dissociates in this way.

ii - C-C bond cleavage

$$CX_3CX_2O \rightarrow CX_3 + CX_2O$$

This reaction always occurs for radicals of the type CX_3CF_2O, independently of the nature of CX_3. The situation is not as clear for CX_3CHFO or CX_3CHClO radicals, since they can either undergo a C-C bond cleavage or react with oxygen. It seems however that the C-C bond cleavage is the most favourable process for these radicals. In a study of Cl atom sensitized oxidation of chlorinated ethanes, in one atmosphere of air, Spence and Hanst (1978) showed that the radicals CCl_3CHClO, $CHCl_2CHClO$, $CH_2ClCHClO$ and CH_3CHClO essentially yield formyl chloride as a result of the C-C bond cleavage. Small amounts of acid chlorides CX_3CClO have, however, been detected, resulting from the reaction with oxygen. The same conclusion was reached in the study of the Cl atom sensitized oxidation of chlorinated ethylenes (Sanhueza et al. 1976). It can be expected that CX_3CHFO radicals react in the same way.

Apparently, the Cl atom detachment from CX_3CClHO has not been observed.

iii - Reaction with oxygen

$$CX_3CXHO \rightarrow CX_3CXO + HO_2$$

Obviously, this reaction preferentially occurs in the cases of radicals of the type CX_3CH_2O, yielding a halogenated acetaldehyde molecule. This has been shown for CCl_3CH_2O (Nelson et al. 1984; Sperce and Henst, 1978) and for CH_2ClCH_2O (Sperce and Henst, 1978). As shown above, the reaction with oxygen seems to be a minor process for CX_3CHXO radicals. However, it will be considered as a possible channel in the compounds relevant to this review. The rate constant for this reaction is assumed to be one tenth of the equivalent reaction for C_2H_5O, taking into account the effect of the halogen atom on the H atom reactivity.

iv - Oxidation of the CF_3O radical

The oxidation of the CF_3O radical is one of the major uncertainties in the mechanism of degradation of perfluorocompounds. This radical is formed in the degradation of CF_3 via CF_2O_2 and the major C-containing product in laboratory systems appears to be CF_2O_2. According to current thermochemical knowledge, the elimination of an F atom either thermally or by reaction with O_2 is too endothermic to be important in the atmosphere :

$$CF_3O + M \rightarrow CF_2O + F + M \qquad \Delta H^0 = +36 \text{ kJ mol}^{-1}$$

$$CF_3O + O_2 \rightarrow CF_2O + FO_2 \qquad \Delta H^0 = +42 \text{ kJ mol}^{-1}$$

Accordingly it has been hypothesized that heteregeneous reactions are responsible for the formation of CF_2O in laboratory systems. It is important therefore to establish whether other homogeneous pathways may occur in the atmosphere.

6 - Photochemical reactions

Halogenated hydroperoxides

Information on the photolysis of halogenated hydroperoxides is sparse. By analogy with the alkyl hydroperoxides, photolysis is likely to be rather slow and to occur via dissociation of the central O-O bond leading to the same alkoxy radical as that produced by reaction of the original peroxy radical with NO. For modeling purposes, it is recommended to use $J(CH_3OOH)$ for the reaction :

$$CX_3OOH + h\nu \rightarrow CX_3O + OH$$

Carbonyl Halides

The absorption spectra of the carbonyl halides, CX_2O, have been determined for CF_2O, CFClO and CCl_2O (Baulch et al. 1980). The molecules absorb only in the deep UV and are virtually unaffected by sunlight in the troposphere. Photolysis leads to elimination of a halogen atom :

$$CX_2O + h\nu \rightarrow CXO + X$$

The fragment radical ClCO is unstable with respect to decomposition to Cl + CO and the same is probably true for FCO, although the thermodynamic stability of this radical is still uncertain.

The photochemistry of CHXO (X = F or Cl) has been investigated in the case of CHFO (Okabe, 1978). It appears that substitution of halogen on the carbonyl carbon atom, X-C = O, has the effect of shifting the $n \rightarrow \Pi^*$ electronic absorption in the C = O group to higher energies (blue shift in wavelength), thus reducing the rate of photoabsorption in the lower part of the atmosphere quite dramatically. Photodissociation rates are therefore likely to be reduced in consequence, although the effect may be modified by changes in the quantum yields, which are not known. These arguments are also expected to apply to fully halogenated carbonyls of the type CX_3CXO.

Halogenated aldehydes

Although there is little information on the photochemistry of the halogenated aldehydes of the type CX_3CHO, there is considerable information on the photochemistry of the halogenated ketones e.g. CX_3COCX_3, which photolyse in the near UV following $n \rightarrow \Pi^*$ excitation (Macket and Phillips, 1962). Since the absorption by aldehydes in the corresponding near UV band is also an $n \rightarrow \Pi^*$,absorption of fully halogenated ketones, $(CF_3)_2CO$, $(CF_2Cl)_2CO$ and $(CCl_3)_2CO$, is shifted up to 20 nm to the red, making these molecules more strongly absorbing in the solar UV troposphere. Moreover, the quantum yields for photodissociation near 300 nm are 0.8 (Whytock and Kutsche, 1988), i.e. substantially higher than for simple aliphatic ketones. Comparing this analogy for aldehydes of the type CX_3CHO, we may expect rather rapid photolysis of these compounds according to the reaction :

$$CX_3CHO + h\nu \rightarrow CX_3 + HCO$$

However, at short wavelength, another photodissociation pathway may occur :

$$CX_3CHO + h\nu \rightarrow CHX_3 + CO$$

A reasonable approximation would be to use the same J value as for HCHO photodissociation via the H + HCO channels for modelling this process in the atmosphere.

A novel process observed in the chloro-substituted ketones is the elimination of a Cl atom rather than C-C bond rupture e.g.

$$CF_2ClCOCF_2Cl + h\nu \rightarrow CF_2ClCOCF_2 + Cl$$

This channel may be open for the (slower) photolysis of CX_3CXO type carbonyls :

$$CX_2ClCXO + h\nu \rightarrow CX_2CXO + Cl$$

7 - Reaction of OH with halogenated peroxides and aldehydes

Halogenated hydroperoxides and aldehydes (containing the -CH0 group) can degrade through OH attack. The reactions can be written as follows :

$$CX_3CHO + OH \rightarrow H_2O + CX_3CO$$

$$CX_3OOH + OH \rightarrow H_2O + CX_3OO$$

For the hydroperoxides, the H-atom attached to the C atom (relative to the peroxy link) are less likely to be abstracted than the H_{00} atom, due to the deactivating effect of the nearby halogen atoms in both C_1 and C_2 fragments. For the rate coefficients the preferred estimates are those for reaction of OH + H_20_2 reduced by a factor of 2 to compensate for the lower number of abstractable H-atoms. The only halogen substituted aldehyde for which the rate coefficient for OH attack appears to have been measured is chloral, CCl_3CHO, derived from the photo-oxidation of methyl chloroform (Nelson et al. 1984) for which a value of 6.2×10^{-12} cm^{3}molecule^{-1}s^{-1} was obtained at 298 K. In the same study, the rate coefficient for OH attack on acetyl chloride :

$$OH + CH_3CClO \rightarrow H_2O + CH_2CClO$$

was determined to be 7.2×10^{-14} cm^3 molecule^{-1} s^{-1} showing that the C-ClO group also reduces the rate of H abstraction. Fluorine substitution is also expected to show a similar deactivating effect in analogous fluorocarbonyl compounds.

The rate of the HCFO and HCClO molecules with OH is unknown :

$$OH + HCXO \rightarrow H_2O + CXO$$

A value of approximately 1×10^{-12} cm^{3}molecule^{-1}s^{-1} is estimated, taking into account the effect of deactivation by the halogen atom for H-abstraction.

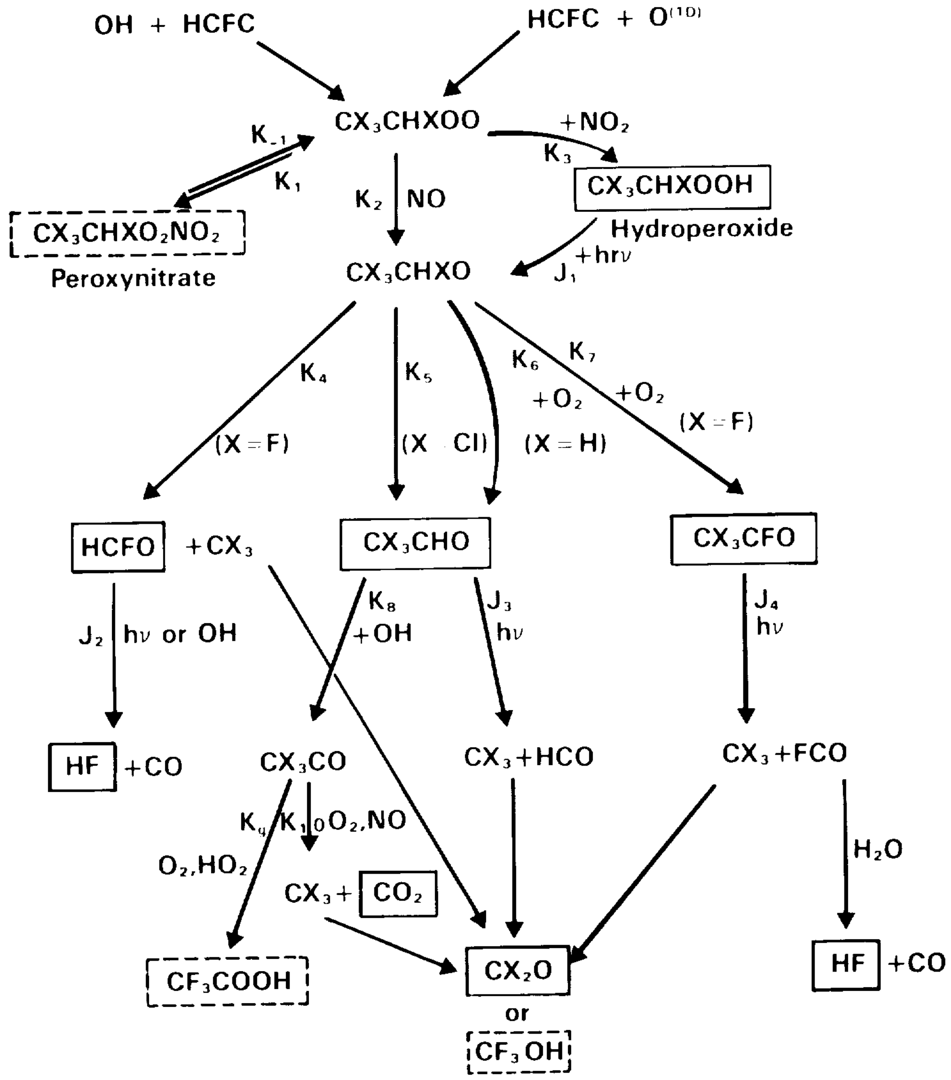
8 - Rainout, washout and dry deposition processes

All oxygenated secondary products from the oxidation of HCFC's and CFC's, hydroperoxides, halogenated aldehydes, carbonyl halides and acid halides (e.g. CX_3CFO), will be subject to removal by solution/hydrolysis in the precipitation elements and also by dry deposition at the earth surface. Knowledge of the solubility and Henry's law constants for these gases is required in order to assess the importance of removal in the precipitation elements for the carbonyl halides CCl_2O, $CFClO$ and CF_2O. Since these molecules are very stable towards gas phase removal, removal by wet and dry deposition probably has an important role in determining their atmospheric lifetime. Recent estimates of the lifetime of phosgene, based on measured concentrations and the estimated source strength (Wilson et al. 1989), are about 2 months.

APPENDIX III (R.A. COX AND R. LESCLAUX)

Recommended rates coefficients for modelling atmospheric degradation of hydrochlorofluorocarbons

A schematic diagram illustrating the degradation pathways of a typical hydrochlorofluocarbon is shown in Figure 1. In order to formulate the basic chemistry, knowledge of the rate coefficients for 10 thermal reactions and 4 photochemical reactions are required. The best estimates of the rate coefficients are summarised in Table A and for the photochemical parameters in Table B.



Minor products shown in "broken" boxes, major products in "full" boxes

Figure 1. Tropospheric Degradation Pathways for typical CFC substrates.

