N92-15441

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

Roger Atkinson

Statewide Air Pollution Research Center
University of California
Riverside, California 92521

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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	Upper Troposphere
M (N_2 + O_2)	2.5 x 10^{19}	4.5 x 10^{18}
O_2	5 x 10^{18}	9 x 10^{17}
O_3	7 x 10^{11}	4 x 10^{11}
NO	2.5 x 10^{8}	2.5 x 10^{8}
NO_2	2.5 x 10^{8}	2.5 x 10^{8}
OH	1.5 x 10^{6}	1.5 x 10^{6}
HO_2	10^{9}	10^{8}
$CH_3\dot{O}_2$	2.5 x 10^{8}	6 x 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 $CF_3CCl_2\dot{O}_2$,

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

with a rate constant k $\geq$5 x 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 x 10^{-6} s.

B. $CF_3CCl_2\dot{O}_2$. The expected reactions of this peroxy radical are,

$$CF_3CCl_2\dot{O}_2 + NO \rightarrow CF_3CCl_2\dot{O} + NO_2 \quad \text{(a)}$$

$$CF_3CCl_2\dot{O}_2 + NO_2 \xrightarrow{M} CF_3CCl_2OONO_2 \quad \text{(b)}$$

$$CF_3CCl_2\dot{O}_2 + HO_2 \rightarrow CF_3CCl_2OOH + O_2 \quad \text{(c)}$$

$$CF_3CCl_2\dot{O}_2 + CH_3\dot{O}_2 \rightarrow CF_3CCl_2\dot{O} + CH_3\dot{O} + O_2 \quad \text{(d1)}$$

$$CF_3CCl_2\dot{O}_2 + CH_3\dot{O}_2 \rightarrow CF_3CCl_2OH + HCHO + O_2 \quad \text{(d2)}$$

with rate constants (cm^3 $molecule^{-1}$ s^{-1} units) of k_a ~1.5 x 10^{-11} $(T/300)^{-1.2}$, k_b ~1.0 x 10^{-11}, k_c = 3.4 x 10^{-13} $e^{800/T}$, and k_{d1} + k_{d2} ~2 x 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), 3.8×10^{-3} and 5.4×10^{-3}; reaction (b), 2.5×10^{-3} and 2.5×10^{-3}; reaction (c), 5×10^{-3} and 1.3×10^{-3}; and reaction (d), 5×10^{-5} and 1.2×10^{-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 $2 \times 10^{-7}\ s^{-1}$ 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 ~ 5 days.

Hence, in the lower troposphere the dominant loss process of $CF_3CCl_2OONO_2$ will be thermal decomposition, with a lifetime of ~ 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 ~ 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 $CF_3CCl_2O_2^{\cdot}$ radical

$$OH + CF_3CCl_2OOH \rightarrow H_2O + CF_3CCl_2O_2^{\cdot}$$

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 $H_2O + RO_2^{\cdot}$ 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

$$k(OH + ROOH \rightarrow H_2O + RO_2^{\cdot}) = 1.7 \times 10^{-12} e^{220/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The calculated OH radical reaction rates during daylight hours of (5-7) 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. <u>$CF_3CCl_2O^{\cdot}$</u>. Based upon the discussion in Section 4.3, the reactions of the $CF_3CCl_2O^{\cdot}$ radical which need to be considered are

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

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

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 ΔH_f[C-(X)(Y)(Z)(C)] and ΔH_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

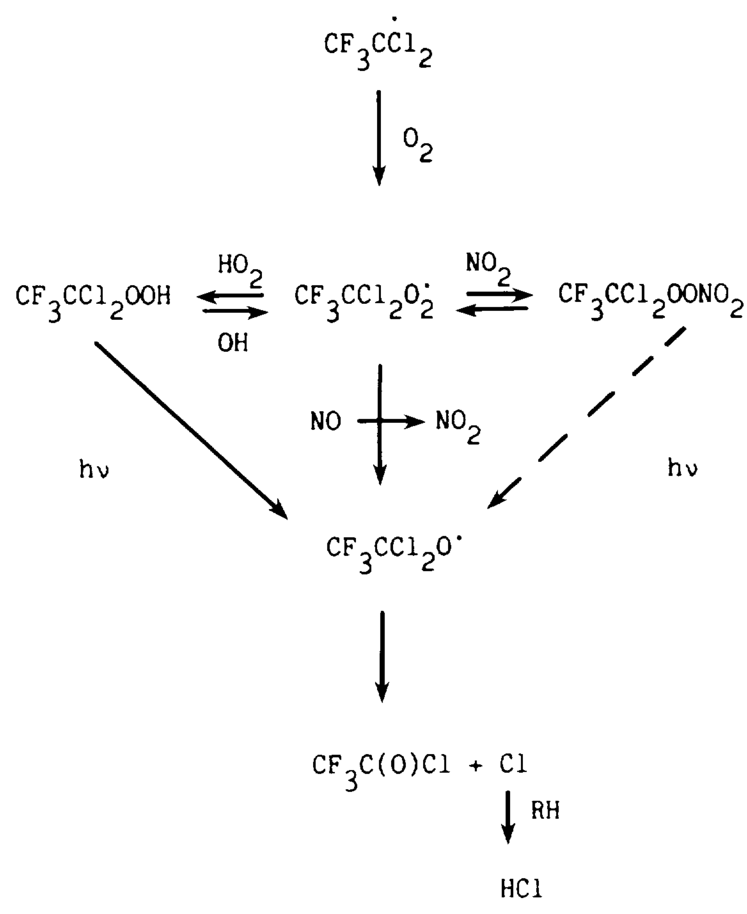
$$OH + HCl \rightarrow H_2O + Cl$$

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,

$$CFCl_2\dot{C}H_2 + O_2 \xrightarrow{M} CFCl_2CH_2\dot{O}_2$$

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. $CFCl_2CH_2\dot{O_2}$. As discussed in Section 2.1, the $CFCl_2CH_2\dot{O_2}$ radical will react with NO, NO_2 and the HO_2 radical,

$$CFCl_2CH_2\dot{O_2} + NO \rightarrow CFCl_2CH_2\dot{O} + NO_2$$

$$CFCl_2CH_2\dot{O_2} + NO_2 \xrightarrow{M} CFCl_2CH_2OONO_2$$

$$CFCl_2CH_2\dot{O_2} + HO_2 \rightarrow CFCl_2CH_2OOH + O_2$$

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 $CFCl_2CH_2\dot{O_2}$ 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

$$CFCl_2CH_2OONO_2 \xrightarrow{M} CFCl_2CH_2\dot{O_2} + NO_2$$

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

$$CFCl_2CH_2OONO_2 + h\nu \rightarrow CFCl_2CH_2\dot{O_2} + NO_2$$

$$CFCl_2CH_2OONO_2 + h\nu \rightarrow CFCl_2CH_2\dot{O} + NO_3$$

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

$$CFCl_2CH_2OOH + h\nu \rightarrow CFCl_2CH_2\dot{O} + OH$$

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.

