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

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1. INTRODUCTION

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

2. THE ATMOSPHERIC DEGRADATION PROCESS

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

$$RH + OH \rightarrow R + H \qquad (1)$$

$$RH + O(^1D) \rightarrow R + OH \qquad (2)$$

$$R + O_2 + M \rightarrow RO_2 + M \qquad (3)$$

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

$$R'Cl + O(^1D) \rightarrow R' + ClO \qquad (4)$$

$$R' + O_2 + M \rightarrow R'O_2 + M \qquad (5)$$

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

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

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

I-1 - Structure of the peroxy radicals

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

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

Table I : List of compounds and corresponding peroxy radicals

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

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

I-2 - Reactions of peroxy radicals

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

Reactions with NO

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

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

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

Reactions with NO_2

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

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

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

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

Reactions with HO_2

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

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

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

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

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

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

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

II-1 - General reactions of alkoxy radicals

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

DEGRADATION MECHANISMS

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

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

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

(X = H,Cl or F)

- Chlorine atom detachment, yielding a carbonyl compound

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

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

- Thermal dissociation into a carbonyl compound and a radical.

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

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

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

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

- CX_3CH_2O radicals react with oxygen by hydrogen abstraction;

- CX_3CCl_2O and CX_3CClFO undergo Cl atom detachment;

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

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

HCFC 22 $CHClF_2$

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

$$CClF_2O \rightarrow CF_2O + Cl$$

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

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

Principal product from HCFC 22 : CF_2O

HCFC 123 $CHCl_2CF_3$

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

$$CF_3CCl_2O \rightarrow CF_3CClO + Cl$$

$$CF_3CHClO \rightarrow CF_3 + CHClO$$

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

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

HCFC 124 CF_3CHClF

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

$$CF_3CClFO \rightarrow CF_3CFO + Cl$$

$$CF_3CHFO \rightarrow CF_3 + CHFO$$

The reaction of CF_3CHFO with oxygen would yield again CF_3CFO.

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

HCFC 141b CH_3CCl_2F

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

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

$$CH_3CClFO \rightarrow CH_3CFO + Cl$$

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

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

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

HCFC 142b CH_3CClF_2

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

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

$$CH_3CF_2O \rightarrow CH_3 + CF_2O$$

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

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

HFC 125 CF_3CHF_2

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

$$CF_3CF_2O \rightarrow CF_3 + CF_2O$$

Principal product from HFC 125 : CF_2O.

HFC 134a CF_3CH_2F

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

$$CF_3CHFO \rightarrow CF_3 + CHFO$$

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

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

HFC 152a CH_3CHF_2

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

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

$$CH_3CF_2O \rightarrow CH_3 + CF_2O$$

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

Principal product from HFC 152a : CF_2O.

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

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

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

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

)[a] : Probably a minor product

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

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

The carbonyl products containing chlorine are CClFO, CHClO, CF_3CClO and possibly some small amounts of phosgene, CCl_2O, formed as a side product in the HCFC 123 oxidation (by C-C bond cleavage in CF_3CCl_2O radical). For the same reason given above, the photolysis of such compounds is likely to be negligible in the troposphere but could become significant in the lower stratosphere, particularly for compounds such as CHClO or CF_3CClO. The photolysis rate of this class of compounds, i.e. RCClO, should be carefully investigated in the conditions of upper troposphere/lower stratosphere. In particular, it should be verified that the photolysis of CF_3CClO do not produce CF_3Cl which would be a long lived chlorine carrier in the atmosphere. These compounds are not expected to react with OH, with the exception of CHClO which will be converted to CO and HCl in the troposphere. Reaction with $O(^1D)$ atoms in the lower stratosphere may be significant and an evaluation of this sink could be obtained from models, assuming rate constants for $O(^1D)$ reactions of about 2×10^{-11} $cm_3 molecule^{-1} s^{-1}$ (value for CFClO).

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

CONCLUSIONS

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

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

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

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

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

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

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

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

Summary of degradation mechanisms of volatile organic compounds in the atmosphere

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

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

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

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

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

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

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

$$RO + O_2 \rightarrow R_1R_2CO + HO_2 \qquad (4)$$

(R_1 and R_2 are H or organic fragment)

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

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

$$\rightarrow R_1R_2CO + H_2O + O_2 \qquad (5b)$$

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

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

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

or

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

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

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

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

or

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Source : IUPAC evaluation, 1989

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

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

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

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

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

Source : IUPAC evaluation, 1989

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

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

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

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

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

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

Source : IUPAC evaluation, 1989

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

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

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

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

$$\rightarrow CX_2O + H_2O + O_2$$

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

5 - Decomposition of halogen substituted alkoxy radicals.