Table A: Rate constants for selective reactions of the degradation mechanism of HCFC's and HFC's

	RO_2+NO_2,M RO_2NO_2+M	RO_2+NO	RO_2+HO_2	$RO \rightarrow CX_3+CX_2O$	$RO \rightarrow CX_3CXO+Cl$	$RO+O_2 \rightarrow CX_3CHO+HO_2$	$RO+O_2 \rightarrow CX_3CXO+HO_2$	$OH+CX_3CHO$	CX_3CO+HO_2	CX_3CO+NO
HCFC's	k_1 & k_{-1}	k_2 x 10^{11} $cm^3\ s^{-1}$	k_3 x 10^{11} $cm^3\ s^{-1}$	k_4	k_5	k_6	k_7	k_8 $cm^3\ s^{-1}$	k_9 x 10^{11} $cm^3\ s^{-1}$	k_{10} x 10^{11} $cm^3\ s^{-1}$
HCFC 22										
$CClF_2O_2$	IUPAC*	1.6	1.0***	NA	y^S	-	-	-	-	-
CHF_2O_2	use k_∞ (CH^3O^2)	1.6	"	NA	-	-	o.1k$(CH_3O+O_2)^S$	-	-	-
HCFC 123										
$CF_3CCl_2O_2$	use k_∞ $(CFCl_2O_2)$	1.5	"	-	as $CFCl_2O^X$	-	-	-	-	-
CF_3CHClO_2	use k_∞ (CF_2ClO_2)	1.6	"	$CF_3+HCClO$		-	-	2.1 x 10^{-12}	-	-
HCFC 124										
CF_3CClFO_2	use k_∞ (CF_2ClO_2)	1.6	"	-	y	-	-	-	-	-
CF_3CHFO_2	" "	1.6	"	CF_3+HCFO^t	-	-	0.1k(CH_3O+O_2)	-	-	-
HCFC 141b										
$CCl_2FCH_2O_2$	use $k_\infty(CH_3O_2)$	0.9**	"	-	-	as CH_3O	-	2.1x10^{-12}	0.5^Z	1.4^W
CH_3CClFO_2	use $k_\infty(CClF_2O_2)$	1.6	"	-	y	-	-	as CH_3CCl_3	-	-
HCFC 142b										
$CClF_2CH_2O_2$	use k_∞ (CH_3O_2)	0.9	"	-	-	as CH_3O	-	2.1x10^{-12}	0.5	1.4
$CH_3CF_2O_2$	use k_∞ (CF_2ClO_2)	1.6	"	CH_3+CF_2O		-	-	as CH_3CCl_3	-	-
HCF 125										
$CF_3CF_2O_2$	use k_∞ (CF_2ClO_2)	1.6	"	$CF_3+CF_2O^t$	-	-	-	-	-	-
HCFC 134										
CF_3CFHO_2	use k_∞ (CF_2ClO_2)	1.6	"	CF_3+HFCO^t	-	-	0.1k (CH_3O+O_2)	-	-	-
HCFC 152a										
$CHF_2CH_2O_2$	use k_∞ (CH_3O_2)	0.9	"	-	-	as CH_3O	-	2.1x10^{-12}	0.5	1.4
$CH_3CF_2O_2$	use k_∞ (CH_2ClO_2)	1.6	"	CH_3+CF_2O	-	-	-	as CH_3CCl_3	-	-

* IUPAC Data evaluation [10]

** as $C_2H_5O_2$ + NO

*** Estimate based on $C_2H_5O_2$ + HO_2

$)^s$ COF_2 is the product

$)^t$ k = 1 x 10^{16}exp(-8110/T)s^{-1} based on an assumed A factor and a rate constant of 1.5 x $10^4 s^{-1}$ at 298K to fit product yields in chlorocarbon photooxidation : see Appendix II

$)^u$ based on a value of 7.2 x $10^{-14} cm^3 s^{-1}$ for CH_3CClO [24]

$)^w$ assume equal to k(CH_3CO_3 + NO) (IUPAC values [10])

$)^x$ k = 1x10^{13} exp(-4965/T) s^{-1}

$)^y$ k = 1x10^{13} exp(-5000/T) s^{-1} estimate based on data for CCl_3O and CCl_2FO

$)^z$ assume equal to k(CH_3CO_3 → $CX_3C(O)OOH$ + O_2)

Table B : Photochemical reactions

Reaction	J_{value} for atmospheric photoylsis*	
$ROOH + h\nu \rightarrow RO + OH$	J_1	use J (CH_3OOH)
$HCFO + h\nu \rightarrow H + FCO$	J_2	use J (CH_3COCH_3)
$CX_3CHO + h\nu \rightarrow CX_3 + HCO$	J_3	use J ($HCHO \rightarrow H + HCO$)
$CX_3CXO + h\nu \rightarrow CX_3 + XCO$	J_4	use J (CH_3CHO)

* Based on arguments presented in Appendix II

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AN ASSESSMENT OF POTENTIAL DEGRADATION PRODUCTS IN THE GAS-PHASE REACTIONS OF ALTERNATIVE FLUOROCARBONS IN THE TROPOSPHERE

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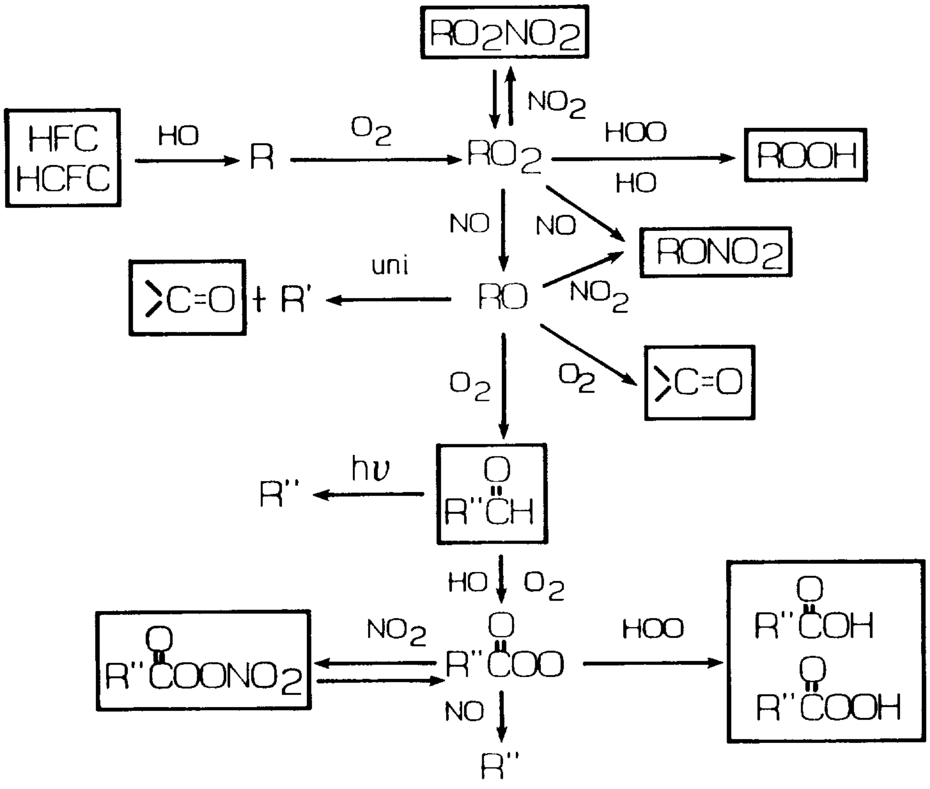
EXECUTIVE SUMMARY

Tropospheric chemical transformations of alternative hydrofluorocarbons (HCFs) and hydrochlorofluorocarbons (HCFCs) are governed by hydroxyl radical initiated oxidation processes, which are likely to be analogous to those known for alkanes and chloroalkanes. A schematic diagram, shown below, illustrates plausible reaction mechanisms for their atmospheric degradation; where R, R' and R'' denote the F- and/or Cl-substituted alkyl groups derived from HCFs and HCFCs subsequent to the initial H atom abstraction by HO radicals. At present, virtually no kinetic data exist for the majority of these reactions, particularly for those involving RO. Potential degradation intermediates and final products include a large variety of fluorine- and/or chlorine-containing carbonyls, acids, peroxy acids, alcohols, hydrogen peroxides, nitrates and peroxy nitrates, as summarized in the attached table. Probable atmospheric lifetimes of these compounds have also been estimated. For some carbonyl and nitrate products shown in this table, there seem to be no significant gas-phase removal mechanisms. Further chemical kinetics and photochemical data are needed to quantitatively assess the atmospheric fate of HCFs and HCFCs, and of the degradation products postulated in this report.



Schematic illustration showing the atmospheric degradation of alternative Fluorocarbons

Fluorine-Containing Products in the Atmospheric Degradation of Selected Fluorocarbons

Compound	Formula	Atom & Radical	Carbonyl	Acid	Hydroxide	Nitrate
HCFC 123	$HCCl_2CF_3$	CF_3CCl_2OO			CF_3CCl_2OOH	$CF_3CCl_2OONO_2$
		CF_3CCl_2O	CF_3CClO			
		CF_3OO			CF_3OOH	CF_3OONO_2
		CF_3O			CF_3OH	CF_3ONO_2
HCFC 141B	CCl_2FCH_3	CCl_2FCH_2OO			CCl_2FCH_2OOH	$CCl_2FCH_2OONO_2$
		CCl_2FCH_2O	CCl_2FCHO			
		CCl_2FOO			CCl_2FOOH	CCl_2FOONO_2
		CCl_2FO	$CClFO$			
		$CCl_2FC(O)OO$		$CCl_2FC(O)OOH$		$CCl_2FC(O)OONO_2$
				$CCl_2FC(O)OH$		
HCFC 142b	$CClF_2CH_3$	$CClF_2CH_2OO$			$CClF_2CH_2OOH$	$CClF_2CH_2OONO_2$
		$CClF_2CH_2O$	$CClF_2CHO$			
		$CClF_2OO$			$CClF_2OOH$	$CClF_2OONO_2$
		$CClF_2O$	CF_2O			
		$CClF_2C(O)OO$		$CClF_2(O)OOH$		$CClF_2C(O)OONO_2$
				$CClF_2C(O)OH$		
HCFC 22	$CHClF_2$	$CClF_2OO$			$CClF_2OOH$	$CClF_2OONO_2$
		$CClF_2O$	CF_2O			
HCFC 124	$CHClFCF_3$	$CF_3CClFOO$			$CF_3CClFOOH$	$CF_3CClFOONO_2$
		CF_3CClFO	CF_3CFO			
		CF_3OO			CF_3OOH	CF_3OONO_2
		CF_3O			CF_3OH	CF_3ONO_2
HCF 134a	CH_2FCF_3	CF_3CHFOO			$CF_3CHFOOH$	$CF_3CHFOONO_2$
		CF_3CHFO	$CHFO$			
			CF_3CHFO			
		CF_3OO			CF_3OOH	CF_3OONO_2
		CF_3O			CF_3OH	CF_3ONO_2
		CFO			$CF(O)OOH$	$CF(O)OONO_2$
HFC 52a	CHF_2CH_3	CH_3CF_2Oo			CH_3CF_2OOH	$CH_3CF_2OONO_2$
		CH_3CF_2O	CF_2O			
		CHF_2CH_2OO			CHF_2CH_2OOH	$CHF_2CH_2OONO_2$
		CHF_2CH_2O	CHF_2CHO			
		CHF_2OO			CHF_2OOH	CHF_2OONO_2
		CHF_2O	$CHFO$			
		$CHF_2C(O)OO$		$CHF_2C(O)OOH$		$CHF_2C(O)OONO_2$
				$CHF_2C(O)OH$		
		CFO		$CF(O)OOH$		$CF(O)OONO_2$
HCF 125	CHF_2CF_3	CF_3CF_2OO			CF_3CF_2OOH	$CF_3CF_2OONO_2$
		CF_3CF_2O	CF_2O			
			CF_3CFO			
		CF_3OO			CF_3OOH	CF_3OONO_2
		CF_3O			CF_3OH	CF_3ONO_2

1. INTRODUCTION

As part of the AFEAS (Alternative Fluorocarbon Environmental Acceptability Study) program for evaluating all relevant current scientific information to determine the environmental acceptability of the alternative fluorocarbons, the following list of questions concerning their atmospheric degradation via gas-phase chemical reactions will be addressed in this report.

1. How will alternative fluorocarbons degraded in the troposphere after initial hydrogen abstraction by hydroxyl (HO) radicals?
2. What are the intermediate and final products of the gas-phase chemical reactions?
3. What are the most probable gas-phase chemical lifetimes of these products in the troposphere?
4. Is it likely that relatively stable fluorine containing products would be formed?
5. How would the degradation products be removed from the atmosphere via gas-phase chemical reactions?

Alternative fluorocarbons under consideration include all HFCs and HCFCs given, respectively, by the formula $CH_{4\text{-}n}F_n$ ($1 \leq n \leq 3$), $C_2H_{6\text{-}n}F_n$ ($1 \leq n \leq 5$), and $CH_{4\text{-}m\text{-}n}Cl_mF_n$ ($1 \leq m \leq 2$; $1 \leq n \leq 2$; $m + n \leq 3$) and $C_2H_{6\text{-}m\text{-}n}Cl_mF_n$ ($1 \leq m \leq 4$; $1 \leq n \leq 4$; $m + n \leq 5$), but emphasis will be placed on HFCs-134a, 152a, 125 and HCFCs-22, 123, 124, 141b and 142b. The formulas for these fluorocarbons are listed in table 1 along with the expected initial radicals following reaction with HO radicals.