$$OH + CFCl_2CH_2OOH \rightarrow H_2O + CFCl_2CH_2\dot{O_2}$$

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 $\sim(5\text{-}15)\%$ 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. $\underline{CFCl_2CH_2\dot{O}}$. Based on the discussion in Section 4.3, the reactions of this radical which need to be considered are

$$CFCl_2CH_2\dot{O} + O_2 \rightarrow CFCl_2CHO + HO_2 \qquad (a)$$

$$CFCl_2CH_2\dot{O} \rightarrow \dot{C}FCl_2 + HCHO \qquad (b)$$

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 $CFCl_2\dot{O}$ radical will eliminate a Cl atom to yield COFCl (instead of the COF_2 formed from the $CF_2Cl\dot{O}$ 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 $CFCl_2CH_2\dot{O}$ 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}, $= 2.7 \times 10^{-15}$ 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 ≥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. $\underline{CFCl_2\dot{C}O}$. This acyl radical will rapidly add O_2, with a rate constant of $\sim 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} (Atkinson, 1989a).

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

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. $\underline{CFCl_2C(O)O_2^{\cdot}}$. Analogous to the alkyl and haloalkyl peroxy ($RO_2^{\cdot}$) radicals and the acetyl peroxy ($CH_3C(O)O_2^{\cdot}$) radical, this acyl peroxy radical will react with NO and NO_2.

$$CFCl_2C(O)O_2^{\cdot} + NO \rightarrow CFCl_2CO_2^{\cdot} + NO_2$$

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

$$CFCl_2C(O)O_2^{\cdot} + NO_2 \xrightarrow{M} CFCl_2C(O)OONO_2$$

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 $CH_3O_2^{\cdot}$ radicals cannot be ruled out as being of importance. The reaction of the $CH_3C(O)O_2^{\cdot}$ 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 $CH_3C(O)O_2^{\cdot}$ radical with the $CH_3O_2^{\cdot}$ radical is rapid, with a rate constant of 1.1×10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 298 K, forming $CH_3O^{\cdot} + CH_3CO_2^{\cdot} + O_2$ and $CH_3COOH + HCHO + O_2$ in equal yield at room temperature (IUPAC, 1989; Moortgat et al., 1989).

The analogous products would then be $CFCl_2CO_2^{\cdot}$, 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.

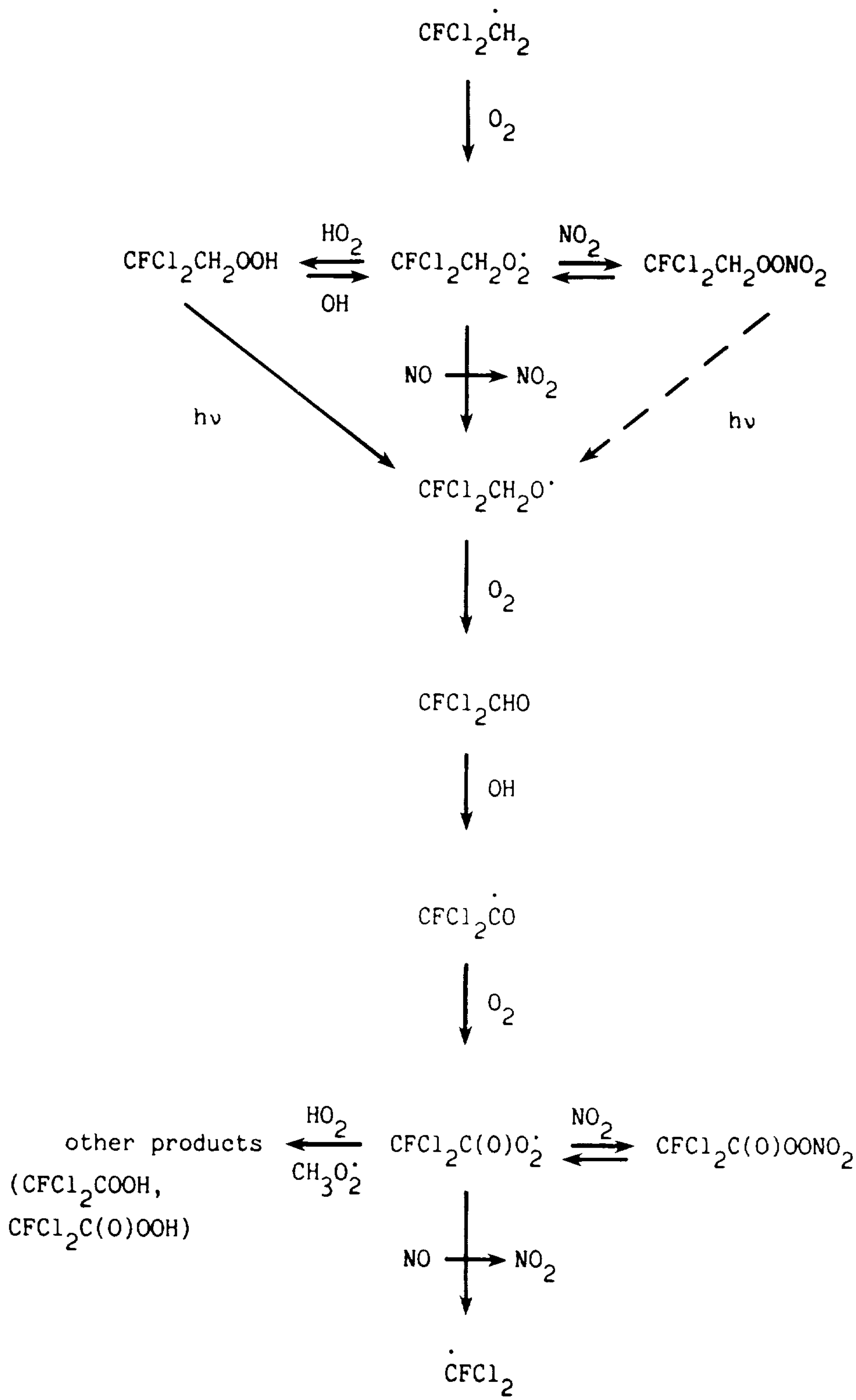
A. $CF_2ClCH_2O^{\cdot}$. The likely reaction pathways are (see Section 2.2.E above)

