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

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EXECUTIVE SUMMARY

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

- HCFC's containing one chlorine atom such as 22 and 142b seem to release their chlorine content essentially instantaneous with the initial attack on the parent by OH radicals. For HCFC 124 such release is apparently prevented.

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

1. INTRODUCTION

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

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

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

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

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

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

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

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

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

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

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

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

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

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

a. R/RO_2 conversion

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

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

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

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

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

b. RO_2/RO conversion

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

(i) RO_2/NO_x interactions:

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

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

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

(3′) $$RO_2 + NO\ (+M) \rightarrow RONO_2\ (+M)$$

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

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

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

Similiar to (3′) this reaction terminates the hydrocarbon oxidation chain. Its rate coefficients are well established for the smaller peroxiradicals with values near10^{-11} cm^3/s in the high pressure limit. However, peroxinitrates have a relatively low bond strength and tend to be unstable at the temperatures of the lower troposphere. For instance, $CH_30_2NO_2$ has a thermal lifetime of < 1 s at 298 K. Only at the lower temperatures of the upper troposphere and lower stratosphere peroxinitrates are more persistent and removal pathways other than thermal decomposition (i.e. photolysis, reaction with OH) may become important. It should be noted that halogen and acyl substitution tends to make peroxinitrates considerably more stable. The lifetimes of $CF_2ClO_2NO_2$ and $CH_3C(O)O_2NO_2$ (PAN) for instance, at 298 K are 20 s and 28 min, respectively, in the high pressure limit (Atkinson et al., 1989). Since these lifetimes will be further enhanced at all pressures prevailing in the troposphere, peroxinitrate formation from these radicals is clearly an important process.

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

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

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

(ii) RO_2/HO_2 interactions:

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

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

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

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

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

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

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

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

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

c. RO/carbonyl compound conversion

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

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

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

d. Carbonyl compound/oxidized fragment conversion

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

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

The subsequent oxidation of this radical occurs in the sequence

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

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

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

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

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

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

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

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

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

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

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

3.1. General considerations

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

- Due to the hydrogen content the initial oxidative attack will be by OH radicals. Compared to CH_4 the reactivity of individual C-H bonds in partially halogenated methanes, including $CHClF_2$, is increased by increasing F and Cl substitution due to a corresponding reduction of the C-H bond strength. An exception being CF_3H, with a C-H bond strength about 1.5 kcal/mol larger than CH_4. The same increase of reactivity applies to F and Cl substituted ethanes, again except when one of the carbon atoms represents a CF_3 group (McMillen and Golden, 1982). Note, however, that the overall reactivity towards OH, as expressed by the rate coefficient, also depends on the number of abstractable H atoms in the molecule. The results for k_{OH}-values are documented elsewhere in this report.
- The fully or partially halogenated alkyl radicals will add O_2 to form the corresponding peroxi radicals. Direct kinetic measurements which are available only for CCl_3, CCl_2F and CF_3 (Atkinson et al., 1989; Caralp et al., 1986) indicate that halogen substitution enhances the rates of these association processes

(for instance k $(CF_3 + O_2)$ / k $(CH_3 + O_2) \simeq 22$). Moreover, since the thermochemistry is expected to be similar for the substituted and unsubstituted case reactions, peroxi radical formation will be the exclusive pathway of oxidation of the halogenated alkyl radicals.

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

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

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

3.2. Discussion of specific examples

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

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

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

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

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

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

(i) HCFC 22: CHF_2Cl

$$CHF_2Cl \xrightarrow{\quad OX \quad} CF_2ClO$$

followed by:

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

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

$$CF_2ClO \rightarrow CFClO + F$$

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

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

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

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

Summary of expected products from CHF_2Cl:

Carbonyl compounds: CF_2O
Others: $CF_2ClO_2NO_2$, CF_2ClOOH

(ii) HCFC 123: $CHCl_2CF_3$

$$CHCl_2CF_3 \xrightarrow{OX} CF_3CCl_2O$$

followed by:

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

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

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

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

Summary of expected products from $CHCl_2CF_3$:

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

(iii) HCFC 124: $CHFClCF_3$

$$CHFClCF_3 \xrightarrow{OX} CF_3CFClO$$

followed by:

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

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

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

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

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

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

$$CF_3O + NO \rightarrow CF_3ONO$$

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

Summary of expected products from $CHFClCF_3$:

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

(iv) HCFC 141b: CCl_2FCH_3

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

followed by:

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

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

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

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

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

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

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

$$CCl_2F + O_2 \rightarrow CCl_2FO_2$$

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

$$CCl_2FO \rightarrow CClFO + Cl$$

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

Summary of expected products from CCl_2FCH_3:

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

(iv) HCFC 142b: $CClF_2CH_3$

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

followed by:

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

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

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

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

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

Summary of expected products from $CClF_2CH_3$:

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

(vi) HFC 125: CHF_2CF_3

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

followed by:

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

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

Summary of expected products from CHF_2CF_3:

Carbonyl compounds: CF_2O
Other products: $CF_3CF_2O_2NO_2$, CF_3CF_2OOH,
(CF_3ONO, CF_3OH)

(vii) HFC 134a: CH_2FCF_3

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

followed by:

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

and, alternatively,

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

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

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

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

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

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

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

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

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

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

Summary of expected products from CH_2FCF_3:

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

(viii) HFC 152a: CH_2CH_3

There are two different initial oxidation pathways, viz.