Questions 1 and 2 deal with the formation of fluorine or chlorine-containing molecular products via the gas-phase HO-initiated reactions of HFCs and HCFCs under representative tropospheric conditions, and questions 3-5 with the subsequent removal of these products by either direct photodissociation or reactions with gaseous tropospheric constituents. These topics are discussed in Sections I and II, respectively. Products with sufficiently long lifetimes are eventually removed from the troposphere by processes such as rain out, deposition to the earth's surface or escape into the stratosphere. These heterogeneous removal processes are evaluated elsewhere in the AFEAS program and will not be discussed in this report.

The HO-radical initiated degradation of HFCs and HCFCs in the troposphere takes place via a large number of reactions involving free radical intermediates. A literature review is given in the appendix. Many of these reaction steps have not been determined experimentally. Thus, when judged plausible, available information on analogous reactions and thermochemical data are also utilized (stated as such) in this evaluation.

2. ATMOSPHERIC DEGRADATION MECHANISMS

Listed in Table 1 are all the possible fluorine- and/or chlorine-substituted haloalkyl (R) radicals initially formed from HFCs and HCFCs after H atom abstraction by HO radicals. As discussed later in the Appendix, atmospheric degradation mechanisms of these R radicals appear to be, in large part, analogous to those of the corresponding alkyl radicals, i.e. CH_3 and C_2H_5 (NASA Report, 1987; CODATA, 1982; Kerr and Calvert, 1984; Atkinson, 1986). These reaction steps involve various types of free radicals and molecular products and are illustrated schematically in Figure 1. In this figure, the molecular products

Table 1: List of Alternative Fluorocarbons and Primary Radicals

Compound	m	n	Formula	Primary Radical
HFC				
$CH_{4-n}F_n$		1	CH_3F	CH_2F
$(1 \leq n \leq 3)$		2	CH_2F_2	CHF_2
		3	CHF_3	CF_3
$C_2H_{6-n}F_n$		1	CH_3CH_2F	CH_3CHF; CH_2FCH_2
		2	CH_3CHF_2 (152a)	CH_3CF_2; CHF_2CH_2
			CH_2FCH_2F	CH_2HCHF
		3	CH_3CF_3	CF_3CH_2
			CH_2FCHF_2	CH_2FCF_2; CHF_2CHF
		4	CH_2FCF_3 (134)	CF_3CHF
			CHF_2CHF_2	CHF_2CF_2
		5	CHF_2CF3 (125)	CF_3CF_2
HCFC				
$CH_{4-m-n}Cl_mF_n$	1	1	CH_2ClF	$CHClF$
$(1 \leq m \leq 2)$	2	1	$CHCl_2F$	CCl_2F
$(1 \leq n \leq 2)$	1	2	$CHClF_2$ (22)	$CFlF_2$
$(2 \leq m+n \leq 3)$				
$C_2H_{6-m-n}Cl_mF_n$	1	1	CH_2ClCH_2F	CH_2ClCHF; CH_2FCHCl
$(1 \leq m \leq 4)$			CH_3CHClF	CH_3CClF; $CHClFCH_2$
$(1 \leq n \leq 4)$	1	2	$CHClFCH_2F$	$CHClFCHF$; CH_2FCClF
$(2 \leq m+n \leq 5)$			$CH_2FCHClF$	CH_2FCClF; $CHClFCHF$
			CH_2ClCHF_2	CH_2ClCF_2; CHF_2CHCl
			CH_3CClF_2	$CClF_2CH_2$
	1	3	$CClF_2CH_2F$	$CClF_2CHF$
			CHF_2CHClF	CHF_2CClF; $CHClFCF_2$
			CH_2FCClF_2	$CClF_2CHF$
			CH_2ClCF_3	CF_3CHCl
	1	4	CF_3CHClF (124)	CF_3CClF
			CCF_2CHF_2	$CClF_2CF_2$
	2	1	CH_3CCl_2F (141b)	CCl_2FCH_2
			$CH_2ClCHClF$	$CH_2ClCClF$; $CHClFCHCl$
	2	2	$CHClFCHClF$	$CHClFCClF$
			CH_2FCCl_2F	CCl_2FCHF
			$CH_2ClCClF_2$	$CClF_2CHCl$
	2	3	$CClF_2CHClF$	$CClF_2CClF$
			CHF_2CCl_2F	CCl_2FCF_2
			$CHCl_2CF_3$ (123)	CF_3CCl_2
	3	1	CCl_3CH_2F	CCl_3CHF
			$CHCl_2CHClF$	$CHCl_2CClF$; $CHClFCClF$
			CH_2ClCCl_2F	CCl_2FCHCl
	3	2	$CCl_2FCHClF$	CCl_2FCClF
			CCl_3CHF_2	CCl_3CF_2
			$CHCl_2CClF_2$	$CClF_2CCl_2$
	4	1	$CHCl_2CCl_2F$	CCl_2FCCl_2
			CCl_3CHClF	CCl_3CClF

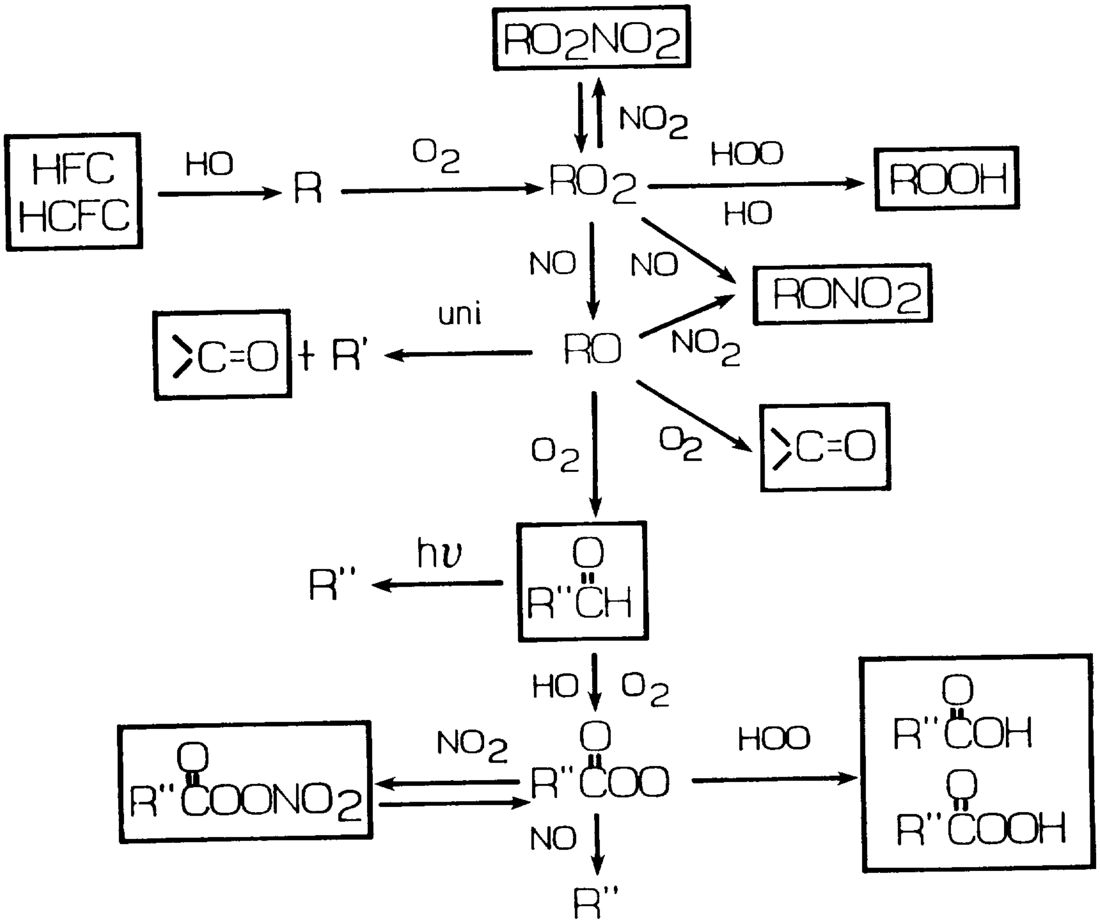


Figure 1: Schematic illustration showing the atmospheric degradation of alternative Fluorocarbons

are enclosed in boxes to differentiate them from the free radical intermediates. Note that under tropospheric conditions the initial haloalkyl (R) radicals exclusively add to O_2 to form the corresponding peroxy RO_2 radicals, (reaction 1).

(1a) $R + O_2\ (+M) \rightarrow ROO\ (+M)$

The most likely reaction partners for these RO_2 radicals in the troposphere are NO, NO_2 or HOO radicals, (reactions 2a-2c) (See, for example, Logan et al., 1981).

(2a) $ROO + NO \rightarrow RO + NO_2$

(2b) $ROO + NO_2\ (+M) \rightarrow ROONO_2\ (+M)$

(2c) $ROO + HOO \rightarrow ROOH + O_2$

In reaction 2a, the ROO radicals are converted by NO into the corresponding haloalkoxy RO radicals, while reactions 2b and 2c yield molecular products haloalkylperoxy nitrate $ROONO_2$ and hydroperoxide

ROOH, respectively (Niki et al., 1979, 1980b; Simonaitis and Heicklen, 1979; Lesclaux and Caralp, 1984). Although the $ROONO_2$ products are thermally unstable and readily redissociate back to ROO radicals and NO_2 at temperatures near 300 K, they become sufficiently stable to be the major intermediate products at the colder temperatures encountered in the upper troposphere Simonaitis and Heicklen, 1979. To illustrate, adopting the temperature tabulations in the US standard atmosphere: 288 K (z = 0 km), 249 K (z = 6 km), and 235 K (z = 8 km), the thermal lifetime of CCl_3OONO_2 will be 10 s, 70 min, and 16 hr, respectively Simonaitis and Heicklen, 1979. Also, the haloalkyl hydroperoxides ROOH are the intermediate products which probably react with HO to regenerate ROO radicals, analogous to the HO-reaction of the CH_3OOH produced in the atmospheric oxidation of CH_4 (NASA Report, 1987).

The subsequent fate of the RO radicals appears to vary greatly depending upon the type of the R group, as discussed in detail later. In general, RO radicals are known to lead to the formation of carbonyl compounds, e.g. CF_2O, CClFO, CF_3CFO, CF_3CClO, etc. via unimolecular dissociation, (reaction 3a), and H-atom abstraction by O_2 for those R groups containing hydrogen attached to the oxygenated carbon, (reaction 3b) (Sanhueza, Hisatsune and Heicklen, 1976).

(3a) $$RO \rightarrow {>}C{=}O + R'$$

(3b) $$RO + O_2 \rightarrow {>}C{=}O + HOO$$

where R′ can be either a Cl-atom or a haloalkyl group attached to the oxygenated carbon in the parent R radicals. The R′ radicals, in turn, undergo a series of degradation steps similar to those for the R radicals. However, for CF_3O radicals, neither the unimolecular dissociation nor the O2-reaction are thermochemically feasible, and bimolecular reactions with other reactive atmospheric species such as NO_2, O_2, or HOO are likely to be operative, (reactions 3c - 3e).

(3c) $$CF3O + NO_2\ (+M) \rightarrow CF_3ONO_2\ (+M)$$

(3d) $$CF_3O + O_3 \rightarrow CF_3OO + O_2$$

(3e) $$CF_3O + HOO \rightarrow CF_3OH + O_2$$

Among the carbonyl products, those containing aldehydic hydrogen [-CHO] group probably undergo both photodissociation, (reaction 4a), and bimolecular reaction with HO-radicals to yield peroxycarbonyl radicals, (reactions 4b - 4c).

(4a) $$R'CHO + h\nu \rightarrow R'' + CHO$$

(4b) $$R'CHO + HO \rightarrow R'CO + H_2O$$

(4c) $$R'CO + O_2\ (+M) \rightarrow R''C(O)OO\ (+M)$$

where R″ represents a haloalkyl group. The R″C(O)OO radicals then react with NO, NO_2 and HOO to form R″ radicals, peroxy nitrates $R''C(O)OONO_2$, and acids R″C(O)OOH, R″C(O)OH, (reactions 5a - 5c), in a manner analogous to $CH_3C(O)OO$ (NASA Report, 1987; CODATA, 1984).