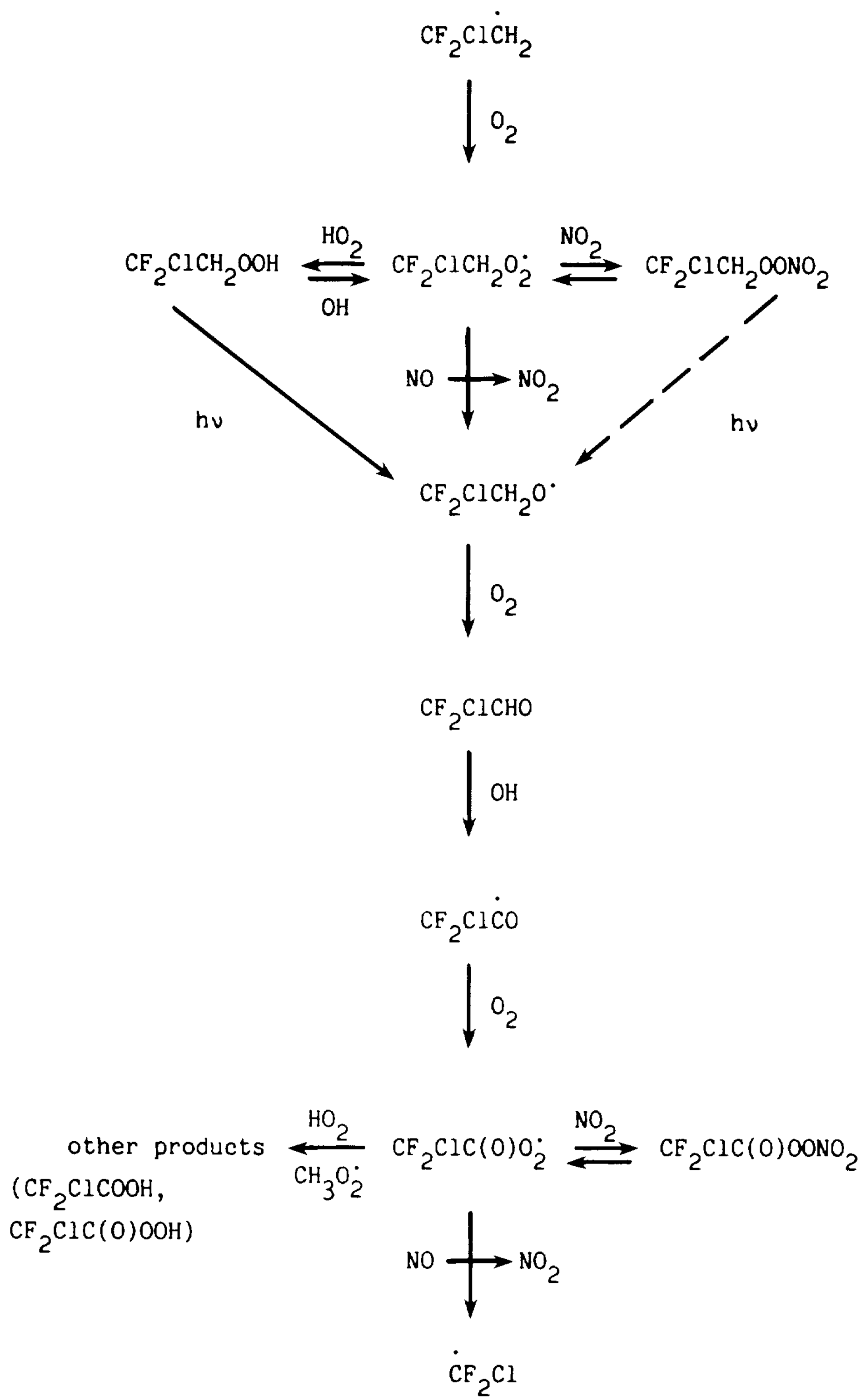
$$CF_2ClCH_2O^{\cdot} + O_2 \rightarrow CF_2ClCHO + HO_2 \quad \text{(a)}$$

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

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.


CFCl2CH2
O2
CFCl2CH2OOH
HO2
OH
CFCl2CH2O2
NO2
CFCl2CH2OONO2
NO
NO2
hν
hν
CFCl2CH2O
O2
CFCl2CHO
OH
CFCl2CO
O2
other products
(CFCl2COOH,
CFCl2C(O)OOH)
HO2
CH3O2
CFCl2C(O)O2
NO2
CFCl2C(O)OONO2
NO
NO2
CFCl2


CF2ClCH2
O2
CF2ClCH2OOH
HO2
OH
CF2ClCH2O2
NO2
CF2ClCH2OONO2
hν
NO
NO2
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.

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

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

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

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. $\underline{CF_2ClOONO_2}$. As in Sections 2.1 and 2.2 above, this peroxynitrate can undergo thermal decomposition or photolyze. The thermal decomposition

$$CF_2ClOONO_2 \xrightarrow{M} CF_2ClO_2^{\cdot} + NO_2$$

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 $\sim$15 s in the lower troposphere to $\sim$(2-3) x 10^7 s ($\sim$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 $\sim$5 days. The photolysis products are not known, but are expected to be mainly the peroxy radical plus NO_2.