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

$$CX_2ClO \rightarrow CX_2O + Cl$$

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

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

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

Table IV - Decomposition of halogen substituted alkoxy radicals.

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

Reactions of hydrochlorofluoroethoxy radicals

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

i - Chlorine atom detachment

$$CX_3CYClO \rightarrow CX_3CYO + Cl$$

(X and Y = H, Cl or F)

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

ii - C-C bond cleavage

$$CX_3CX_2O \rightarrow CX_3 + CX_2O$$

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

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

iii - Reaction with oxygen

$$CX_3CXHO \rightarrow CX_3CXO + HO_2$$

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

iv - Oxidation of the CF_3O radical

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

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

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

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

6 - Photochemical reactions

Halogenated hydroperoxides

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

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

Carbonyl Halides

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

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

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

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

Halogenated aldehydes

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

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

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

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

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

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

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

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

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

7 - Reaction of OH with halogenated peroxides and aldehydes

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

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

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

For the hydroperoxides, the H-atom attached to the C atom (relative to the peroxy link) are less likely to be abstracted than the H_{00} atom, due to the deactivating effect of the nearby halogen atoms in both C_1 and C_2 fragments. For the rate coefficients the preferred estimates are those for reaction of OH + H_2O_2 reduced by a factor of 2 to compensate for the lower number of abstractable H-atoms. The only halogen substituted aldehyde for which the rate coefficient for OH attack appears to have been measured is chloral, CCl_3CHO, derived from the photo-oxidation of methyl chloroform (Nelson et al. 1984) for which a value of 6.2×10^{-12} $cm^3molecule^{-1}s^{-1}$ was obtained at 298 K. In the same study, the rate coefficient for OH attack on acetyl chloride :

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

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

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

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

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

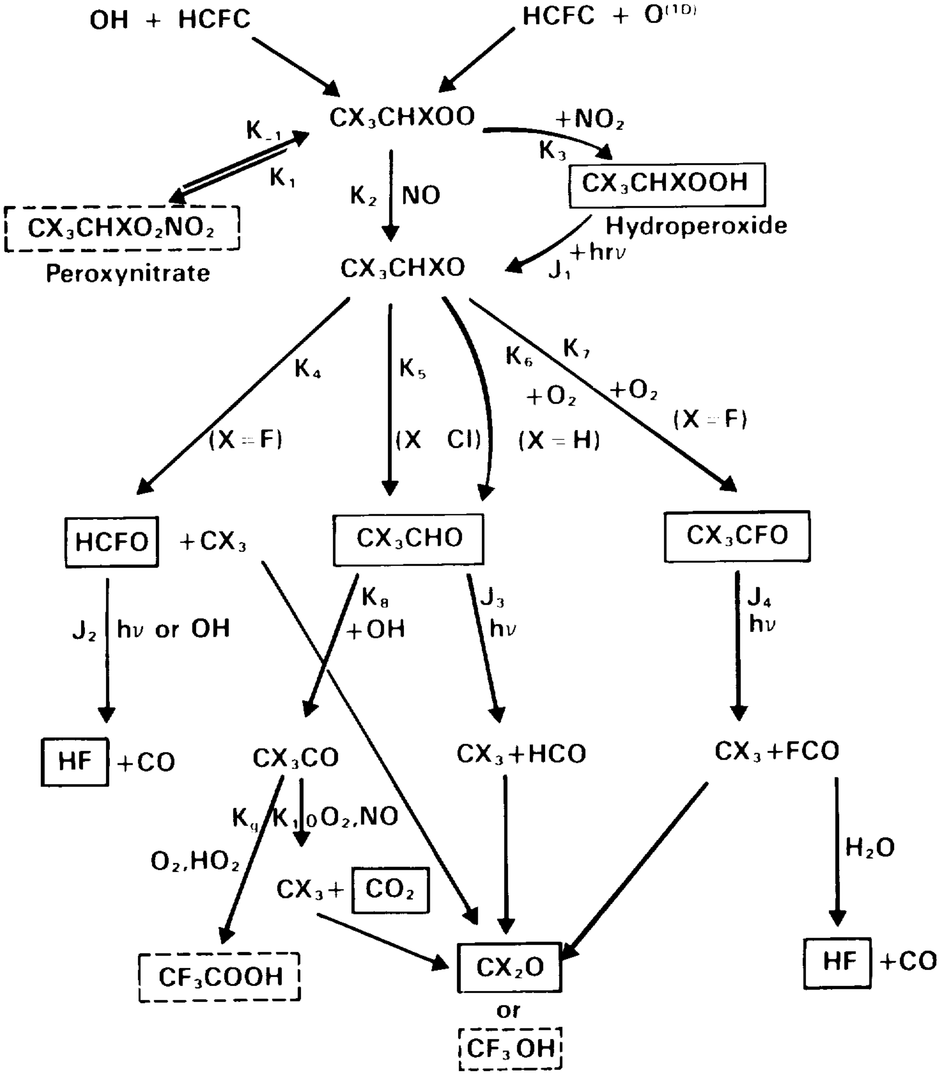
8 - Rainout, washout and dry deposition processes