(5a) $$R''C(O)OO + NO \rightarrow R'' + CO_2 + NO_2$$

(5b) $$R''C(O)OO + NO_2\,(+M) \rightarrow R''C(O)OONO_2\,(+M)$$

(5c) $$R''C(O)OO + HOO \rightarrow R''C(O)OOH + O_2\ (\text{or } R''C(O)OH + O_3)$$

The peroxy nitrates $R''C(O)OONO_2$ are thermally unstable, but can persist in colder regions of the troposphere because of the strong temperature dependence of reaction 5b, analogous to the behavior of $CH_3C(O)OONO_2$ (PAN) (NASA Report, 1987; CODATA, 1982, 1984), i.e. 3 days at 288 K (0 km); 1 month at 262 K (4 km); 1 yr at 249 K (6 km); 15 yrs at 235 K (8 km). However, the long lifetime probably will not be realized because of the possibility of photodissociation. Notably, while there is no evidence for the existence of the H-substituted carbonylperoxy nitrate $HC(O)OONO_2$, presumably due to thermal instability of its precursor radicals HC(O)OO, the corresponding fluorine- and chlorine-substituted peroxy nitrates, $FC(O)OONO_2$ and $ClC(O)OONO_2$ produced via reaction 5b, have been observed in the laboratory, and their thermal dissociation lifetimes appear to be comparable to that of PAN (Edney, Spence and Hanst, 1979).

Summarized in Table 2 are the fluorine- and/or chlorine-containing free radicals and molecular products to be expected in the atmospheric degradation of those HFCs and HCFCs that are of particular interest to the AFEAS assessment, i.e. HFCs-134a, 152a, 125 and HCFCs-22, 123, 124, 141b and 142b. The molecular products include carbonyls, acids, hydroxides and nitrates formed via the reactions illustrated in Figure 1. These products are listed for each alternative fluorocarbon in the consecutive order of occurrence during the course of their degradation. Listed in the 3rd column to the left of the products appearing in each row are their free radical precursors. The H-containing carbonyl products indicated by asterisks are the precursors for those radicals indicated also by asterisks. It can be noted from Table 2 that some free radical precursors and molecular products, particularly fluorinated carbonyls such as CHFO, CF_2O and CClFO, are common to degradation of many of the HFCs and HCFCs. The expected carbonyl products from all the C1- and C_2-HFCs and HCFCs are listed in Table 3.

3. GAS-PHASE CHEMICAL LIFETIMES IN THE TROPOSPHERE

As already indicated in the preceding section, the atmospheric reactivity of various fluorine- and/or chlorine-containing molecular products can be assessed in terms of three different types of gas-phase chemical reaction, i.e. thermal decomposition, photolysis, and bimolecular reaction with atmospheric species, particularly HO radicals.

Thermal decomposition is important for the peroxy nitrates, $ROONO_2$ and $RC(O)OONO_2$, listed in Table 2. In colder regions of the troposphere, the acylperoxy nitrates $RC(O)OONO_2$ have thermal lifetimes longer than one year and can be considered "stable," while haloalkylperoxy nitrates $ROONO_2$ are short-lived (<1 day) intermediate products. Notably, these peroxy nitrates are present in the troposphere at concentrations equal to or greater than those determined by the equilibrium with their precursors ROO and NO_2, and they can persist significantly longer than predicted solely from their dissociation rate constants.

Solar radiation in the troposphere contains photons in the near-UV (≤ 295 nm) region which are energetically capable of dissociating various atmospheric compounds (NASA Report, 1987). However, the

Table 2: Degradation Products in the Tropospheric Oxidation of Selected Fluorocarbons

Compound	Formula	Atom & Radical	Carbonyl	Acid	Hydroxide	Nitrate
HCFC 123	$HCCl_2CF_3$	CF_3CCl_2OO			CF_3CCl_2OOH	$CF_3CCl_2OONO_2$
		CF_3CCl_2O	CF_3CClO			
		CF_3OO			CF_3OOH	CF_3OONO_2
		CF_3O			CF_3OH	CF_3ONO_2
HCFC 141B	CCl_2FCH_3	CCl_2FCH_2OO			CCl_2FCH_2OOH	$CCl_2FCH_2OONO_2$
		CCl_2FCH_2O	*CCl_2FCHO			
		CCl_2FOO			CCl_2FOOH	CCl_2FOONO_2
		CCl_2FO	$CClFO$			
		*$CCl_2FC(O)OO$		$CCl_2FC(O)OOH$		$CCl_2FC(O)OONO_2$
				$CCl_2FC(O)OH$		
HCFC 142b	$CClF_2CH_3$	$CClF_2CH_2OO$			$CClF_2CH_2OOH$	$CClF_2CH_2OONO_2$
		$CClF_2CH_2O$	*$CClF_2CHO$			
		$CClF_2OO$			$CClF_2OOH$	$CClF_2OONO_2$
		$CClF_2O$	CF_2O			
		*$CClF_2C(O)OO$		$CClF_2(O)OOH$		$CClF_2C(O)OONO_2$
				$CClF_2C(O)OH$		
HCFC 22	$CHClF_2$	$CClF_2OO$			$CClF_2OOH$	$CClF_2OONO_2$
		$CClF_2O$	CF_2O			
HCFC 124	$CHClFCF_3$	$CF_3CClFOO$			$CF_3CClFOOH$	$CF_3CClFOONO_2$
		CF_3CClFO	CF_3CFO			
		CF_3OO			CF_3OOH	CF_3OONO_2
		CF_3O			CF_3OH	CF_3ONO_2
HCF 134a	CH_2FCF_3	CF_3CHFOO			$CF_3CHFOOH$	$CF_3CHFOONO_2$
		CF_3CHFO	*$CHFO$			
			CF_3CHFO			
		CF_3OO			CF_3OOH	CF_3OONO_2
		CF_3O			CF_3OH	CF_3ONO_2
		*CFO			$CF(O)OOH$	$CF(O)OONO_2$
HFC 52a	CHF_2CH_3	CH_3CF_2Oo			CH_3CF_2OOH	$CH_3CF_2OONO_2$
		CH_3CF_2O	CF_2O			
		CHF_2CH_2OO			CHF_2CH_2OOH	$CHF_2CH_2OONO_2$
		CHF_2CH_2O	*CHF_2CHO			
		CHF_2OO			CHF_2OOH	CHF_2OONO_2
		CHF_2O	*$CHFO$			
		*$CHF_2C(O)OO$		$CHF_2C(O)OOH$		$CHF_2C(O)OONO_2$
				$CHF_2C(O)OH$		
		*CFO		$CF(O)OOH$		$CF(O)OONO_2$
HCF 125	CHF_2CF_3	CF_3CF_2OO			CF_3CF_2OOH	$CF_3CF_2OONO_2$
		CF_3CF_2O	CF_2O			
			CF_3CFO			
		CF_3OO			CF_3OOH	CF_3OONO_2
		CF_3O			CF_3OH	CF_3ONO_2

Table 3: List of Alternative Fluorocarbons and Carbonyl Radicals

Compound	m	n	Formula	Carbonyl Radical
HFC				
$CH_{4\text{-}n}F_n$		1	CH_3F	$CHFO$
$(1 \le n \le 3)$		2	CH_2F_2	CF_2O
		3	CHF_3	
$C_2H_{6\text{-}n}F_n$		1	CH_3CH_2F	$CHFO$, CH_3CFO, CH_2FCHO
$(1 \le n \le 5)$		2	CH_3CHF_2 (152a)	$CHFO$, CF_2O, CHF_2CHO
			CH_2FCH_2F	$CHFO$, CH_2FCFO
		3	CH_3CF_3	CF_3CHO
			CH_2FCHF_2	$CHFO$, CF_2O, CHF_2CFO
		4	CH_2FCF_3	$CHFO$, CF_3CFO
			CHF_2CHF_2	CF_2O
		5	CHF_2CF_3	CF_2O
HCFC				
$CH_{4\text{-}m\text{-}n}Cl_mF_n$	1	1	CH_2ClF	$CHFO$
$(1 \le m \le 2)$	2	1	$CHCl_2F$	$CClFO$
$(1 \le n \le 2)$	1	2	$CHClF_2$ (22)	CF_2O
$(2 \le m+n \le 3)$				
$C_2H_{6\text{-}m\text{-}n}Cl_mF_n$	1	1	CH_2ClCH_2F	$CHFO$, $CHClO$, CH_2FCHOH, CH_2ClCFO
$(1 \le m \le 4)$			CH_3CHClF	$CClFO$, CH_3CFO, $CHClFCHO$
$(1 \le n \le 4)$	1	2	$CHClFCH_2F$	$CHFO$, $CClFO$, $CHClFCFO$, CH_2FCFO
$(2 \le m+n \le 5)$			$CH_2FCHClF$	$CHFO$, $CHClFCFO$, CH_2FCFO, CH_2FCFO
			CH_2ClCHF_2	$CHClO$, CF_2O, CHF_2CHO
			CH_3CClF_2	CF_2O, $CClF_2CHO$
	1	3	$CClF_2CH_2F$	$CHFO$, CF_2O, $CClF_2CFO$
			CHF_2CHClF	$CHFO$, CF_2O, $CClFO$, CHF_2CFO
			CH_2FCClF_2	$CHFO$, CF_2O, $CClF_2CFO$
			CH_2ClCF_3	$CHClO$, CF_3CHO
	1	4	CF_3CHClF	CF_3CFO
			CCF_2CHF_2	CF_2O
	2	1	CH_3CCl_2F	$CClFO$, CCl_2FCHO
			$CH_2ClCHClF$	$CHFO$, $CClFO$, CH_2ClCFO, $CHClFCHO$
	2	2	$CHClFCHClF$	$CClFO$, $CHClFCFO$
			CH_2FCCl_2F	$CHFO$, $CClFO$, CCl_2FCFO
			$CH_2ClCClF_2$	$CHClO$, $CClF_2CHO$
	2	3	$CClF_2CHClF$	CF_2O, $CClFO$, $CClF_2CFO$
			CHF_2CCl_2F	CF_2O, $CClFO$
			$CHCl_2CF_3$	CF_2CClO, CCl_2O
	3	1	CCl_3CH_2F	$CHFO$, CCl_2O, CCl_3CFO
			$CHCl_2CHClF$	$CHFO$, $CHClO$, $CHCl_2CFO$, $CHClFCClO$
			CH_2ClCCl_2F	$CHClO$, $CClFO$, CCl_2FCHO
	3	2	$CCl_2FCHClF$	$CCLFO$, CCl_2CFO
			CCl_3CHF_2	CF_2O, CCl_2O
			$CHCl_2CClF_2$	CF_2O, CCl_2O, $CClF_2CClO$
	4	1	$CHCl_2CCl_2F$	$CClFO$, CCl_2O, CCl_2FCClO
			CCl_3CHClF	$CClFO$, CCl_2O, CCl_3CFO

data for UV absorption cross sections and quantum yields required for determining photodissociative lifetimes are not available for the majority of the fluorine-containing products listed in Table 2. Carbonyl compounds such as CF_2O, CClFO and CCl_2O Mare known to lack absorptions in the near-UV region and thus, are photochemically inactive in the troposphere (NASA Report, 1987). On the other hand, those RCHO compounds with R = haloalky group are known to absorb UV at wavelengths longer than 300 nm (Calvert and Pitts; 1967), but their quantum yields for the formation of R + HCO and RH + CO under atmospheric conditions have not been determined. In the absence of the necessary information, all the carbonyls listed in Table 2 should be regarded as being potentially photochemically stable. The haloalkyl acids also appear to be photochemically inactive, since the first UV absorption bands of the organic acids generally lie below 250 nm (Calvert and Pitts; 1967). The onset of absorption for the ROOH compounds listed in Table 2 is likely to occur at wavelengths longer than 295 nm, by analogy to H_2O_2 and CH_3OOH (NASA Report; 1987). The latter peroxides can decay photochemically in the troposphere, splitting the O-O bond, at noon photolysis rates of approximately 1 day-1 and thus, short photochemical lifetimes are also expected for the haloalkyl hydroperoxides. There appears to be no information on the photochemical properties of the haloalkyl-substituted $RC(O)OONO_2$ compounds, although they are not expected to be strong absorbers in the near-UV region. The UV spectrum of even the most common compound of this type, i.e. PAN (R = CH_3), is not sufficiently well-characterized to exclude significant photolysis in the middle and upper troposphere.