D. $\underline{CF_2ClOOH}$. 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 $\sim$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. $\underline{CF_2ClO^{\cdot}}$. 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).

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

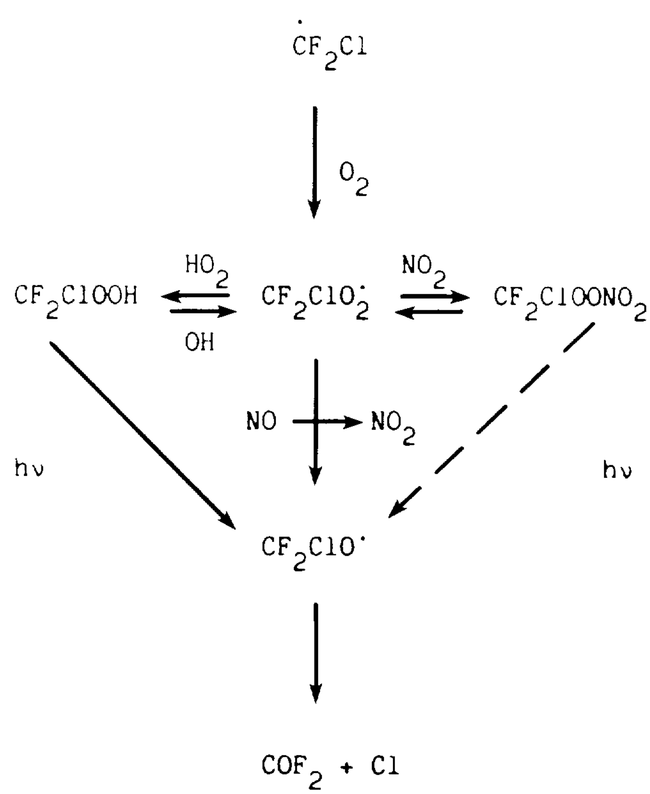
The $CFCl_2O^{\cdot}$ radical decomposes in an analogous manner

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

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

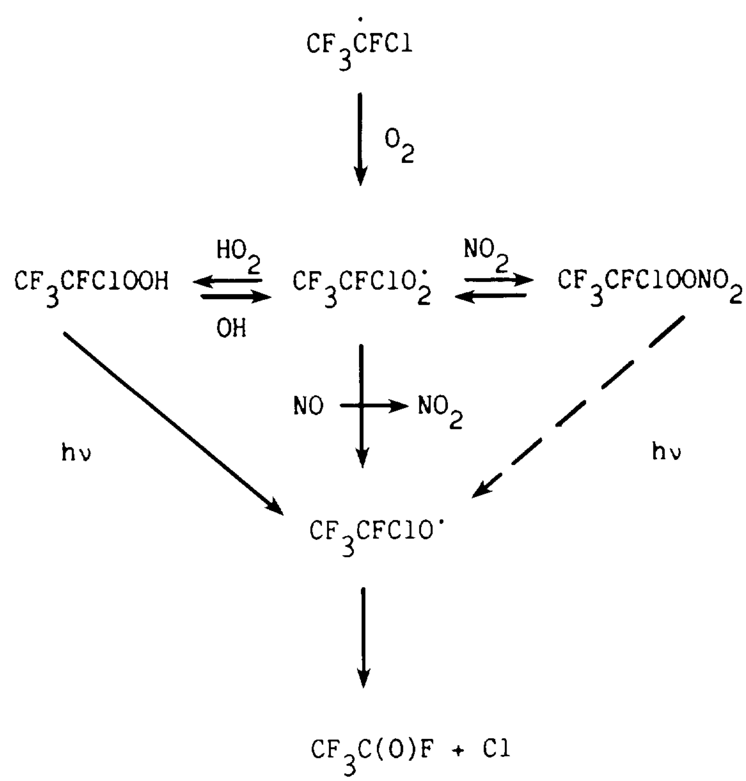
$$CF_3CFClO^{\cdot} \rightarrow CF_3C(O)F + Cl \quad (a)$$

$$CF_3CFClO^{\cdot} \rightarrow \dot{C}F_3 + COFCl \quad (b)$$

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

$$CF_3CHFO_2^{\cdot} + NO \rightarrow CF_3CHFO^{\cdot} + NO_2 \quad \text{(a)}$$

$$CF_3CHFO_2^{\cdot} + NO_2 \xrightarrow{M} CF_3CHFOONO_2 \quad \text{(b)}$$

$$CF_3CHFO_2^{\cdot} + HO_2 \rightarrow CF_3CHFOOH + O_2 \quad \text{(c)}$$

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

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

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

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

$$CF_3CHFO^{\cdot} \rightarrow CF_3CHO + F \quad \text{(d)}$$

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.

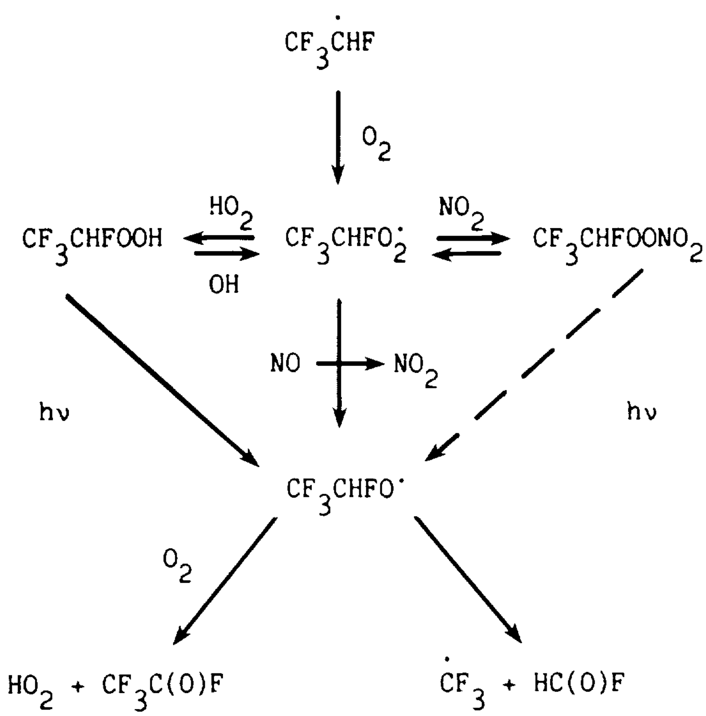
G. HC(O)F. The expected tropospheric removal routes for formyl fluoride are photolysis, reaction with the OH radical and wet deposition. Reaction with the OH radical