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

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

Recommended rates coefficients for modelling atmospheric degradation of hydrochlorofluorocarbons

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



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

Figure 1. Tropospheric Degradation Pathways for typical CFC substrates.

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

	$RO_2 + NO_2M$ $RO_2NO_2 + M$	$RO_2 + NO$	$RO_2 + HO_2$	$RO \rightarrow CX_3 + CX_2O$	$RO \rightarrow CX_3CXO + Cl$	$RO + O_2 \rightarrow CX_3CHO + HO_2$	$RO + O_2 \rightarrow CX_3CXO + HO_2$	$OH + CX_3CHO$	$CX_3CO + HO_2$	$CX_3CO + NO$
HCFC's	k_1 & k_{-1}	k_2 x 10^{11} cm^3 s^{-1}	k_3 x 10^{11} cm^3 s^{-1}	k_4	k_5	k_6	k_7	k_8 cm^3 s^{-1}	k_9 x 10^{11} cm^3 s^{-1}	k_{10} x 10^{11} cm^3 s^{-1}
HCFC 22										
$CClF_2O_2$	IUPAC*	1.6	1.0***	NA	y^s	-	-	-	-	-
CHF_2O_2	use k_∞ (CH^3O^2)	1.6	"	NA	-	-	0.1k$(CH_3O+O_2)^s$	-	-	-
HCFC 123										
$CF_3CCl_2O_2$	use k_∞ $(CFCl_2O_2)$	1.5	"	-	as $CFCl_2O^x$	-	-	-	-	-
CF_3CHClO_2	use k_∞ (CF_2ClO_2)	1.6	"	$CF_3+HCClO$		-	-	2.1 x 10^{-12}	-	-
HCFC 124										
CF_3CClFO_2	use k_∞ (CF_2ClO_2)	1.6	"	-	y	-	-	-	-	-
CF_3CHFO_2	" "	1.6	"	CF_3+HCFO^t	-	-	0.1k(CH_3O+O_2)	-	-	-
HCFC 141b										
$CCl_2FCH_2O_2$	use $k_\infty(CH_3O_2)$	0.9**	"	-	-	as CH_3O	-	2.1x10^{-12}	0.5^z	1.4^w
CH_3CClFO_2	use $k_\infty(CClF_2O_2)$	1.6	"	-	y	-	-	as CH_3CCl_3	-	-
HCFC 142b										
$CClF_2CH_2O_2$	use k_∞ (CH_3O_2)	0.9	"	-	-	as CH_3O	-	2.1x10^{-12}	0.5	1.4
$CH_3CF_2O_2$	use k_∞ (CF_2ClO_2)	1.6	"	CH_3+CF_2O		-	-	as CH_3CCl_3	-	-
HCF 125										
$CF_3CF_2O_2$	use k_∞ (CF_2ClO_2)	1.6	"	$CF_3+CF_2O^t$	-	-	-	-	-	-
HCFC 134										
CF_3CFHO_2	use k_∞ (CF_2ClO_2)	1.6	"	CF_3+HFCO^t	-	-	0.1k (CH_3O+O_2)	-	-	-
HCFC 152a										
$CHF_2CH_2O_2$	use k_∞ (CH_3O_2)	0.9	"	-	-	as CH_3O	-	2.1x10^{-12}	0.5	1.4
$CH_3CF_2O_2$	use k_∞ (CH_2ClO_2)	1.6	"	CH_3+CF_2O	-	-	-	as CH_3CCl_3	-	-

* IUPAC Data evaluation [10]

** as $C_2H_5O_2$ + NO

*** Estimate based on $C_2H_5O_2$ + HO_2

)^s COF_2 is the product

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

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

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

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

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

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

Table B : Photochemical reactions

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

* Based on arguments presented in Appendix II