Reaction with HO radicals can be responsible, at least in part, for the subsequent degradation of various hydrogen-containing products listed in Tables 2 and 3, depending on their HO-radical reactivity. Among the aldehydic products RCHO, all those containing R = haloalkyl group probably react rapidly with HO radicals. For instance, a room temperature rate constant of 2×10^{-12} cm^3 $molecule^{-1}$ s^{-1} for the HO + CCl_3CHO reaction (Logan et al.; 1981; Crutzen, 1982; WMO Report; 1985) combined with the global average HO concentration of 5×10^5 molecule cm^{-3} (Crutzen, 1982) gives a lifetime of about 12 days. Although not firmly established experimentally, halogen-substitution for the aldehydic products RCHO (R = F or Cl atom) should greatly reduce their reactivity towards HO radicals [cf. Appendix], and their corresponding atmospheric lifetimes are likely to be as long as several months. For the carbonyls and other products containing hydrogen in the haloalkyl groups only, rate constants for H-abstraction are expected to be comparable to those for the corresponding haloalkanes, leading to lifetimes typically longer than one year. The HO-reactivity of the haloalkyl-substituted acidic products RC(O)OH is expected to be similar to that of HC(O)OH and $CH_3C(O)OH$ (Atkinson, 1985), and their estimated atmospheric lifetimes are about a month or longer. On the other hand, the HO-group in a peroxy acid RC(O)OOH is expected to be much less reactive towards HO radicals due to internal hydrogen-bonding to the C=O group. It remains to be determined whether H abstraction from the HO groups in haloalkyl-substituted alcohols and hydroperoxides will occur at rates comparable to those of their alkyl counterparts. For comparison, room temperature rate constants for the H abstraction from the CH_3 groups of CH_3OH and CH_3OOH are approximately 1×10^{-13} and 5×10^{-12} cm^3 $molecule^{-1}$ s^{-1}, i.e. lifetimes of 8 months and 5 days, respectively. Among the $RONO_2$ and $RC(O)OONO_2$ compounds listed in Table 2, only $CHF_2C(O)OONO_2$ formed from HFC-152a contains hydrogen. This compound is expected to react with HO radicals more slowly than $CH_3C(O)OONO_2$ [PAN]. The rate constant for PAN is 1.4×10^{-13} cm^3 $molecule^{-1}$ s^{-1} at 298 K, corresponding to a lifetime of approximately 6 months.

The preceding semi-quantitative discussion concerning atmospheric reactivity of various degradation products suggests that F- and/or Cl-substituted alkyl compounds generally have substantially longer lifetimes than their alkyl counterparts. There appear to be no known gas-phase reactions for the removal of fully halogenated carbonyls and nitrates.

4. SUMMARY

Tropospheric gas-phase degradation mechanisms and products of alternative fluorocarbons have been assessed based on available laboratory data. The fluorine- and/or chlorine-substituted haloalkyl radicals formed from HFCs and HCFCs after H atom abstraction by HO radicals appear to undergo atmospheric transformations largely analogous to those of the corresponding alkyl radicals. The molecular products include a large variety of fluorine- and/or chlorine-containing carbonyls, acids, peroxy acids, alcohols, hydrogen peroxides, nitrates and peroxy nitrates. Probable atmospheric lifetimes of these compounds have also been estimated. For some carbonyl and nitrate products there seem to be no significant gas-phase removal mechanisms.

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APPENDIX: LITERATURE REVIEW OF THE RELEVANT GAS-PHASE REACTIONS

This review focuses primarily on aspects of the literature information which are not included in the kinetic data evaluation reports published by the NASA and CODATA panels (NASA Report, 1987; CODATA, 1982, 1984). Some of the studies cited are highly qualitative but provide important information for the present assessment. It is not intended as recommendation for modeling purposes.

$HO + RH \rightarrow R + H_2O$ (RH = HFC and HCFC)

The rate constants for these reactions appear to be well established (NASA Report, 1987). For those C_2 -fluorocarbons containing H atoms attached to both the A- and B-carbon atoms, H-atom abstraction from either carbon can occur, but the product distribution is largely unknown. The only available experimental value is that for CH_3CH_2F; 85% ± 4% for abstraction from the A-carbon ($HO + CH_3CH_2F \rightarrow H_2O + CH_3CHF$) (Singleton, Paraskevopoulos and Irwin; 1980). Empirical correlations between the rate constant and C-H bond energy do not work well for predicting product distributions (Atkinson, 1985). Recommendations based on transition-state-theory calculations and the above-mentioned single experimental measurement at room temperature are also available for extrapolation to other temperatures and to other fluorocarbons (Cohen and Westberg, 1988). In the present assessment, all possible primary radicals and their reaction products are considered, as indicated in Tables 1-3.

$R + O_2 + M \rightarrow RO_2 + M$

Limiting high pressure rate constants of $>10^{-12}$ cm^3 molecule^{-1} s^{-1} have been reported for R = CF_3 (Ryan and Plumb, 1982), CCl_2F (Caralp and Lesclaux, 1983; Caralp, Dognon and Lesclaux, 1984), and CCl_3 (Cooper et al., 1980; Ryan and Plumb, 1984). These rate constants are comparable to those for R = CH_3 (NASA Report, 1987; CODATA, 1982, 1984). Similar values are expected for all the R species listed in Table 1. Under tropospheric conditions, these addition reactions seem likely to be the exclusive reaction path for R radicals.

$RO_2 + NO \rightarrow RO + NO_2$

The rate constants for R = CF_3, CF_2Cl, $CFCl_2$, and CCl_3 are recommended by the NASA panel report are based on existing experimental data (Caralp, Dognon and Lesclaux, 1984; Ryan and Plumb, 1984; Lesclaux and Caralp, 1984; Dognon, Caralp and Lesclaux, 1985; Plumb and Ryan, 1982). The room-temperature rate constants of $1.5\text{-}1.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} are comparable to the NASA-recommended value of 7.6×10^{-12} cm^3 molecule^{-1} s^{-1} for R = CH_3 (NASA Report, 1987). In these reactions NO_2 has been shown to be the major nitrogen-containing product (Ryan and Plumb, 1984). Some of the RO_2 radicals may yield $RONO_2$ as well as $RO + NO_2$ upon reaction with NO under atmospheric conditions, analogous to the alkyl radicals ($\geq C_4$) (Carter and Atkinson, 1985). Thus, in the present assessment, both possibilities are indicated in Figure 1 and Tables 2-3.

$RO_2 + NO_2 (+M) \rightarrow RO_2NO_2 (+M)$

These reactions appear to be highly competitive with reaction 2a under tropospheric conditions. For

R = CCl_3, the ratio of rate constants k_{2b}/k_{2a} = 0.68 has been reported at 1 atmosphere, independent of temperature (Simonaitis and Heicklen, 1979; Lesclaux and Caralp, 1984). For R = $CFCl_2$, a high pressure limit of $k_{2b} = 6.0\ (\pm\ 1.0) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} has been determined based on extrapolation from the data obtained at the diluent O_2 pressures of 1-12 torr. The unimolecular rate constants for the thermal dissociation of the haloalkyl and alkylperoxy nitrates are probably all similar, e.g. $k_{-2b} = 10^{15.56 \pm 1.00} \exp[(-11\ 000 + 600/T]$ s^{-1} for R = CCl_3 (Simonaitis and Heicklen, 1979).

ROO + HOO → ROOH + O_2

By analogy to ROO = CH_3OO (NASA Report, 1987; CODATA, 1982, 1984), the HOO-reactions of haloalkyl-substituted ROO radicals are probably competitive with reactions 2a and 2b. No kinetic data are available for these reactions. For R = CH_2Cl and $CHCl_2$, there is IR spectroscopic evidence for the formation of ROOH products (Niki et al., 1980b). However, the possibility of an alternative mechanism to form $>C=O + H_2O +$ O2 via formation of an adduct [ROOOOH] complex formation has not been entirely ruled out. The products, haloalkyl hydroperoxides, are intermediate products which are likely to react further with HO radicals to regenerate ROO radicals, in analogy to the reaction of CH_3OOH (NASA Report, 11987; CODATA, 1982, 1984).

Reactions Involving RO Radicals

The atmospheric reactions of the haloalkoxy RO radicals are less well established. Product studies have been carried out at room temperature and atmospheric pressure of air for the following RO radicals; $CH_2ClO + O_2 \rightarrow CHClO + HO_2$ (Simonaities and Heicklen, 1979; Sanhueza and Heicklen, 1975a); $CHCl_2O \rightarrow CHClO + Cl$ (Simonaitis and Heicklen, 1979; Sanhueza and Heicklen, 1975a); $CF_{3-x}Cl_xO \rightarrow CF_{3-x}Cl_{x-1}O + Cl\ (1 \leq x \leq 3)$ (Jayanty, Simonaitis and Heicklen, 1975; Gillespie, Garraway and Donovan, 1977; Suong and Carr, 1982); $CCl_3CCl_2O \rightarrow (CCl_3CClO + Cl)/(CCl_3 + CCl_2O) = 6.0$ (Mathias et al., 1974; Hybrechts, Olbregts and Thomas, 1967); $CHCl_2CCl_2O \rightarrow (CH_2ClCClO + Cl)/(CHCl_2 + CCl_2O) > 6.0$ (Hybrechts and Meyers, 1966; Bertrand et al., 1968); $CH_2ClCCl_2O \rightarrow (CH_2ClCClO + Cl)/(CH_2Cl + CCl_2O) < 50$ (Sanhueza and Heicklen, 1975b); $CHCl_2CHClO \rightarrow (CHCl_2CHO + Cl)/(CHCl_2 + CHClO) < 50$ (Sanhueza and Heicklen, 1975c); $CH_2ClHCHClO \rightarrow (CH_2ClHCHO + Cl)/(CH_2ClH + CHClO) > 10$ (Sanhueza and Heicklen, 1975c); $CClF_2CCl_2O \rightarrow (CClF_2CClO + Cl)/(CClF_2 + CCl_2O) > 10$ (Simonaitis and Heicklen, 1979); $CF_2ClCF_2O \rightarrow CF_2Cl + CF_2O$ (Simonaitis and Heicklen, 1979). Some general trend in the degradation mechanisms can be inferred from these studies (Simonaitis and Heicklen, 1979), i.e.

* The strong C-F bonding is not broken during the course of the degradation.

* H atom abstraction by O_2 is the dominant reaction for those R radicals containing two H atoms attached to the oxygenated carbon atom, and also for one carbon RO containing only H and F atoms.

* For R = R''CHFO where R'' is a haloalkyl group, the predominant reaction is unimolecular decomposition.

* For those R groups containing one H and one or more Cl attached to the oxygenated carbon atom, the ROO radicals may predominantly undergo unimolecular dissociation by either breaking the C-Cl

and/or C-C bond depending upon the exothermicity of these two channels. In this assessment, both possibilities are included for all these ROO radicals.

For R = CF_3O, the O_2-reaction $CF_3O + O_2 \rightarrow CF_2O + FO_2$ and the unimolecular dissociation $CF_3O \rightarrow CF_2O + F$ are endothermic by 29 and 22 kcal/mole (Herron, 1989), respectively, so other bimolecular reactions such as those with NO_2, HOO or O_3 are likely to occur, as indicated in the text.

Reactions Involving RCHO (R = F, Cl or haloalkyl group)

Although no data seem to be available, both photodissociation and HO-reaction may play a role in the atmospheric removal of the RCHO compounds. Note that if UV absorption spectra of HCFO and HCClO resemble those of CF_2O and CCl_2O rather than that of HCHO (NASA Report, 1987), these RCHO compounds cannot photodissociate in the troposphere. Also, F- or Cl-substitution should greatly reduce their reactivity towards HO radicals analogous to the Cl-atom reaction of HCHO and HCClO (Sanhueza and Heicklen, 1975a; Niki et al., 1980a). On the other hand, those RCHO compounds with R = haloalky group are known to absorb UV at wavelength longer than 300 nm (Calvert and Pitts, 1967), but the quantum yields for the formation of R + HCO and RH + CO under atmospheric conditions have not been determined. The HO-reactions of these RCHO compounds and their subsequent reactions are probably analogous to that of CH_3CHO (NASA Report, 1987; CODATA, 1982,1984), but their HO-rate constants are probably much smaller than 1.4×10^{-11} cm^3 $molecule^{-1}$ s^{-1} for CH_3CHO at 298 K. For instance, a room temperature value of 2×10^{-12} cm^3 $molecule^{-1}$ s^{-1} has been determined for CCl_3CHO (Nelson, Treacy and Sidebottom, 1984). This value may be used as an upper limit for estimating the atmospheric lifetimes of the RCHO compounds in this assessment.

The F, Cl or haloalkyl-substituted RC(O)OO radicals are expected to undergo reactions with NO, NO_2 and HOO,(reactions 5a - 5c), analogous to $CH_3C(O)OO$ radicals (NASA Report, 1987; CODATA, 1982,1984). Except for the IR spectroscopic observation of $FC(O)OONO_2$ and $ClC(O)OONO_2$ and the thermal dissociation of $ClC(O)OONO_2$ (Edney, Spence and Hanst, 1979), no quantitative data are available on the kinetics of these reactions. The rate constants for the reaction $ClC(O)OONO_2 \rightarrow ClC(O)OO + NO_2$ have been determined over the temperature range of 293.7 to 300.3 K in air at 1 atm pressure to be $10^{16.8 \pm 1.5} \exp(-27.7 \pm 2.3 \text{ kcal/mol})$ s^{-1} (Edney, Spence and Hanst, 1979). This expression is comparable to the rate expression of $1.12 \times 10^{16} \exp(-13330/T)$ for R = CH_3 (CODATA, 1982,1984).