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

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

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

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

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

The alternative C-C-bond fission

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

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

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

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

$$CHF_2 + O_2 \rightarrow CHF_2O_2$$

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

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

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

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

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

Summary of expected products from CHF_2CH_3:

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

4. SUMMARY AND RECOMMENDATIONS

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

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

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

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

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

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

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

a) Benson, 1976

b) McMillen and Golden, 1982

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

d) Batt, 1977

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

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

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

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

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

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

k) JANAF Tables, 1979

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

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

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

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

VII. LIQUID PHASE PROCESSES

Possible Atmospheric Lifetimes and Chemical Reaction Mechanisms for Selected HCFCs, HFCs, CH_3CCl_3, and their Degradation Products Against Dissolution and/or Degradation in Seawater and Cloudwater

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EXECUTIVE SUMMARY

The rates at which eight potential alternative HCFCs and HFCs and methyl chloroform (CH_3CCl_3) can be removed from the atmosphere by dissolution and reaction in the oceans and in cloudwater have been estimated from the species' thermodynamic and chemical properties using simple mathematical formulations to simulate the transfer of gases from the atmosphere to the aqueous phase. The HCFCs and HFCs considered are $CHCl_2CF_3$ (HCFC-123), $CFCl_2CH_3$ (HCFC-141b), CF_2ClCH_3 (HCFC-142b), CHF_2Cl (HCFC-22), $CHFClCF_3$ (HCFC-124), CH_2FCF_3 (HFC-134a), CHF_2CH_3 (HFC-152a), and CHF_2CF_3 (HFC-125).

Cloudwater is found to be of no importance as an atmospheric sink for any of the above compounds. Best-estimate lifetimes for all eight HCFCs and HFCs toward removal in the oceans are greater than 77 years, with only HCFC-22, HCFC-123, and HCFC-141b having lifetimes shorter than 200 years. The most reactive of the nine species considered toward removal in the oceans is methyl chloroform with a best-estimate lifetime of 42 years and a minimum reasonable lifetime of 22 years. Important removal mechanisms for methyl chloroform, HCFC-22, HCFC-123, and HCFC-141b in seawater are hydrolysis and reaction with hydrated electrons. Improved hydrolysis kinetics data and Henry's law solubility data for methyl chloroform, HCFC-22, HCFC-123, and HCFC-141b would help to reduce the uncertainties in the aqueous phase removal rates of these species, as would improved estimates of the hydrated electron concentration in seawater.

Gas phase degradation products of the eight HCFCs and HFCs include a large variety of halo-substituted carbonyls, acids, peroxyacids, hydroperoxides, alcohols, nitrates, peroxynitrates, and peroxyacetylnitrates. Although handicapped by the total absence of Henry's law solubility data for any of the compounds of interest and the limited availability of relevant kinetic data, an assessment of the rates and mechanisms of aqueous phase removal of the gas phase degradation products has been carried out.

The species X_2CO, HXCO, CH_3CXO, CF_3OH, CX_3OONO_2, and ROOH (X = F or Cl, R = halo-substituted methyl or acetyl) are all expected to be removed from the atmosphere on time scales limited by transport to cloudy regions or the marine boundary layer (i.e. about 1 month); aqueous phase reactions of these species result in the formation of chloride, fluoride, and carbon dioxide, as well as formic, acetic, and oxalic acids. The species CX_3CXO, CX_3CX_2OOH, $CX_3CX_2OONO_2$, $CX_3C(O)OONO_2$, and $CX_3C(O)OOH$ are also expected to be removed from the atmosphere rapidly, and their aqueous phase reactions result in the formation of halo-substituted acetates, $CX_3C(O)O^-$.

The species $CX_3C(O)OH$ are very acidic and, as a result, are highly soluble in cloudwater. These acids are expected to be rapidly removed from the atmosphere by rainout. However, the aqueous phase species $CX_3C(O)O^-$ are expected to be resistant to chemical degradation. Trichloroacetate can thermally decompose on a time scale of 2-10 years to yield carbon dioxide and chloroform. In fresh water, the reaction of $CCl_3C(O)O^-$ with the hydrated electron is also expected to occur on a time scale of a few years. The species $CFCl_2C(O)O^-$, $CF_2ClC(O)O^-$, and $CF_3C(O)O^-$ may have very long aqueous phase lifetimes. The longest lived species, $CF_3C(O)O^-$, could have a lifetime in natural waters as long as several hundred years. Processes which could possibly degrade $CF_nCl_{3-n}C(O)O^-$ on shorter time scales than suggested above, but whose rates cannot be estimated with any degree of confidence at this time, include oxidation by photochemically generated valence band holes in semiconductor particles and hydrolysis catalyzed by enzymes in microorganisms and plants; further research aimed at characterizing these processes is needed.

One possible gas phase degradation product about which very little is known is CF_3ONO_2. This compound has never been observed, and may be thermally unstable. If CF_3ONO_2 is thermally stable, then it may have a long lifetime toward aqueous phase removal. Henry's law solubility data and hydrolysis kinetics data for CF_3ONO_2 are needed before its aqueous phase removal rate can be assessed with any degree of confidence.