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

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 ~ 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 ~ 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,

$$CHF_2CH_2O^{\cdot} + O_2 \rightarrow CHF_2CHO + HO_2 \tag{a}$$

$$CHF_2CH_2O^{\cdot} \rightarrow \dot{C}HF_2 + HCHO \tag{b}$$

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.

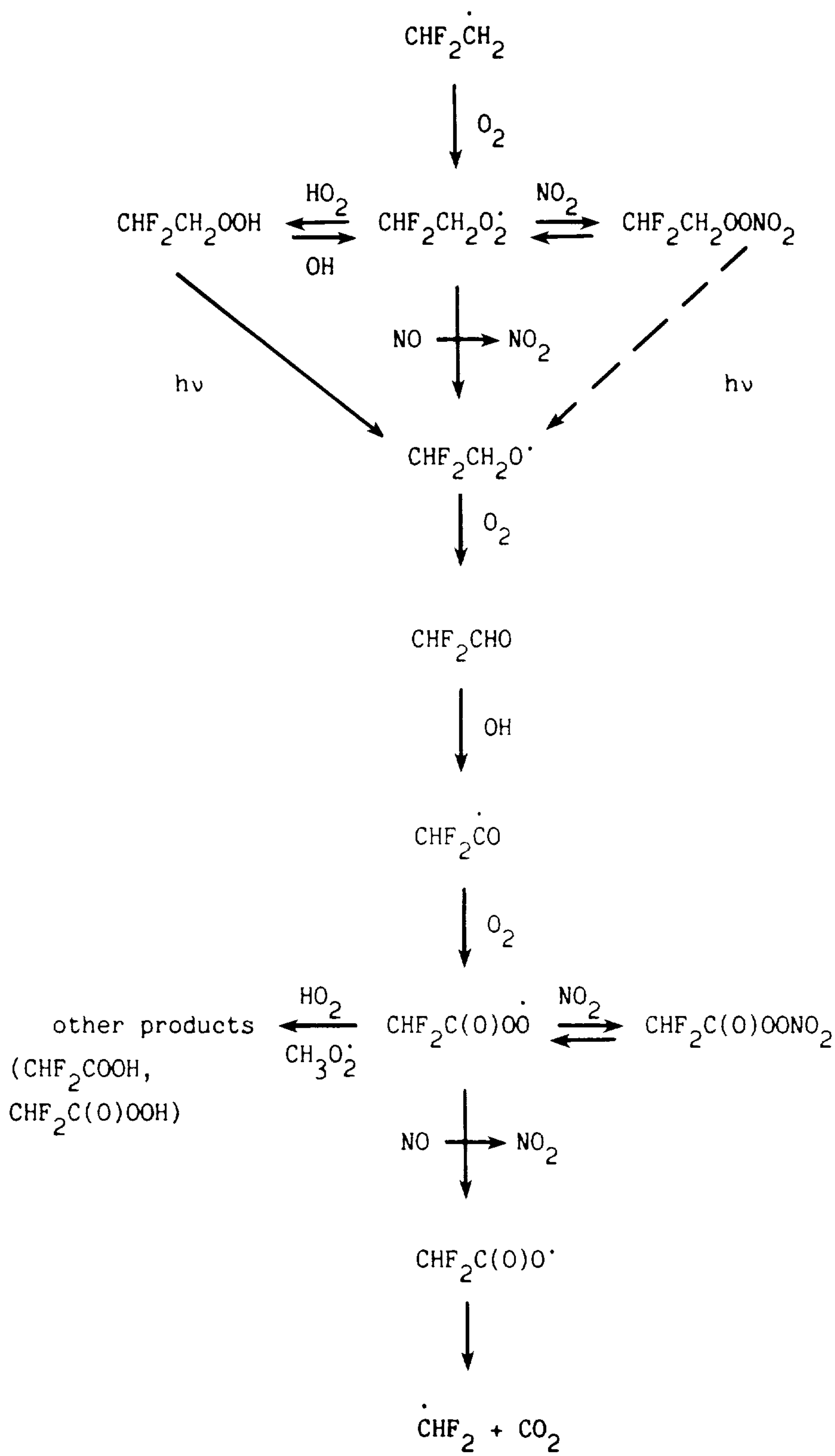
B. CHF_2CHO. Difluoroacetaldehyde will react in a similar manner to CF_2ClCHO and $CFCl_2CHO$ discussed above in Sections 2.2 and 2.3. The OH radical reaction

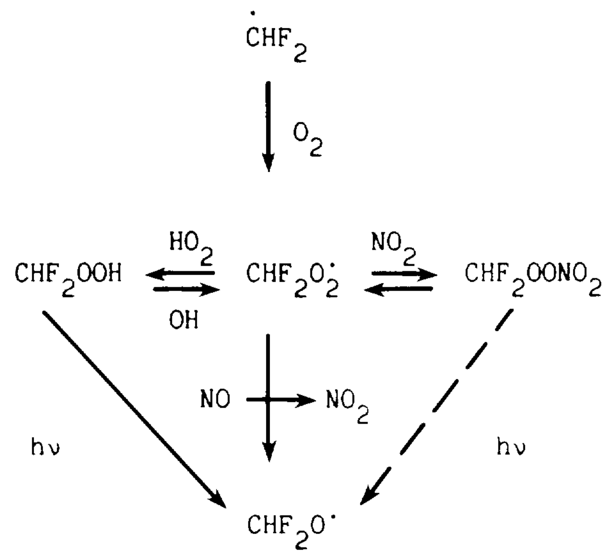
$$OH + CHF_2CHO \rightarrow H_2O + CHF_2\dot{C}O$$

will proceed as shown, with an estimated rate constant of $\sim$1.6 x 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 x 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.