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ATMOSPHERIC DEGRADATION MECHANISMS OF HYDROGEN CONTAINING CHLOROFLUOROCARBONS (HCFC) AND FLUOROCARBONS (HFC)

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EXECUTIVE SUMMARY

The current knowledge of atmospheric degradation of hydrogen containing chlorofluorocarbons [HCFC 22 ($CHClF_2$), HCFC 123 ($CHCl_2CF_3$), HCFC 124 ($CHClFCF_3$), HCFC 141b ($CFCl_2CH_3$), HCFC 142b (CF_2ClCH_3)] and fluorocarbons [HFC 125 (CHF_2CF_3), HFC 134a (CH_2FCF_3), HFC 152a (CHF_2CH_3)] is assessed. Except for the initiation reaction by OH radicals there are virtually no experimental data available concerning the subsequent oxidative breakdown of these molecules. However, from an analogy to the degradation mechanisms of simple alkanes, some useful guidelines as to the expected intermediates and final products can be derived. A noteable exception from this analogy, however, appears for the oxi-radicals. Here, halogen substitution induces new reaction types (C-Cl and C-C bond ruptures) which are unknown to the unsubstituted analogues and which modify the nature of the expected carbonyl products. Based on an evaluation of these processes using estimated bond strength data, the following simplified rules with regards to the chlorine content of the HCFC's may be deduced:

- HCFC's containing one chlorine atom such as 22 and 142b seem to release their chlorine content essentially instantaneous with the initial attack on the parent by OH radicals. For HCFC 124 such release is apparently prevented.
- HCFC's such as 123 and 141b with two chlorine atoms are expected to release only one of these instantaneously. The second chlorine atom may be stored in potentially long-lived carbonyl compounds such as CF_3CClO or CClFO.

1. INTRODUCTION

According to current knowledge volatile organic compounds are removed from the atmosphere predominantly by gas phase oxidation processes. These are always initiated photochemically, either by direct photolysis or - more importantly - by photochemically generated species such as OH, $O(^1D)$, HO_2, Cl, NO_3 and O_3. Due to the high energies of the first electronic absorption bands of saturated hydrocarbons and their halogen containing analogues, direct photodissociation is only possible in the middle and upper stratosphere where solar photon fluxes become sufficiently intense below 270 nm.

Among the photochemically generated oxidants, the OH radical is by far the most important species. It is present at all altitudes from ground to well above the stratopause with a maximum density of several 10^7 cm^{-3} during the daytime near 40 km. Due to its photochemical origin and due to the spatial variation of its main source and sink species (O_3, H_2O, NO, CO), OH is highly variable in space and time; the globally and annually averaged concentration is normally assumed to be $\sim 5 \times 10^5$ cm^{-3}.

OH is important not only because of its concentration level but also because of its reactivity. Due to the strong HO-H bond, it reacts readily in an exothermic reaction with all saturated hydrocarbons by H-atom abstraction. Only the atoms $O(^1D)$ and Cl are capable of performing similar abstraction processes. In general the reactions of these species have higher rate coefficients than those of the OH radical, their importance however is limited to those regions of the atmosphere (> 30 km) where sufficient concentrations of these species prevail.

Conventional CFC's owe their long tropospheric lifetime and effective stratospheric chlorine injections - as expressed by their ozone depletion potential (ODP) - to their stability against OH attack in the troposphere. Reactions such as $CX_3Cl + OH \rightarrow CX_3 + HOCl$ are endothermic and have not been observed in the laboratory (DeMore et al. 1987). Hydrogen containing HCFC's and HFC's on the contrary may be degraded by initial OH attack in the troposphere and hence are expected to have correspondingly lower ODP values. The most relevant question with regard to the environmental acceptability of this class of compounds is

- What is the flux of chlorine across the tropopause relative to CFC 11 and per unit mass emitted?

An answer to this question can only be found by addressing to the following problem areas:

- Reactivity towards OH, the global distribution of tropospheric OH and its temporal evolution
- Other potential tropospheric sinks (i.e. solubility, hydrolysis)
- Tropospheric lifetime and fate of oxidation intermediates.

In this review an attempt is being made to delineate the current knowledge of the tropospheric oxidation mechanisms of HCFC's and HFC's with particular view to assessing their ultimate role as chlorine sources in the stratosphere. Since some of the mechanistic details remain speculative at the present time, we will first highlight what is known about the tropospheric oxidation of simple hydrocarbons and on which some of the analogies presented later are based.

2. THE OXIDATION MECHANISM OF SIMPLE HC'S IN THE TROPOSPHERE

Following the initial attack of HC's (alkanes) by OH radicals, viz.

(1) $$OH + RH \rightarrow H_2O + R$$

the subsequent oxidation of the alkyl radicals (R) under tropospheric conditions is known to proceed by the general sequence:

$$\text{alkyl} \xrightarrow{(a)} \text{alkylperoxi} \xrightarrow{(b)} \text{alkoxi} \xrightarrow{(c)} \text{carbonyl compound} \xrightarrow{(d)} \text{oxidized fragments}$$

The rates of these individual steps, including the oxidation of the carbonyl compound are generally faster than that of reaction (1) such that the initial OH attack is rate determining and the lifetime of the hydrocarbon is given by the space and time average of $(k_1 [OH])^{-1}$. Other potential loss processes of hydrocarbons in the troposphere (i.e. reactions with HO_2 and O_3, photolysis, hydrolysis) are unimportant.

a. R/RO_2 conversion

Step (a) of the above sequence reflects the universal conversion of alkyl radicals to alkylperoxi radicals, viz.

(2) $$R + O_2 (+M) \rightarrow RO_2 (+M)$$

This reaction is extremely fast under all tropospheric conditions. Due to the relatively high $R\text{-}O_2$ bond strength (> 25 kcal/mol), reaction (2) is not reversible and RO_2 is the only form in which R exists in perceivable levels in the troposphere. Alternative interactions between R and O_2 leading to an unsaturated HC and HO_2, viz.

(2^1) $$R'CH_2 + O_2 \rightarrow R'_{-H} = CH_2 + HO_2$$

account for less than 0.1% ($R' = CH_3$) of the overall reaction and can safely be discarded for the simpler HC's.

b. RO_2/RO conversion

Unlike step (a), the conversion mechanism of alkylperoxi radicals to alkoxi radicals - step (b) - depends on the ambient conditions.

(i) RO_2/NO_x interactions:

In the continental boundary layer as well as in the upper troposphere/lower stratosphere, sufficient nitrogen oxides are normally present for the alkylperoxi radical chemistry to be dominated by the fast reaction with NO, viz.

(3) $$RO_2 + NO \rightarrow RO + NO_2$$

The rate constants for this process at 298 K are of the order of 8 x 10^{-12} cm^3/s for R = CH_3, C_2H_5, n-C_3H_7 and i-C_3H_7 (Atkinson et al., 1989). However, with the exception of R = CH_3, the interaction between RO_2 and NO may also proceed in recombination forming alkylnitrates,

$$RO_2 + NO\ (+M) \rightarrow RONO_2\ (+M) \tag{3'}$$

The importance of this process increases somewhat with chain length and amounts to < 1.5%, 2% and 4.4% for R = C_2H_5, n-C_3H_7 and i-C_3H_7, respectively.

Under conditions where RO_2 radicals interact predominantly with NO_x another reaction pathway of general application also needs to be considered: the recombination between RO_2 and NO_2 to form peroxinitrates, viz.

$$RO_2 + NO_2\ (+M) \Longleftrightarrow RO_2NO_2\ (+M) \tag{4,-4}$$

Similiar to (3') this reaction terminates the hydrocarbon oxidation chain. Its rate coefficients are well established for the smaller peroxiradicals with values near10^{-11} cm^3/s in the high pressure limit. However, peroxinitrates have a relatively low bond strength and tend to be unstable at the temperatures of the lower troposphere. For instance, $CH_3O_2NO_2$ has a thermal lifetime of < 1 s at 298 K. Only at the lower temperatures of the upper troposphere and lower stratosphere peroxinitrates are more persistent and removal pathways other than thermal decomposition (i.e. photolysis, reaction with OH) may become important. It should be noted that halogen and acyl substitution tends to make peroxinitrates considerably more stable. The lifetimes of $CF_2ClO_2NO_2$ and $CH_3C(O)O_2NO_2$ (PAN) for instance, at 298 K are 20 s and 28 min, respectively, in the high pressure limit (Atkinson et al., 1989). Since these lifetimes will be further enhanced at all pressures prevailing in the troposphere, peroxinitrate formation from these radicals is clearly an important process.

Taking peroxinitrates as relevant temporary reservoir species of HC oxidation intermediates, the question arises whether and how the oxidation chain may be continued other than by the "do-nothing" sequence (4,-4)? It appears that there is at present insufficient knowledge to assess alternatives such as photolysis or reactions with OH. One may speculate that the photolysis products of RO_2NO_2 may be $RO_2 + NO_2$ or $RO + NO_3$ which would correspond to "do-nothing" or the standard RO_2/RO conversion of step (b), respectively. The OH reactions of RO_2NO_2 except for PAN (Wallington et al., 1984; leBras, 1988), have apparently not been investigated. Assuming that their mechanisms occur by α - hydrogen abstraction, viz.

$$OH + R'CH_2O_2NO_2 \rightarrow H_2O + R'CHO_2NO_2$$

these processes may provide direct access to the carbonyl compound since the product radical is expected to decompose readily to $R'CHO + NO_3$.

(ii) RO_2/HO_2 interactions:

In the background middle troposphere where the concentration of NO_x is very low, RO_2 can only be removed in mutual interactions or in reaction with other free radicals such as OH, HO_2 or Cl. Considerations of the concentration levels of each of these species suggest that HO_2 will be the dominant oxidant of RO_2 leading primarily to the formation of hydroperoxides, viz.

(5) $$RO_2 + HO_2 \rightarrow ROOH + O_2$$

The rate constant of this type of reaction is only well established by direct techniques for $R = CH_3$ ($k = 6.3 \times 10^{-12}$ cm^3/s at 298 K). However, there is evidence of a still larger reactivity of $R = CH_3CO$ (Moortgat et al., Veret et al., private communications). Recent product studies performed on reaction (5) ($R = CH_3$) also suggest that there may be an alternative reaction channel forming formaldehyde + H_2O directly, viz.

(5′) $$CH_3O_2 + HO_2 \rightarrow CH_2O + H_2O + O_2$$

Whereas (5′) as well as the subsequent oxidation of the hydroperoxide by OH

(6) $$OH + ROOH \rightarrow H_2O + R_1R_2CO + OH$$

both produce carbonyl compounds directly (thereby circumventing the alkoxi oxidation stage) alkoxi radicals are formed in the competitive photolysis of ROOH, viz.

(7) $$ROOH + h\nu \rightarrow RO + OH$$

This process however is slow in the troposphere since simple hydroperoxides absorb only weakly in the actinic range of the solar spectrum (Molina and Arguello, 1979). It should be noted that hydroperoxides resulting from simple organics are expected to be highly soluble in water and their formation may therefore provide an efficient route of heterogenous removal via rain out. Whether peroxiradicals themselves may also undergo this pathway is presently open to speculation.

c. RO/carbonyl compound conversion

The dominant oxidation pathway of simpler alkoxi radicals is by direct abstraction of the α -H-atom in reaction with O_2, viz.

(8) $$RO + O_2 \rightarrow R_1R_2CO + HO_2$$

The rate coefficient for this type of reaction is relatively small ($k = 1.9 \times 10^{-15}$ cm^3/s at T = 298 K for $R = CH_3$ (DeMore et al., 1987) and 1.1×10^{-14} cm^3/s at T = 298 K for $R = C_2H_5$ (Gutman et al., 1982; Hartmann et al., 1989). However due to the atmospheric O_2 content, the "lifetime" of RO radicals with respect to this process is <0.2 ms. For RO radicals with a chainlength $\geq C_4$, alternative reaction pathways (isomerization, decomposition) forming hydroxyalkyl radicals and carbonyl compounds + alkyl radical are also important (Balla et al., 1985, Dobe et al., 1986).

d. Carbonyl compound/oxidized fragment conversion

It is apparent from the above discussion that carbonyl compounds are the primary oxidation products of any HC oxidation in the atmosphere. Apart from the decomposition routes possible for larger RO radicals, the number of carbon atoms of the parent HC has been conserved. However, carbonyl compounds are further oxidized, mainly in reaction with OH. In case of an aldehyde, R_1HCO, this oxidation occurs almost exclusively by abstraction of the weakly-bonded carbonyl-H-atom leading to the formation of an acyl radical, viz.

(9) $$OH + R_1HCO \rightarrow H_2O + R_1CO$$

The subsequent oxidation of this radical occurs in the sequence

$$R_1CO + O_2 \rightarrow R_1C(O)O_2$$

$$R_1C(O)O_2 + NO \rightarrow R_1C(O)O + NO_2$$

$$R_1C(O)O \rightarrow R_1 + CO_2$$

leading eventually to the split of the α -C-C bond and the formation of CO_2.

Acylperoxiradicals of the type $R_1C(O)O_2$ also tend to react readily with NO_2 to form relatively stable acylperoxinitrates, viz.

$$R_1C(O)O_2 + NO_2 \rightarrow R_1C(O)O_2NO_2$$

The kinetics of formation and decay of the simplest of these species, PAN ($CH_3C(O)O_2NO_2$), are well documented (Atkinson et al., 1989).

Carbonyl compounds have weak near UV (230 - 340 nm) absorption bands arising from the "forbidden" n — π^* singlet-singlet transition. The band maxima appear around 280 - 290 nm with absorption coefficients near 6 x 10^{-20} cm^2 (Calvert and Pitts, 1967). Therefore photolysis is a minor but non negligible alternative pathway of degradation. The photolysis products are alkyl + acyl radicals, i.e.

(10) $$R_1R_2CO + h\nu \rightarrow R_1 + R_2CO$$

both of which will be further oxidized according to the mechanisms delineated above.

3. THE OXIDATION MECHANISMS OF SIMPLE HYDROGEN CONTAINING HCFC's AND HFC's

3.1. General considerations

In light of the above discussion and in view of additional evidence, the following similarities/differences of the atmospheric oxidation of partially halogenated alkanes can be formulated

- Due to the hydrogen content the initial oxidative attack will be by OH radicals. Compared to CH_4 the reactivity of individual C-H bonds in partially halogenated methanes, including $CHClF_2$, is increased by increasing F and Cl substitution due to a corresponding reduction of the C-H bond strength. An exception being CF_3H, with a C-H bond strength about 1.5 kcal/mol larger than CH_4. The same increase of reactivity applies to F and Cl substituted ethanes, again except when one of the carbon atoms represents a CF_3 group (McMillen and Golden, 1982). Note, however, that the overall reactivity towards OH, as expressed by the rate coefficient, also depends on the number of abstractable H atoms in the molecule. The results for k_{OH}-values are documented elsewhere in this report.

- The fully or partially halogenated alkyl radicals will add O_2 to form the corresponding peroxi radicals. Direct kinetic measurements which are available only for CCl_3, CCl_2F and CF_3 (Atkinson et al., 1989; Caralp et al., 1986) indicate that halogen substitution enhances the rates of these association processes (for instance k (CF_3 + O_2) / k (CH_3 + O_2) $\simeq$ 22). Moreover, since the thermochemistry is expected to be similar for the substituted and unsubstituted case reactions, peroxi radical formation will be the exclusive pathway of oxidation of the halogenated alkyl radicals.

- Halogenated peroxi radicals will be reduced to the corresponding oxi radicals in reactions with NO. The limited direct evidence available for CCl_3O_2, $CFCl_2O_2$, CF_2ClO_2, CF_3O_2 suggests that these reactions have rate constants in the order $\sim$ 1.6 x 10^{-11} cm^3/s at 298 K, i.e. a factor of two larger than the corresponding reaction of CH_2O_2 (Atkinson et al., 1989; Dognon et al., 1985). An alternative formation of nitrates from the recombination of halogenated RO_2 with NO is uncertain; for the C_1 case it is most probably unimportant. The recombination of halogenated peroxi radicals with NO_2 occurs with similar rate coefficients to those of the unsubstituted radicals, i.e. k $\cong$ 10^{-11} cm^3/s in the high pressure limit (Atkinson et al., 1989). The pernitrates formed, however, are considerably more stable in the halogenated series (Caralp et al., 1988a) with an increase of the RO_2 -NO_2 bond strength of approximately 4.3 kcal/mol.

- Reactions of halogenated RO_2 with HO_2 have apparently not yet been studied. However, there appears to be no reason to assume that they would not occur and that hydroperoxides will be the products in complete analogy to the unsubstituted systems. Since the RO_2/HO_2-interactions, however, are in competition with the RO_2/NO_x-interactions and since the latter are faster in the substituted cases, we expect reactions between halogenated RO_2 and HO_2 to be generally less important.

- As a result of modified bond strengths, halogenated oxi radicals present new types of reactions. Whereas simple alkoxi radicals such as CH_3O and C_2H_5O only react with O_2 (to form aldehyde + HO_2) and not by C-H or C-C bond rupture, the latter reaction is induced upon halogen substitution. As a result, C-Cl and C-C bond dissociations may become competitive events, even when there are remaining H atoms in the oxi radical (Betrand et al., 1971). Fluorine subsitution in the α-position does not significantly affect the C-Cl bond strength, but it tends to make C-C bonds more stable (McMillen and Golden, 1982). These processes are considered in more detail in the subsequent section.

3.2. Discussion of specific examples

In the following we will discuss the possible atmospheric degradation pathways of a number of specific HCFC's and CFC's in the light of the above principles. The available kinetic information from laboratory studies is too weak to make a firm assessment except perhaps for the more simple cases, i.e. $CHClF_2$.

For the sake of brevity we will condense the initiation reactions as long as they are expected to follow the general pattern of HC oxidation, i.e. we will use the symbol

$$\xrightarrow{\text{OX}}$$

to indicate the sequence: H atom abstraction by OH/O_2 addition/reduction with NO, and will concentrate on the subsequent fate of the oxi radicals. This is done because from the reactions of these radicals the largest differences compared to the hydrocarbon system and between the individual substituted cases are to be expected. It must be understood, though, that in each case presented, additional products such as peroxinitrates and hydroperoxide which arise as chain termination steps from the interactions of peroxi radicals with NO_2 and HO_2 will also occur. They are listed together with the carbonyl compounds in the individual lists of expected products.

As a general rule we have used thermochemical arguments as a guideline of discussing the atmospheric fate of the individual oxi radicals. This has two substantial shortcomings:

- The thermodynamic data base is derived using group additivity rules (Benson, 1976; see appendix). Although this leads generally to acceptable accuracy it is expected to be less reliable for halogen substituted compunds due to polar effects, in particular for F-substitution (Chen et al., 1975). As a consequence the calculated enthalpies of reaction, which in cases comprising fluorinated compounds are the difference between large numbers, may even be uncertain with regards to the sign of their values.
- There is no direct way to relate enthalpies of reaction to a kinetic quantity such as an activation energy. However, we may assume that intrinsic activation barrieres for C-C or C-Cl fission in a radical are small such that the likelihood of these processes to occur will be governed by thermochemistry.

(i) HCFC 22: CHF_2Cl

$$CHF_2Cl \text{ ---- } OX \longrightarrow CF_2ClO$$

followed by:

$$CF_2ClO \rightarrow CF_2O + Cl \qquad \Delta H_R = -30 \text{ kcal/mol}$$

There is evidence from various laboratory studies (Carr et al., 1986; Sanhueza, 1977; Hauteclogue, 1980; Lesclaux et al., 1987; Zellner), mainly performed on the photo-oxidation of CHX_3 type compounds, which indicate that a Cl atom is readily released from CX_3O. A rate coefficient of 7×10^5 s^{-1} at 298 K has been determined for CF_2ClO (Carr et al., 1986). The alternative dissociation pathway

$$CF_2ClO \rightarrow CFClO + F$$

is endothermic by 10 kcal/mol and can safely be discarded. The thermal decay rate of CF_2ClO under atmospheric conditions is comparable to the rate of reaction of CH_3O with O_2. It ensures the rapid transformation of CHF_2Cl to CF_2O with accompanied release of the Cl atom and negligible build-up of CF_2ClO.

CF_2O is considered to be stable with regards to reaction with any of the tropospheric oxidants. However, it is very susceptible to hydrolysis (yielding CO_2 and HF) and is therefore most likely to be removed from the troposphere by this pathway. In the stratosphere CF_2O may be degraded by reaction with $O(^1D)$, viz.

$$CF_2O + O(^1D) \rightarrow CO_2 + F_2$$

($k = 2.2 \times 10^{-11}$ cm^3 (Atkinson et al., 1989)) or by photolysis. However, its UV absorption is very weak even at 220 nm ($\sigma \sim 5 \times 10^{-22}$ cm^2 (DeMore et al., 1987).

Summary of expected products from CHF_2Cl:

Carbonyl compounds: CF_2O
Others: $CF_2ClO_2NO_2$, CF_2ClOOH

(ii) HCFC 123: $CHCl_2CF_3$

$$CHCl_2CF_3 \xrightarrow{OX} CF_3CCl_2O$$

followed by:

$$CF_3CCl_2O \rightarrow CF_3CClO + Cl \qquad \Delta H_R = -3 \text{ kcal/mol}$$

There is no direct evidence that this reaction occurs. It is suggested on the basis of its exothermicity. The alternative dissociation pathway

$$CF_3CCl_2O \rightarrow CF_3 + CCl_2O \qquad \Delta H_R = +2 \text{ kcal/mol}$$

is thermodynamically less favourable and therefore not expected to be competitive with the α -Cl-elimination. The subsequent fate of trifluoroacetylchloride (CF_3CClO) is uncertain. In the troposphere it is not expected to react with OH. Similarly, on the basis of the CCl_2O/CH_2O analogy its photolysis is expected to be slower than that of CH_3CHO. However, CF_3CClO is known to be highly soluble and easily hydrolyzed with trifuoroacetic acid as a product (Beilstein, 1960). Therefore we may expect the lifetime of CF_3CClO to be determined by wash-out or by transport to the ocean. There is therefore little potential for chlorine transport into the stratosphere.

Summary of expected products from $CHCl_2CF_3$:

Carbonyl compounds: CF_3CClO
Other products: $CF_3CCl_2O_2NO_2$, CF_3CCl_2OOH.

(iii) HCFC 124: $CHFClCF_3$

$$CHFClCF_3 \xrightarrow{OX} CF_3CFClO$$

followed by:

$$CF_3CFClO \rightarrow CF_3 + CFClO \qquad \Delta H_R = -4 \text{ kcal/mol}$$

C-C bond fission of CF_3CFClO seems to be the most favourable reaction of this radical. The altemative α - Cl - elimination

$$CF_3CFClO \rightarrow CF_3CFO + Cl \qquad \Delta H_R = +4 \text{ kcal/mol}$$

is thermodynamically less likely and may not be competitive with the former. Therefore we expect the Cl-atom of $CHFClCF_3$ to be stored in $CFClO$.

The atmospheric fate of $CFClO$ is presently not well known. It must be considered stable with regards to reaction with any of the tropospheric oxidants and its photolysis is very slow in the troposphere (DeMore et al., 1987). However, $CFClO$ may be subject to hydrolysis (yielding CO_2, HF and HCl) and is expected to be removed from the troposphere by this pathway.

The subsequent oxidation of the CF_3 radical in the troposphere is highly speculative. It is expected to undergo the normal oxidation chain producing CF_3O radicals. However, there is no apparent thermodynamically allowed pathway for decomposition or reaction with O_2 of this radical. Therefore, CF_3O may be expected to react with other trace gases such as NO or HO_2, viz.

$$CF_3O + NO \rightarrow CF_3ONO$$

$$CF_3O + HO_2 \rightarrow CF_3OH + O_2$$

Summary of expected products from $CHFClCF_3$:

Carbonyl compounds: $CFClO$, (CF_3CFO)
Other products: $CF_3CFClO_2NO_2$, $CF_3CFClOOH$
(CF_3ONO, CF_3OH)

(iv) HCFC 141b: CCl_2FCH_3

$$CCl_2FCH_3 \xrightarrow{\quad OX \quad} CCl_2FCH_2O$$

followed by:

$$CCl_2FCH_2O + O_2 \rightarrow CCl_2FCHO + HO_2 \qquad \Delta H_R = -32 \text{ kcal/mol}$$

Due to the remaining α - atoms the CCl_2FCH_2O radical is expected to react predominantly with O_2 to produce a perhalogenated acetaldehyde in accordance with the standard hydrocarbon oxidation chain. Chlorine release from the oxi radical is not possible. Moreover, β - scission of CCl_2FCHO, viz

$$CCl_2FCH_2O \rightarrow CCl_2F + CH_2O \qquad \Delta H_R = +7 \text{ kcal/mol}$$

is endothermic and may therefore not be competitive with the O_2 reaction.

The subsequent fate of the aldehyde will most likely be degradation via initial OH attack to yield CO_2 + CCl_2F ($CClFO$), viz.

$$CCl_2FCHO \xrightarrow{\quad OX \quad} CCl_2FC(O)O$$

$$CCl_2FC(O)O \rightarrow CCl_2F + CO_2$$

$$CCl_2F + O_2 \rightarrow CCl_2FO_2$$

$$CCl_2FO_2 + NO \rightarrow CCl_2FO + NO_2$$

$$CCl_2FO \rightarrow CClFO + Cl$$

Due to the higher OH reaction rate of the aldehyde compared to the initial HCFC, this sequence corresponds essentially to the release of one chlorine atom instantaneous with the degradation of the HCFC. The second one is being stored in $CClFO$, the fate of which has been discussed under (iii). It may be worthy of note that β-scission of the oxiradical will produce the same products.