CHF2CH2
O2
CHF2CH2OOH
HO2
OH
CHF2CH2O2
NO2
CHF2CH2OONO2
NO
NO2
hν
hν
CHF2CH2O
O2
CHF2CHO
OH
CHF2CO
O2
other products
(CHF2COOH,
CHF2C(O)OOH)
HO2
CH3O2
CHF2C(O)OO
NO2
CHF2C(O)OONO2
NO
NO2
CHF2C(O)O
CHF2 + CO2



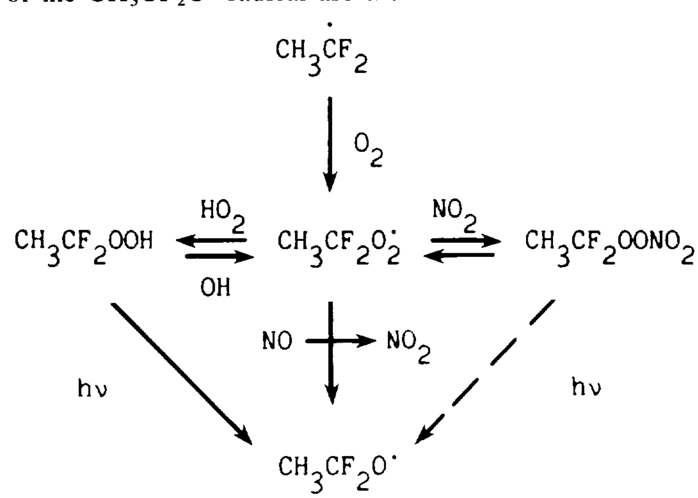
C. $CHF_2O^{\cdot}$. Reaction with O_2 will be the only important reaction pathway

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

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 $CH_3CF_2O^{\cdot}$ need to be considered, as discussed below.

A. $CH_3CF_2O^{\cdot}$. The reactions of this radical which can occur are

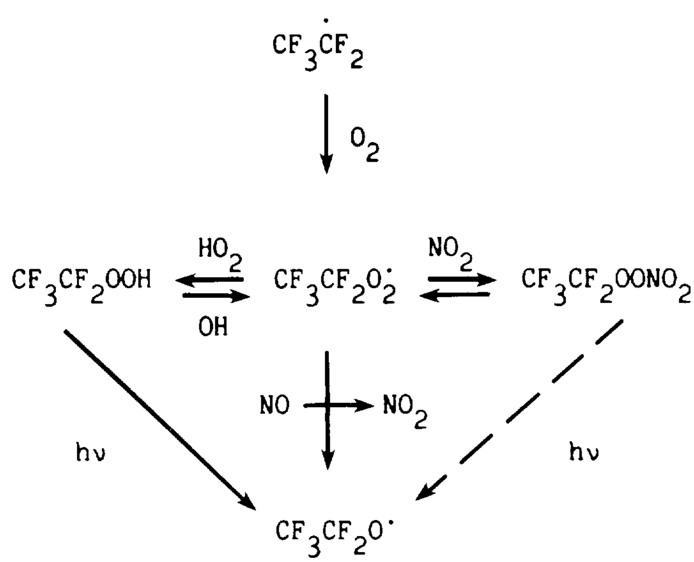
$$CH_3CF_2O^{\cdot} \rightarrow \dot{C}H_3 + COF_2 \tag{a}$$

$$CH_3CF_2O^{\cdot} \rightarrow CH_3C(O)F + F \tag{b}$$

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 $CF_3CF_2O^{\cdot}$ haloalkoxy radical will be as shown below.



A. $CF_3CF_2\dot{O}$. The reactions of the $CF_3CF_2O^{\cdot}$ 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):

$$CF_3CF_2O^{\cdot} \rightarrow \dot{C}F_3 + COF_2 \tag{a}$$

$$CF_3CF_2O^{\cdot} \rightarrow CF_3C(O)F + F \tag{b}$$

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

$$\dot{C}F_3 + O_2 \xrightarrow{M} CF_3\dot{O}_2$$

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 $CF_3\dot{O}_2$ 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 $CF_3\dot{O}_2$ 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

$$CF_3\dot{O}_2 + NO \rightarrow CF_3O^{\cdot} + NO_2$$

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 $CF_3\dot{O}_2$ radicals with NO proceeded, presumably through the expected intermediate CF_3OONO, to yield COF_2 and FNO_2

$$CF_3\dot{O}_2 + NO \rightarrow COF_2 + FNO_2$$

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 $CF_3\dot{O}_2$ 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

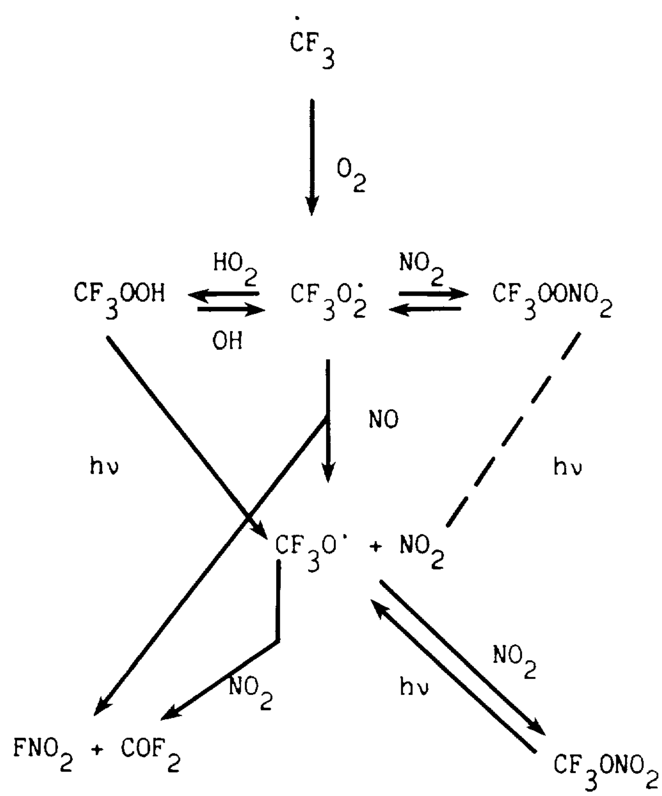
$$CF_3OO^{\cdot} + NO \xrightarrow{M} CF_3ONO$$