Summary of expected products from CCl_2FCH_3:

Carbonyl compounds: CCl_2FCHO, $CClFO$, (CH_2O)
Other products: $CCl_2FCH_2O_2NO_2$, CCl_2FCH_2OOH,
$CCl_2FC(O)O_2NO_2$ (from the oxidation of CCl_2FCHO),
$CCl_2FO_2NO_2$, CCl_2FOOH (from the oxidation of CCl_2FCHO)

(iv) HCFC 142b: $CClF_2CH_3$

$$CClF_2CH_3 \text{ —— } OX \longrightarrow CClF_2CH_2O$$

followed by:

$$CClF_2CH_2O + O_2 \rightarrow CClF_2CHO + HO_2 \qquad \Delta H_R = -29 \text{ kcal/mol}$$

In complete analogy to Cl_2FCH_2O we expect $CClF_2CH_2O$ to react predominantly with O_2 to form perhalogenated acetaldehyde. Chlorine release from $CClF_2CH_2O$ is not possible. Moreover, the β- scission reaction

$$CClF_2CH_2O \rightarrow CClF_2 + CH_2O \qquad \Delta H_R = +10 \text{ kcal/mol}$$

is more endothermic than in the 141b case and hence may be entirely negligible.

The subsequent oxidation of $CClF_2CHO$ will lead to $CClF_2 + CO_2$; whereupon $CClF_2$ radicals will oxidize to CF_2O. As a consequence we expect the release of the chlorine content of HCFC 142b instantaneous with the initial OH attack. However, since HCFC 142b has a relatively long tropospheric lifetime (~ 28 years), some of this degradation will always occur in the stratosphere.

Summary of expected products from $CClF_2CH_3$:

Carbonyl compounds: $CClF_2CHO$, CF_2O, (CH_2O)
Other compounds: $CClF_2CH_2O_2NO_2$, $CClF_2CH_2OOH$
$CClF_2C(O)O_2NO_2$, $CClF_2O_2NO_2$, $CClF_2OOH$
(from the oxidation of $CClF_2CHO$).

(vi) HFC 125: CHF_2CF_3

$$CHF_2CF_3 \text{ —— } OX \longrightarrow CF_3CF_2O$$

followed by:

$$CF_3CF_2O \rightarrow CF_3 + CF_2O \qquad \Delta H_R = -23 \text{ kcal /mol}$$

The perfluorinated oxi radical CF_3CF_2O is expected to be thermally unstable with respect to C-C bond fission. The alternative elimination of an F-atom to yield CF_3CFO is endothermic by ~ 25 kcal/mol and can safely be discarded. The subsequent atmospheric fates of CF_3 and CF_2O have been discussed above (compare (iii) and (i)).

Summary of expected products from CHF_2CF_3:

Carbonyl compounds: CF_2O
Other products: $CF_3CF_2O_2NO_2$, CF_3CF_2OOH,
(CF$_3$ONO, CF_3OH)

(vii) HFC 134a: CH_2FCF_3

$$CH_2FCF_3 \text{——} OX \longrightarrow CF_3CHFO$$

followed by:

$$CF_3CHFO + O_2 \rightarrow CF_3CFO + HO_2 \qquad \Delta H_R = -38 \text{ kcal/mol}$$

and, alternatively,

$$CF_3CHFO \rightarrow CF_3 + CHFO \qquad \Delta H_R = 8 \text{ kcal/mol}$$

Due to the hydrogen content of CF_3CHFO this radical is expected to react readily with O_2 yielding perfluoroacetylfluoride. The alternative C-C bond fission is sufficiently exothermic to be expected as a competitive reaction pathway. Thermal elimination of an H atom from CF_3CHFO on the other hand is endothermic (+ 11 kcal/mol) and can safely be discarded.

The product CF_3CFO is not expected to react with any of the tropospheric oxidants, nor to be subject to photolysis. However, in analogy to CF_2O and CF_3CClO it may readily hydrolyze yielding CF_3OOH and HF as products. Therefore its removal rate from the troposphere may be determined by the rate of wash-out or by transport to the ocean surface.

The atmospheric fate of the CF_3 product has been discussed above (cf (iii)). For the second product resulting from this channel, CHFO, we expect both photolysis and reaction with OH as possible degradation pathways, viz.

$$\begin{aligned} CHFO + h\nu &\rightarrow CFO + H \\ &\rightarrow CO + HF \\ OH + CHFO &\rightarrow CFO + H_2 \end{aligned}$$

The consecutive reactions of the CFO radical are highly uncertain. Due to the strong C-F bond we must expect other reactions than for CHO and propose the following sequence

$$\begin{aligned} CFO + O_2 &\rightarrow FC(O)O_2 \\ FC(O)O_2 + NO_2 &\rightarrow FC(O)O_2NO_2 \end{aligned}$$

$$FC(O)O_2 + NO \rightarrow FC(O)O + NO_2$$

$$FC(O)O + HO_2 \rightarrow FC(O)\ OH + O_2$$

with fluorinated formic acid as a product, which may further stabilize by HF elimination.

Summary of expected products from CH_2FCF_3:

Carbonyl compounds: CF_3CFO, $CHFO$,
Other products: $CF_3CHFO_2NO_2$, $CF_3CHFOOH$,
$FC(O)O_2NO_2$, $FC(O)OH$ (from the oxidation of CHFO)

(viii) HFC 152a: CH_2CH_3

There are two different initial oxidation pathways, viz.

(a) $$CHF_2CH_3 \xrightarrow{OX} CHF_2CH_2O$$

(b) $$\xrightarrow{OX} CH_3CF_2O \longrightarrow$$

arising from α-and β-H-abstraction from the parent by OH radicals. Apparently, the relative rates of these processes have not been directly measured. However, there is indirect evidence from reactions of OH and Cl radicals with fluorinated alkanes (Martens et al., 1976, Tschuikow-Roux et al., 1985, Singleton et al., 1980) that suggest preferential attack of the α-(fluorinated) position yielding predominantly CH_3CF_2O (channel b) despite the statistical advantage of the β-position. However, in the subsequent presentation we will still consider the possible final products arising from both types of oxi radicals.

For CHF_2CH_2O we expect the reaction with O_2 as the most likely pathway of its subsequent removal, viz.

$$CHF_2CH_2O + O_2 \rightarrow CHF_2CHO + HO_2 \qquad \Delta H_R = -29 \text{ kcal/mol}$$

The alternative C-C-bond fission

$$CHF_2CH_2O \rightarrow CHF_2 + CH_2O \qquad \Delta H_R = +11 \text{ kcal/mol}$$

is sufficiently endothermic to be safely discarded. The product, difluoro-ace-taldehyde, will readily oxidize to yield CO_2 and CF_2O as final products, viz.

$$CHF_2CHO \xrightarrow{OX} CHF_2C(O)O$$

$$CHF_2C(O)O \rightarrow CHF_2 + CO_2$$

$$CHF_2 + O_2 \rightarrow CHF_2O_2$$

$$CHF_2O_2 + NO \rightarrow CHF_2O + NO_2$$

$$CHF_2O + O_2 \rightarrow CF_2O + HO_2$$

The oxi-radical formed in channel (b) on the hand is expected to undergo rapid C-C-bond fission, viz.

$$CH_3CF_2O \rightarrow CH_3 + CF_2O \qquad \Delta H_R = -24 \text{ kcal/mol}$$

eventually leading to $CO_2 + CF_2O$, the same products as expected from CHF_2CH_2O. As a consequence the relative Initiation rate (α- or β-H -atom abstraction) does not modify the main product distribution. It will influence, however, products such as pernitrates and hydroperoxides.

Summary of expected products from CHF_2CH_3:

Carbonyl compounds: CHF_2CHO, CF_2O,
Other products: $CHF_2CH_2O_2NO_2$, CHF_2CH_2OOH,
$CH_3CF_2O_2NO_2$, CH_3CF_2OOH,
$CHF_2C(O)O_2NO_2$, $CHF_2O_2NO_2$ (from the oxidation of CHF_2CHO)
CHF_2OOH (from the oxidation of CHF_2CHO)

4. SUMMARY AND RECOMMENDATIONS

- The mechanisms of the tropospheric degradation of HCFC's such as 22 and 142b suggest that their chlorine content will be released essentially instantaneous with the initial attack of the HCFC by OH. For HCFC 124 this release is prevented due to competitive C-C bond fission.

- HCFC's such as 123 and 141b with two chlorine atoms are expected to release only one of these instantaneously. The second chlorine atom may be stored in relatively long-lived species such as CF_3CClO or CClFO.

- The photochemistry of compounds such as CF_3CClO and CClFO should be investigated in order to assess their potential for chlorine release in the stratosphere.

- The effect of Cl atom release on the chemistry of the troposphere should be assessed.

- The experimental data base is too weak to allow firmer assessment of the degradation mechanism of HCFC's and HFC's. A large uncertainty arises for the reactions of the oxi radicals. Even the thermodynamic data base is too speculative to draw more substantiated conclusions. It is absolutely essential to initiate direct experimental studies in order to validate these assessments.

APPENDIX TABLE: Summary of standard enthalpies of formation used in the present evaluation: (in units of kcal/mol). Calculated quantities are underlined.

Radicals		Carbonyl compounds	
F	18.9 a)	CH_2O	- 26 a)
Cl	28.9 a)	CHFO	- $\underline{88.9}$ f)
HO_2	2.5 b)	CF_2O	-152 a)
CH_3	35.1 b)	CFClO	-102 k)
CHF_2	- 59 b)	CCl_2O	- 52.6 a)
CF_3	-112 a, b)	CHF_2CHO	-$\underline{127}$ l)
CF_2Cl	- 64 b)	$CFCl_2CHO$	- $\underline{90}$ m)
$CFCl_2$	- 23 b)	CF_2ClCHO	-$\underline{131}$ m)
CCl_3	18.5 a)	CF_3CFO	-$\underline{235}$ n)
CF_3O	-$\underline{145}$ c), -157 d)	CF_3CClO	-$\underline{198}$ o)
CF_2ClO	- 93 e), - $\underline{97}$ f)		
$CFCl_2O$	- $\underline{49}$ g), - $\underline{49}$ f)		
CF_3CF_2O	-$\underline{241}$ h)		
CF_3CHFO	-$\underline{193}$ i)		
CHF_2CH_2O	- $\underline{96}$ j)		
CH_3CF_2O	- $\underline{93}$ j)		
CF_3CFClO	-$\underline{210}$ j)		
CF_3CCl_2O	-$\underline{166}$ j)		
CF_2ClCH_2O	-$\underline{100}$ j)		
$CFCl_2CH_2O$	- $\underline{56}$ j)		

a) Benson, 1976

b) McMillen and Golden, 1982

c) Calculated from bond additivity rules (Benson, 1976) using [C-(F)} (O)] $\sim$ [C-$(F)_3$(C)] = - 158.4 and a correction for the oxi group of [O -(C)]= + 13.6 as derived from Δ H_f (CH_3O) = [C-$(H)_3$(O)] + [O - (C)] = 3.5

d) Batt, 1977

e) Calculated using [C-$(F)_2$(Cl)(O)] $\sim$ (C-$(F)_2$(Cl)(C)]= - 106.3 (Benson, 1976)

f) MNDO-calculation from Rayez et al., 1987

g) Calculated from Δ H_f (CF_2ClO) using a correction for F/Cl-exchange as derived from Δ H_f's for substituted CX_3 radicals

h) Calculated using [C-$(F)_3$(C)] = - 158.4, [C-$(F)_2$ (C) (O)] $\sim$ [C-$(F)_2(C)_2$] = - 97 (Benson, 1976) and a correction for the oxi group of [O-(C)] = + 14.3 as derived from Δ H_f (C_2H_5O) = - 4 and the corresponding group contributions.

i) Calculated as for h) and with [C-(H)(F)(O)] = - 49 (Benson, 1976)

j) Calculated according to h) with group contributions from Benson, 1976

k) JANAF Tables, 1979

l) Calculated from [C-(CO)$(F)_2$(Cl)] = - 102 and a correction for substitution of Cl by H according to Benson, 1976 and [CO-(C)(H)] = - 26.9

m) Calculated as for l) and by applying a correction for F exchange by Cl

n) Calculated from [C-(CO)$(F)_3$] = - 158 (Benson, 1976) and [CO-(C)(F)] = - 77, where the latter was obtained from [CO-(C)(Cl)] (see o.)) and a correction for Cl/F exchange.

o) Calculated from [C-(CO)$(F)_3$] = - 158 (Benson, 1976) and [CO-(C)(Cl)] = - 40, where the latter was obtained from the experimental Δ H_f for CH_3COCl (-60.5 (Pritchard and Skinner, 1950)) and [C-(CO)$(Cl)_3$] = - 20.7 (Benson, 1976)