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

$$CF_3\dot{O} + NO_2 \xrightarrow{M} CF_3ONO_2$$

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 $CF_3\dot{O}_2$ 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 $CF_3\dot{O}$ radical under tropospheric conditions need to be investigated, and the formation of $CF_3\dot{O}$ from the reaction of $CF_3\dot{O}_2$ 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 ($\dot{R}$) radicals with O_2

				10^{12} x k (cm^3 $molecule^{-1}$ s^{-1})[a]		
$\dot{R}$	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
$\dot{C}H_3$	8×10^{-31} $(T/300)^{-(3.3 \pm 1)}$	2.2×10^{-12} $(T/300)^{1 \pm 1}$	0.27	1.0	0.76	IUPAC (1989)
$C_2\dot{H}_5$	2.0×10^{-28} $(T/300)^{-(3.8 \pm 1)}$	5×10^{-12}	0.7	4.8	4.8	IUPAC (1989)
$CH_3CH_2\dot{C}H_2$		6×10^{-12}		6		IUPAC (1989)
$(CH_3)_2\dot{C}H$		1.5×10^{-11}		15		IUPAC (1989)
$CH_3CH_2CH_2\dot{C}H_2$		$(7.5 \pm 1.4) \times 10^{-12}$[b] (room temperature)				Lenhardt et al. (1980)
$CH_3CH_2\dot{C}HCH_3$		$(1.66 \pm 0.22) \times 10^{-11}$[b] (room temperature)				Lenhardt et al. (1980)
$(CH_3)_3\dot{C}$		$(2.34 \pm 0.39) \times 10^{-11}$[b] (room temperature)				Lenhardt et al. (1980)
$(CH_3)_2CH\dot{C}H_2$		$(2.9 \pm 0.7) \times 10^{-12}$[b] ($298 \pm 2$ K)				Wu and Bayes (1986)
$(CH_3)_3C\dot{C}H_2$		$(1.6 \pm 0.3) \times 10^{-12}$[b] ($298 \pm 2$ K)				Wu and Bayes (1986)
		2.1×10^{-12} $(T/300)^{-2.1}$[b] (266-374 K)				Xi et al. (1988)
$\dot{C}F_3$	1.9×10^{-29} $(T/300)^{-(4.7 \pm 1)}$	1×10^{-11}	0.4-0.5	7.9	8.2	IUPAC (1989)
$\dot{C}FCl_2$	5×10^{-30} $(T/300)^{-(4 \pm 2)}$	6×10^{-12}	0.6	4.7	4.7	IUPAC (1989)
$\dot{C}Cl_3$	1.5×10^{-30} $(T/300)^{-(4 \pm 2)}$	5×10^{-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 $R\dot{O}_2$ radical can decompose to the alkene and the HO_2 radical

$$\begin{array}{ccccc} \dot{R} + O_2 = & [R\dot{O}_2]^* & \rightarrow & HO_2 + \text{alkene} \\ & \Big\downarrow M & & \\ & R\dot{O}_2 & & \end{array}$$

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
$CH_3O_2^{\cdot}$	$4.2 \times 10^{-12}\, e^{(180\pm180)/T}$	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)
$CF_3O_2^{\cdot}$	$1.6\times10^{-11}\ (T/300)^{-1.2}$	16	298	IUPAC (1989)
$CF_2ClO_2^{\cdot}$	$1.6\times10^{-11}\ (T/300)^{-1.5}$	16	298	IUPAC (1989)
$CFCl_2O_2^{\cdot}$	$1.5\times10^{-11}(T/300)^{-1.3}$	15	298	IUPAC (1989)
$CCl_3O_2^{\cdot}$	$1.8\times10^{-11}\ (T/300)^{-1.0}$	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 $C_2H_5\dot{O}_2$ + 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 $CF_3\dot{O}_2$, $CF_2Cl\dot{O}_2$, $CFCl_2\dot{O}_2$ and $CCl_3\dot{O}_2$ radicals suggest that the major reaction pathway is

$$CX_3\dot{O}_2 + NO \rightarrow CX_3\dot{O} + NO_2 \ (X = F \text{ and/or } Cl)$$

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 $CH_3\dot{O}_2$ and of Lesclaux and Caralp (1984), Lesclaux et al. (1986) and Caralp et al. (1988) for the $CX_3\dot{O}_2$ 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 ($R\dot{O}_2$) radicals with NO_2

				10^{12} x k (cm^3 $molecule^{-1}$ s^{-1})a		
$\dot{R}$	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
$CH_3\dot{O}_2$	2.3×10^{-30} $(T/300)^{-(4.0\pm2)}$	8×10^{-12}	0.4	4.1	4.0	IUPAC (1989)
$C_2H_5\dot{O}_2$		$(1.25\pm0.07)\times10^{-12}$b (room temperature)				Adachi and Basco (1979b)
$(CH_3)_2CH\dot{O}_2$		$(5.65\pm0.17)\times10^{-12}$b (room temperature)				Adachi and Basco (1982)
$(CH_3)_3C\dot{O}_2$		$\geq5\times10^{-13}$ (298 K)				Anastasi et al. (1978)
$CF_3\dot{O}_2$	2.7×10^{-29} $(T/300)^{-(5\pm2)}$	9×10^{-12} $(T/300)^{-(0.7\pm1)}$	0.49	7.6	9.6	IUPAC (1989)
$CF_2Cl\dot{O}_2$	4.0×10^{-29} $(T/300)^{-(5\pm2)}$	1.0×10^{-11} $(T/300)^{-(0.7\pm1)}$	0.45	8.4	11	IUPAC (1989)
$CFCl_2\dot{O}_2$	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)
$CCl_3\dot{O}_2$	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 $R\dot{O}_2$ radicals with NO_2 are,

$$k_\infty(R\dot{O}_2 + NO_2) \cong 1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

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).

$$R\dot{O}_2 + NO_2 \overset{M}{\rightleftarrows} ROONO_2$$

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 $CH_3\dot{O}_2$ and $C_2H_5\dot{O}_2$, and these data are given in Table 5. The IUPAC (1989) recommended rate constant expressions for these reactions are $k(CH_3\dot{O}_2 + HO_2) = 1.7 \times 10^{-13} e^{1000/T}$ cm^3 molecule^{-1} s^{-1} (4.9×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K) and $k(C_2H_5\dot{O}_2 + HO_2) = 6.5 \times 10^{-13} e^{650/T}$ 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 $R\dot{O}_2$+ HO_2 reactions are similar to those for these two reactions, a room temperature rate constant of

$$k(R\dot{O}_2 + HO_2) \cong 5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K}$$

and

$$k(R\dot{O}_2 + HO_2) \cong 3.4 \times 10^{-13} e^{800/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

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 $CH_2Cl\dot{O}_2$ is significantly slower than the corresponding HO_2 radical reaction rate constant for the $CHCl_2\dot{O}_2$ radical.

These reactions have been assumed to proceed by the pathway.

$$R\dot{O}_2 + HO_2 \rightarrow ROOH + O_2$$

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 $\sim\pm$ 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

$$R_2R_2CHO_2^{\cdot} + R_3R_4CHO_2^{\cdot} \rightarrow R_1R_2CHO^{\cdot} + R_3R_4CHO^{\cdot} + O_2 \quad \text{(a)}$$

$$R_1R_2CHO_2^{\cdot} + R_3R_4CHO_2^{\cdot} \rightarrow R_1R_2CHOH + R_3R_4CO + O_2 \quad \text{(b)}$$

$$R_1R_2CHO_2^{\cdot} + R_3R_4CHO_2^{\cdot} \rightarrow R_1R_2CHOOCHR_3R_4 + O_2 \quad \text{(c)}$$

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 $\sim$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.

$$R_1R_2CHO^{\cdot} + NO \rightarrow R_1R_2CHONO$$

$$R_1R_2CHO^{\cdot} + NO \rightarrow R_1R_2CO + HNO$$

$$R_1R_2CHO^{\cdot} + NO_2 \rightarrow R_1R_2CHONO_2$$

$$R_1R_2CHO^{\cdot} + NO_2 \rightarrow R_1R_2CO + HONO$$

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).

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

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 3.7×10^{-14} cm^3 molecule^{-1} s^{-1} leads to

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

(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 1.8×10^{-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).

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

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 $4.0 \times 10^4\ s^{-1}$.

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 $4 \times 10^4\ s^{-1}$ 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^{-8}[b]	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^{-8}[b]	298	Batt et al. (1986)
$CF_2ClO^{\cdot} \rightarrow COF_2 + Cl$	$\sim 1 \times 10^{14}$	6240[c]	8×10^{4}[b]	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^{4}[b]	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^{4}[b]	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^{5}[b] $>10^{5}$	298 298	Rayez et al. (1987) 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^{-6}[b]	298	Rayez et al. (1987)
$CHF_2O^{\cdot} \rightarrow COF_2 + H$	$\sim 1 \times 10^{14}$	17770[c]	1×10^{-12}[b]	298	Rayez et al. (1987)
$CHFClO^{\cdot} \rightarrow COFCl + H$	$\sim 1 \times 10^{14}$	14800[c]	3×10^{-8}[b]	298	Rayez et al. (1987)
$CH_2ClO^{\cdot} \rightarrow HC(O)Cl + H$	$\sim 1 \times 10^{14}$	14900[c]	2×10^{-8}[b]	298	Rayez et al. (1987)
$CHCl_2O^{\cdot} \rightarrow COCl_2 + H$	$\sim 1 \times 10^{14}$	13340[c]	4×10^{6}[b]	298	Rayez et al. (1987)
$CH_2FO^{\cdot} \rightarrow HC(O)F + H$	$\sim 1 \times 10^{14}$	14540[c]	6×10^{-8}[b]	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 $CX_3CH_2\dot{O}$ 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 $CX_3CF_2\dot{O}$ 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

$$CFCl_2CFCl\dot{O} \rightarrow CFCl_2C(O)F + Cl$$

$$CF_2ClCCl_2\dot{O} \rightarrow CF_2ClC(O)Cl + Cl$$

$$CCl_3CF_2\dot{O} \rightarrow COF_2 + \dot{C}Cl_3$$

$$CF_2ClCF_2\dot{O} \rightarrow COF_2 + \dot{C}F_2Cl$$

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, $CH_2Cl\dot{O}$ and $CH_2Cl\dot{O}$ 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 $CH_2Cl\dot{O}$ radical, consistent with Table 8).

The differences in the heats of reaction, $\{[\Delta HO_{2\,reaction} - \Delta H_{decomposition}]\} = \Delta(\Delta H)$, in kcal mol^{-1} (rounded to the nearest kcal mol^{-1}) are then: $C_2H_5\dot{O}$, 45; 2-butoxy, 42; $CH_2Cl\dot{O}$, 48; and $CHCl_2\dot{O}$, 30. At room temperature and atmospheric pressure of air, the removal processes of these $R\dot{O}$ radicals are: $C_2H_5\dot{O}$, 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); $CH_2Cl\dot{O}$, reaction with O_2 (Niki et al., 1980); and $CHCl_2\dot{O}$, 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^{-1} [a]
$CH_3CH_2O^{\cdot}$	$CH_3CH_2O^{\cdot} + O_2 \rightarrow CH_3CHO + HO_2$	-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,

C-3

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 ($2.0 \times 10^{-13}\ cm^3\ molecule^{-1}\ s^{-1}$ 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,

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

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 $\leq$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

$ROONO_2$	k_0 (cm^3 molecule^{-1} s^{-1})	k_∞ (s^{-1})	F (298 K)	k (s^{-1}) 298 K 760 Torr	k (s^{-1}) 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).

Acknowledgments

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